Master Quality Assurance Project Plan Implementation of U.S. EPA Cleanup Grants for Petroleum & Hazardous Substance Brownfields – City of Spokane; Cooperative Agreement Nos. BF-01J39501-1, BF-01J39601-1 & BF-01J39701-1

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July 17, 2018

Stantec

Sign-off Sheet

This document entitled Master Quality Assurance Project Plan Implementation of U.S. EPA Cleanup Grants for Petroleum & Hazardous Substance Brownfields – City of Spokane; Cooperative Agreement Nos. BF-01J39501-1, BF-01J39601-1 & BF-01J39701-1 was prepared by Stantec Consulting Services Inc. ("Stantec") for the account of City of Spokane (the "Client"). Any reliance on this document by any third party is strictly prohibited. The material in it reflects Stantec's professional judgment in light of the scope, schedule and other limitations stated in the document and in the contract between Stantec and the Client. The opinions in the document are based on conditions and information existing at the time the document was published and do not take into account any subsequent changes. In preparing the document, Stantec did not verify information supplied to it by others. Any use which a third party makes of this document is the responsibility of such third party. Such third party agrees that Stantec shall not be responsible for costs or damages of any kind, if any, suffered by it or any other third party as a result of decisions made or actions taken based on this document.

Approved by Deborah Burgess via email July 17, 2018	
Deborah Burgess, U.S. EPA Project Officer	Date
Donald M. Brown, U.S. EPA Quality Assurance Manager	Date
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Teri Stripes, City of Spokane Grantee Project Manager	Date
	06/26/18
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	06/26/18
Kim Vik, LG, Stantec Consultant QA Manager	Date
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Randee Arrington, TestAmerica, Laboratory Project Manager	Date

MASTER QUALITY ASSURANCE PROJECT PLAN IMPLEMENTATION OF U.S. EPA CLEANUP GRANTS FOR PETROLEUM & HAZARDOUS SUBSTANCE BROWNFIELDS – CITY OF SPOKANE; COOPERATIVE AGREEMENT NOS. BF-01J39501-1, BF-01J39601-1 & BF-01J39701-1

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Master Quality Assurance Project Plan Distribution List

The following have received a copy of this QAPP:

- Deborah Burgess, U.S. EPA, Project Officer
- Donald M. Brown, U.S. EPA, Quality Assurance Manager
- Teri Stripes, City of Spokane, Grantee Project Manager
- Chris Gdak, Stantec, Project Manager
- Cyrus Gorman, Stantec, Consultant Technical Lead
- David Holmes, Stantec, Consultant Brownfields Grant Specialist & Senior Technical Reviewer
- Kim Vik, Stantec, QA Manager
- Randee Arrington, TestAmerica, Laboratory Project Manager
- Terri Torres, TestAmerica, Laboratory QA Manager

Abbreviations

ABCA	Analysis of Brownfield Cleanup Alternatives
ASTM	American Society for Testing and Materials
Cascade	Cascade Drilling, L.P.
City	City of Spokane
COC	Chain of Custody
CUL	Cleanup level
DQA	Data Quality Assessment
DQO	Data Quality Objective
Ecology	Washington Department of Ecology
ESN-NW	ESN-NW Environmental Drilling
HASP	Health and Safety Plan
i.e.	id est (Latin word meaning "that is" or "in other words")
LCS	Laboratory Control Sample
L.G.	Licensed Geologist
mL	Milliliter
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MTCA	Model Toxics Control Act
NVLAP	National Voluntary Laboratory Accreditation Program
OSHA	Occupational Safety and Health Administration
PARCCS	Precision, Accuracy, Representativeness, Completeness, Comparability and Sensitivity
Parks Department	Spokane Parks and Recreation Department
PCOC	Potential Contaminant of Concern
P.E.	Professional Engineer
PID	Photoionization Detector
Properties	Canada Island, Havermale Island, and North Bank areas of Riverfront Park, Spokane
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QLs	Quantitation Limits
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SA	Spike Added
SMP	Soil Management Plan
SOPs	Standard Operating Procedures
SR	Sample Result
SRMs	Standard Reference Materials
SSR	Spiked Sample Result
Stantec	Stantec Consulting Services Inc.
TestAmerica	TestAmerica Laboratories Inc.
U.S. EPA	United States Environmental Protection Agency

VOA	Volatile organic analyte
VOC	Volatile organic compound
WAC	Washington Administrative Code

Project Personnel

Contact information for key project personnel is summarized in the table below.

Name & Title	Project Role	Organization	Contact Information
Deborah Burgess	Project Officer	U.S. EPA Region 10	Office of Environmental Cleanup 1200 6th Avenue Seattle, WA 98101 Phone: 206-553-6396 Perkins.Brandon@epa.gov
Sandra Treccani	Technical Project Manager	Washington Department of Ecology	Ecology Eastern Regional Office 4601 N Monroe Spokane, WA 99205 Phone: 509-329-3412 satr461@ecy.wa.gov
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Cyrus Gorman, L.G. *Environmental Associate*	Consultant Technical Lead	Stantec	4100 194th Street SW Suite 400 Lynnwood, WA 98036 Phone: 425-599-9302 cyrus.gorman@stantec.com
Kim Vik, L.G. *Project Geologist*	Consultant Data Manager	Stantec	19101 36th Avenue West, Suite 203 Lynnwood, WA 98036 Phone: 425-977-4994 kim.vik@stantec.com
JR Sugalski, P.E. *Environmental Engineer*	Subconsultant, Project Manager	GeoEngineers	523 E. 2nd Spokane, WA 99202 Phone: 509-209-2830
Bruce Williams *Principal Environmental Scientist*	Subconsultant, Principal	GeoEngineers	523 E. 2nd Spokane, WA 99202 Phone: 509-262-3125
Randee Arrington *Laboratory Project Manager*	Laboratory Project Manager	TestAmerica Laboratories, Inc.	11922 E. 1st Avenue Spokane, WA 99206 Phone: 509-924-9200 randee.arrington@testamericainc.com

Terri Torres *QA Manager*	Laboratory QA Manager	TestAmerica Laboratories, Inc.	5755 8th Street East Tacoma, WA 98424-1317 Phone: 253-922-2310 terri.torres@testamericainc.com

1.0 PROJECT MANAGEMENT

The purpose of this document is to describe the personnel, procedures, and methods for demonstrating that the quality, accuracy, and precision of data associated with the City of Spokane Brownfield Cleanup Project meet quality assurance/quality control (QA/QC) protocols established by the United States Environmental Protection Agency (U.S. EPA). In May of 2017, the City of Spokane, Washington (City) was formally awarded three separate $200,000 U.S. EPA grants for cleanup of petroleum and hazardous substance brownfields sites for three areas within the City's Riverfront Park. These areas include: Havermale Island, Canada Island, and North Bank (Properties). This Quality Assurance Project Plan (QAPP) serves each of the three grants and addresses both petroleum and hazardous substance contaminants that may be encountered during construction at the Properties.

This QAPP was prepared by Stantec Consulting Services Inc. (Stantec), which was selected by the City through a competitive qualifications-based procurement process to serve as the environmental consultant for the project, and to assist with grant management activities on behalf of the City. The procedures outlined in this QAPP will be used to demonstrate the data collected by Stantec meets the project objectives. This QAPP will be valid for the life of the cooperative agreement and will be reviewed and updated annually (from the date of approval), as necessary. This annual review will be documented, and a summary will be forwarded to all QAPP recipients, along with any updated materials (current laboratory certificates, resumes for new key staff, etc.) for insertion into their copies of the QAPP. If substantial changes are anticipated during the project period (new laboratories, additional analyses, new field methods, etc.), a telephone call will be arranged with all parties who reviewed this QAPP to determine the scope of necessary revisions.

In addition to the QAPP, a Soil Management Plan (SMP) was developed to provide guidance to the City and other contractors that perform earthwork activities at the Properties. The SMP provides information on soil categories and definitions (i.e. contaminated soil, impacted soil etc.), soil excavation and handling recommendations and procedures for the discovery of potentially contaminated impacted soil or underground storage tanks. References to the SMP are provided in the applicable sections below. The SMP is included as **Appendix A**.

1.1 PROJECT ORGANIZATION AND RESPONSIBILITIES

Responsibilities of key project personnel are outlined below. Project team communication, management activities, and technical direction will follow this organizational arrangement. Any U.S. EPA directions or communications will be provided to the Grantee project manager. The Grantee project manager will subsequently communicate these items to the Stantec project manager. Stantec will coordinate with the analytical laboratory and subcontractors. The U.S. EPA project manager will be notified of all proposed changes in personnel. Resumes for Stantec personnel referenced below are presented in **Appendix B**. A project organization chart is

presented on **Figure 1,** and a project schedule on **Figure 2**. Roles and responsibilities are summarized below.

U.S. EPA Project Officer (Deborah Burgess)

1. Direct, review, and approve QAPP and Sampling and Analysis Plans (SAPs).
2. Provide technical consultation services to the Grantee project manager and Stantec project manager.
3. Review progress reports detailing work accomplished.
4. Review all final reports.

Washington Department of Ecology (Sandra Treccani)

1. Provide technical consultation services to the Grantee project manager and Stantec project manager.
2. Review progress reports detailing work accomplished.
3. Review all final reports.

U.S. EPA Quality Assurance Reviewer (Donald M. Brown)

1. Review and approve the QAPP.
2. Assist in review of the SAPs.

Grantee Project Manager (Teri Stripes, City of Spokane)

1. Direct project activities.
2. Prepare and submit progress reports detailing work accomplished, funds spent, and the project status.
3. Responsible for review of project deliverables, project plan development, and overview of project strategies.

Consultant Project Manager (Chris Gdak, Stantec)

1. Oversee planning, coordinating, monitoring, and evaluation of project field activities.
2. Before sampling, meet with the quality assurance (QA) manager, and field staff to discuss and establish sampling purposes, sampling methodology, number of samples, size of samples, sample preservation methods, chain-of-custody (COC) requirements, analyses required, and which samples will be duplicated in the field.
3. Resolve technical problems.
4. Meet with team members to discuss and review analytical results prior to completion of reports.

5. Oversee environmental reports and documents.

Stantec Technical & Field Team Lead: Cyrus Gorman

1. Complete a project SAP and Health and Safety Plan (HASP) prior to the start of monitoring activities.
2. Be responsible for oversight of field activities and ensure that procedures for the field activities related to the QAPP are executed and documented properly.
3. Procure, coordinate, and qualify all subcontractors.

Consultant Quality Assurance Manager (Kim Vik, L.G., Stantec)

1. Oversee sampling activities for adherence to sampling methodology, sample preservation methods, and COC procedures.
2. Assist in any QA issues with field or laboratory questions, as needed.
3. Conduct Field Audits.
4. Maintain a record of samples submitted to the laboratory, the analyses being performed on each sample, the final analytical results, and data validation reports.
5. Prepare Data Assessment Report.
6. Conduct annual QAPP review.

Consultant Data Manager (Kim Vik, L.G., Stantec)

1. Maintain a record of all samples collected and the sample identification information for each sample.
2. Manage data acquired from field assessments and laboratory analyses.
3. Assemble data into computer format.

Consultant Field Team Leader (Bruce Williams, GeoEngineers), and Field Team Leader Liaison and Project Manager (JR Sugalski, P.E., GeoEngineers)

1. Maintain a record of all samples collected and the sample identification information for each sample.
2. Manage data acquired from field assessments and laboratory analyses.
3. Assemble data into computer format.
4. Complete a project Health and Safety Plan (HASP) prior to the start of monitoring activities.
5. Oversee field activities and QAPP-related field activity procedures for proper execution and documentation.
6. Procure, coordinate with and qualify subcontractors.

Consultant Field Technical Staff (GeoEngineers Field Staff; Stantec Field Staff)

1. Stantec and GeoEngineers field technical staff will be assigned to the project on an as-needed basis, as field investigation activities are initiated.
2. Before sampling, meet with GeoEngineers project manager to discuss and establish sampling purposes, sampling methodology, number of samples, size of samples, sample preservation methods, COC requirements, analyses required, and which samples will be duplicated in the field.
3. Collect equipment needed for monitoring activities, including personal protective equipment, sampling equipment, sample containers and coolers, monitoring devices, and any other equipment deemed necessary.
4. Oversee sampling activities and follow procedures outlined in this document during each type of monitoring.
5. Monitor hazardous conditions, if present, while conducting field operations.
6. Submit COC records and field paperwork to field team leader.

All Stantec site personnel working at locations where hazardous materials or contaminants may be encountered in soil, water, or other media will be trained as mandated by the Occupational Safety and Health Administration (OSHA) Act regulations (29 Code of Federal Regulations 1910.120). Additionally, all site personnel will be properly trained in procedures for collecting, labeling, packaging, and shipping liquid and solid environmental samples. The Stantec project manager will maintain personnel training records. Field personnel will be trained to use all monitoring devices and other equipment used in the field.

TestAmerica Laboratories, Inc. (TestAmerica) Laboratory QA Manager (Terri Torres)

TestAmerica Laboratories, Inc. (TestAmerica) is selected to provide laboratory analytical services for this project. The responsibilities of the Laboratory QA Manager for TestAmerica include:

1. Ensure the integrity of samples submitted to TestAmerica, including those released to a subcontracted laboratory (although all analyses currently included in Revision 0 of the QAPP will be performed in-house).
2. Summarize QA/QC requirements for the project.
3. Maintain laboratory schedule and ensure that laboratory personnel understand technical requirements.
4. Provide technical guidance to Stantec project manager.
5. Ensure accuracy of laboratory data.
6. Evaluate adherence to policies and establish systems to provide QA/QC as defined in the QAPP.

7. Initiate and oversee audits of corrective action procedures.
8. Perform data reviews.
9. Maintain training documentation.

As described above, TestAmerica located in Spokane, Washington, has been selected to perform the analytical work required for this project. The lab is certified under the State of Washington Programs for analyses of air, potable water, non-potable water, and solid and chemical materials; however, only soil samples will be collected for this project.

As a State of Washington-certified laboratory, TestAmerica has undergone performance evaluations administered by the Washington Department of Ecology (Ecology) Lab Accreditation Unit, per Chapter 173-50 of the Washington Administrative Code (WAC) for method accuracy and precision. The TestAmerica Ecology laboratory accreditation number is C569-18a. A listing of analyses and analytes for which the laboratory is certified through January 6, 2019 is presented in (**Appendix C**). Laboratory analyses that will be performed by TestAmerica as part of this project are summarized on **Table 1**. Reporting and control limits for soil analyses, are summarized on **Table 2**. Copies of TestAmerica's QA Manual and Standard Operating Procedures (SOPs) are presented in **Appendix D**.

ESN NW /GeoEngineers and Environmental West are specialized environmental drilling companies which employ Washington State licensed drillers and geologists. On-site drilling personnel shall have completed the applicable OSHA training. Additionally, drilling personnel will be required to comply with all site safety regulations covered in the HASP prepared for the project. Copies of the HASP will be provided to the drilling companies, which will be responsible for developing and implementing their own HASPs. Additional drillers and other subcontractors may be utilized for project specific requirements (specialty drilling methods, test pits, etc.)

1.2 FACILITY HISTORY AND BACKGROUND INFORMATION

Riverfront Park located at 507 N. Howard Street in the heart of Spokane, Washington occupies approximately 100 acres of land and water with a rich and varied history. Spokane Falls and the surrounding land has long been a gathering place for people. Native Americans gathered and fished at the falls and in the late 1800's, pioneers settled here and started the City then known as Spokane Falls. The railroad industry fueled the City's growth and rail yards covered Havermale Island, the present site of Riverfront Park.

With the steady decline of the railroad in the 1950s, the area around Spokane Falls began to degrade and the City pondered how to revitalize the area. The City's response was to host Exposition '74, "The World's Fair." In preparation for Expo '74, the area around the Spokane Falls and river gorge was cleaned up, the rail yards were removed, and the Great Northern Railroad Depot on Havermale Island was demolished. The Clock tower is the only vestige of the once famous 1902 Great Northern Depot.

Now, over 40 years after its creation following Expo '74, an extensive revitalization and rehabilitation effort is underway by the City's Parks Department to bring new life to this local landmark. This grant is for a portion of the North Bank Development Area of Riverfront Park identified on **Figure 3**.

1.3 PROJECT DESCRIPTION AND SCHEDULE

Area A – Havermale Island:

Originally built as the U.S. Federal Pavilion for Expo '74, the Pavilion was a gift to the Spokane region from the United States government. The Master Plan aims to restore the Pavilion into a flexible use event space. The Pavilion is no longer a central gathering place for Spokane or the region, despite its prominent stature within the urban landscape. Views of the river are difficult from within the Pavilion due to the ice rink roofing structure added in the 1980s. The present layout of the Pavilion makes very little effort to move circulation towards the river; in essence, the Pavilion turns its back on the river it should be celebrating. The state approved of a Progressive Design-Build method on the Pavilion. The Pavilion is at 50% of the design concept which includes removal of the ice rink and roofing structure to restore views of the river and backfilling with soil currently stockpiled on the North Bank area. Site Prep and Asbestos Abatement has begun, and construction shall be completed in 2019.

Area B – Canada Island:

As part of improvements to the North Promenade, a new bridge abutment and utility corridor will be constructed on Canada Island. The construction activities are slated to begin in early 2018.

Area C – North Bank:

During construction of the Ice Ribbon and Looff Carousel impacted soils were hauled to the North Bank and stockpiled for reuse at the Park. The stockpiled soil will be used as backfill material when the Ice Rink is removed as part of renovations to the Pavilion. Construction is anticipated to start in early 2018.

1.4 DATA QUALITY OBJECTIVES

Data collected from this project will be used to meet the following objectives of the project:

1.) To identify the potential presence of potential contaminants of concern (PCOCs);
2.) Minimize risks to worker health/safety and the environment; and
3.) Outline general procedures for handling and disposal of contaminated soil if encountered during construction activities.

Soils at the Site may be classified as Contaminated Soil, Impacted Soil and Clean Soil as described in the SMP. It is the objective of this project that all laboratory reporting limits for soil data will meet applicable Model Toxics Control Act (MTCA) regulatory standards. No groundwater samples will be collected or analyzed as part of Site cleanup and restoration activities.

Data Quality Objectives (DQOs) are qualitative and quantitative statements that clearly state the objective of a proposed project, define the most appropriate type of data to collect, determine the appropriate conditions for data collection, and specify acceptable decision error limits that establish the quantity and quality of data needed for decision making. The DQOs are based on the use of the data that will be generated. Different data uses may require different quantities of data and levels of quality.

1.4.1 Analytical Quality Objectives

Analytical quality objectives are identified so that the analysis will accurately and adequately identify the contaminants of concern, and so that the analysis selected will be able to achieve quantitation limits less than or equal to the target cleanup levels.

1.4.1.1 Field Screening

Field-screening instruments provide a lower quality of analytical data than laboratory equipment in a controlled environment. However, field methods provide rapid "real-time" results for field personnel in order to guide field decision-making processes. These techniques are often used for health and safety monitoring, initial site characterization to locate areas for sample collection, and preliminary comparison of remedial objectives. During sampling and activities, the breathing space of site personnel may be monitored for the presence of volatile organic compounds (VOCs) using a photoionization detector (PID). The PID will also be used to perform field screening of soil in order to assist in the selection of samples submitted for laboratory analysis. In general, the soil interval with the highest PID readings at a boring or sampling location will be submitted to the laboratory. If no VOCs are detected by the PID, samples will be selected for laboratory analysis based on the following:

- The presence of obvious discoloration, odor, or other visible signs of contamination.
- A sample from a depth corresponding to the subsurface zone expected to contain the greatest concentration of contaminants based on the type of release, and the history of the area being investigated will be submitted. This selection will be determined by the GeoEngineers project manager.

Field screening methods are described further in Appendix A of the SMP (**Appendix A**).

1.4.2 Project Quality Objectives

The project quality objectives process is a series of planning steps designed so that the type, quantity, and quality of environmental data used in decision making are appropriate for their intended application. There are five steps in the project quality objectives process which include problem statement, decision identification, decision inputs, assessment boundary, and the decision process. The details of these steps are provided in the following sections.

1.4.2.1 Problem Statement

U.S. EPA cleanup funding will be used to finalize the Draft Analysis of Brownfield Cleanup Alternatives (ABCAs) for each of the Properties, prepare bid specifications, procure remedial contractors and an environmental consultant, and to execute and document the remedial activities. The proposed cleanup plan incorporates use of green or sustainable methods or materials. The ABCA is based on a SMP developed for the Properties in June of 2016 and submitted to the Ecology on May 26, 2015 for review and approved on June 23, 2016. The SMP was revised in May of 2017 to include modifications to Section 8.0 which outlines procedures to mark and record areas where contaminated soil remains at the Properties.

1.4.2.2 Decision Identification

Soil characterization data collected during previous investigations will be used to determine soil excavation and handling recommendations. To assess the potential impacts of each soil category on the feasibility of property redevelopment, the City will ask the following questions:

- Do contaminant levels exceed applicable standards such as those specified by Ecology in MTCA 173-340 for soil cleanup, and/or risk-based cleanup standards?
- Can the contaminants be managed by eliminating exposure pathways through engineering and institutional controls?
- Will the Properties require remediation prior to redevelopment?
- If remediation is too costly based on the expected land use, can the Properties be developed for another use?

1.4.2.3 Decision Inputs

Soil samples will be collected as needed for analysis as described in the Stantec SOPs presented in **Appendix F**. In order to assess the level of contamination, whether the soil is appropriate for reuse at the Properties, and to guide handling recommendations. Soil samples may also be collected to either assess the data gaps identified from work previously completed.

Such data gaps or environmental conditions will be evaluated to provide answers to the following types of questions:

- What is the level of potential exposure to surface or subsurface soils at the Properties?
- What is the level of potential exposure to surface water and associated sediments at the Properties?
- What is the level of potential exposure to groundwater at the Property?
- Have past uses of the Properties (or adjacent properties) impacted the soil, sediment, surface water, or groundwater?
- Did past handling or storage activities, if any, impact the Properties?
- Have former aboveground storage tanks impacted the surrounding media at the Properties?
- Does fill material (such as slag) used at the Properties contain contaminants that may impact soil, sediment, surface water, or groundwater?

1.4.2.4 Assessment Boundary

A site map showing the Project boundary is provided as **Figure 3**. Although the vertical assessment boundary will likely vary based on the end-use of the Properties, full delineation of both the horizontal and vertical extent of contamination is generally required by Ecology for all sites where releases of petroleum or other contaminants have occurred.

1.4.2.5 City Decision Process

Ecology's generic numerical standards may be the applicable State standards for cleanup criteria. Soils may be compared to both to the generic (Method A,) and site-specific risk-based (Method B) soil Cleanup Levels (CULs) contained in MTCA 173-340-700, as applicable. Industrial CULs may be applicable depending on land use regulations and requirements under the MTCA.

Contaminant levels in sediments will be evaluated based upon the guidelines stated in WAC 173-340-760 which refers to standards noted in WAC 173-204.

Should sample results exceed the applicable Ecology cleanup standards, the City's response actions at any individual site will be determined not only by remedial requirements, but a wide range of considerations, restrictions, and legal and other requirements. A general approach is outlined below for the decision-making process that will be used for sites where the City makes a decision to proceed with the remedial alternatives process.

- If contaminant levels exceed the Ecology criteria, then the City may opt to resample the specific locations associated with elevated contaminant levels. If any of the resample results confirm the original data, the City will consider the second option listed below. If all

the resample results are below Ecology limits, no further action will be pursued at the property if there is a basis for considering the second set of results to be more accurate and representative of site conditions.

- If soil contaminant levels exceeding MTCA CULs are associated only with a specific exposure pathway, the City may then conduct a property-specific risk assessment, and pursue an exclusion of exposure pathways through the use of engineering and institutional controls.
- If an exposure pathway cannot be eliminated through engineering or institutional controls, then the City may develop a Cleanup Action Plan to meet the needs of the proposed future use of the property.

1.5 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT

The overall QA objective for each project is to develop and implement procedures for field sampling, COC protocols, laboratory analysis, and reporting in accordance with State of Washington protocols for physical or chemical parameters subject to Ecology regulatory authority. Specific procedures for sampling, COC, laboratory instrument calibration, laboratory analysis, data reporting, internal quality control, audits, preventive maintenance of field equipment, and corrective action are described in other sections of this QAPP.

DQOs for measurements during this project will be addressed in terms of precision, accuracy, representativeness, completeness, comparability, and sensitivity (PARCCS). The numerical PARCCS parameters will be determined from the project DQOs. The DQOs and resulting PARCCS parameters will require that sampling be performed using standard methods with properly operated and calibrated equipment and conducted by trained personnel. The PARCCS parameters are defined below.

1.5.1 Precision

Precision is the degree of agreement among repeated measurements of the same parameter under the same or similar conditions. Precision is reported as either relative percent difference (RPD) or relative standard deviation (RSD), depending on the end use of the data.

1.5.1.1 Field Precision Objectives

Field precision will be assessed through collection and analysis of field duplicate samples. RPDs will be calculated for detected analytes from investigative and field duplicate samples. Analysis results for water matrix samples can be more readily duplicated due to the homogeneous nature of the sample; conversely, the duplication of soil and sediment sample results is much more difficult due to the heterogeneous nature of the samples. Due to this difficulty, RPDs of ±35 percent and ±50 percent for water and soil sample field duplicates, respectively, will be used as advisory limits for analytes detected in both investigative, and field duplicate samples at concentrations greater than or equal to five times its quantitation limit. A summary of field duplicate samples to be collected is presented in **Table 3**, along with the other quality control samples. Per Ecology requirements or guidance, field duplicate samples must be provided for each matrix (sediment, surface water, etc.) sampled. The minimum number of field duplicate samples required for each round of sampling is one for every twenty samples. If there are fewer than twenty samples per matrix, one field duplicate per matrix will be submitted.

1.5.2 Accuracy

Accuracy is the extent of agreement between an observed or measured value and the accepted reference or true value of the parameter being measured.

1.5.2.1 Field Accuracy Objectives

The objective of the field sample collection procedure is to collect the samples using methods that do not allow the samples to be affected by sources external to the sample, such as sample contamination by ambient conditions or inadequate equipment decontamination procedures. Sampling accuracy will be assessed by evaluating the results of equipment and trip blank samples for contamination.

A trip blank will consist of a laboratory-prepared sample of reagent-grade water for water samples. For soil samples, the trip blank will consist of lab-grade sand with methanol (for mid to high range VOCs) or without preservative (for low-level VOCs). Trip blanks will accompany sample containers and be subjected to the same handling procedures as the field samples but will not be opened and will be shipped back to the laboratory with the samples. Trip blanks are required only when VOCs will be analyzed. Trip blanks will be submitted at the rate of one trip blank per shipping container containing field samples for laboratory VOC analysis. The trip blank samples will provide a means for identifying and quantifying potential cross contamination of samples by VOCs during shipment and handling.

When non-dedicated equipment is used for sample collection, equipment blanks will be collected by pouring laboratory-prepared water or distilled water over or through the field sampling equipment and collecting the rinsate in the proper analytical containers. Equipment blanks must be submitted to the laboratory with investigative samples and analyzed for the same parameters as the investigative samples. The minimum required by U.S. EPA is one per twenty field samples per matrix; or, if less than twenty samples are collected, one equipment blank per day per sample matrix.

1.5.2.2 Laboratory Accuracy Objectives

Laboratory accuracy will be assessed by determining percent recoveries from the analysis of laboratory control samples (LCSs) or standard reference materials (SRMs). Matrix spike/matrix spike duplicate (MS/MSD) samples are analyzed and utilized to determine laboratory accuracy by determining percent recoveries. MS/MSD samples will be collected for organic and inorganic analyses at a minimum frequency of one per twenty or fewer samples per matrix. The equation used to determine the analytical accuracy for this project is presented in Section 4.3.2.3.

The accuracy of any organics analyses performed will also be monitored through analysis of surrogate compounds. Surrogate compounds are added to each sample, standard, blank, and QC sample prior to sample preparation and analysis. Surrogate compounds are not expected to

be found in samples either due to natural occurrence or as environmental contaminants of concern, but behave analytically similar to the compounds of interest. Consequently, surrogate compound percent recoveries will provide information on the effect that the sample matrix exhibits on the accuracy of the analyses.

In addition, please see the QA Manuals presented in **Appendix D** of this QAPP for the laboratory.

1.5.3 Representativeness

Representativeness is a qualitative term that describes the extent to which a sampling design adequately reflects the environmental conditions of the site. It also reflects the ability of the sample team to collect samples and laboratory personnel to analyze those samples in a manner such that the data generated accurately and precisely reflect the conditions at the site.

1.5.3.1 Measures to Achieve Representativeness of Field Data

Representativeness will be achieved by establishing the level of allowable uncertainty in the data and then statistically determining the number of samples needed to characterize the population through the DQO process. It will also be achieved by ensuring that sampling locations are properly selected. Representativeness is dependent upon the proper design of the sampling program and will be accomplished by adherence to this QAPP, the property-specific SAPs, and standard procedures. The QA goal is to have all samples and measurements be representative of the media sampled. Soil sample intervals will be homogenized for all analyses except VOCs to promote collection of representative soil samples.

1.5.3.2 Measures to Achieve Representativeness of Laboratory Data

Representativeness of laboratory data cannot be quantified. However, representativeness of laboratory data will be achieved through adherence to the prescribed analytical methods and procedures, including holding times, blanks, and duplicates.

1.5.4 Completeness

Completeness is defined as the measure of the quantity of valid data obtained from a measurement system compared to the quantity that was expected under normal conditions. While a completeness goal of 100 percent is desirable, an overall completeness goal of 90 percent may be realistically achieved under normal field sampling and laboratory analysis conditions.

1.5.4.1 Field Completeness Objectives

The field sampling team will take measures to generate data in the field that are valid and usable to achieve project objectives. However, some samples or sample containers may be lost or broken during handling and transit. Therefore, field completeness goals for this project are to have

valid data for 90 percent of all samples. The equation for calculating completeness is presented in Section 4.3.5.

1.5.5 Comparability

The confidence with which one data set can be compared to another is a measure of comparability. The ability to compare data sets is particularly critical when a set of data for a specific parameter is compared to historical data for determining trends.

1.5.5.1 Measures to Achieve Comparability of Field Data

Comparability of field data will be achieved through adherence to the QAPP and through proper handling and analysis of all samples. Additionally, efforts will be made to have sampling completed in a consistent manner by the same sampling team.

1.5.5.2 Measures to Achieve Comparability of Laboratory Data

Analytical data are comparable when the samples are collected and preserved in the same manner followed by laboratory analysis with the same standard method and reporting limits. Data comparability is limited to data from the same environmental media. Analytical method quality specifications have been established to produce comparable data results. **Table 2** summarize the laboratory reporting limits.

1.5.6 Sensitivity

Sensitivity is the ability of a method or instrument to detect a parameter to be measured at a level of interest.

1.5.6.1 Measures to Achieve Field Sensitivity

The sensitivity of the PID used to screen samples for organic vapors is relative to background readings in ambient air.

1.5.6.2 Measures to Achieve Laboratory Sensitivity

The sensitivity requirements for laboratory analyses will meet any applicable State of Washington or Ecology standards for the environmental media sampled. If analytical methods are deemed insufficiently sensitive, alternative analytical methods may be utilized. Additionally, minimum laboratory reporting limits, which exceed applicable State of Washington or Ecology standards, will be evaluated using the following line of reasoning:

- Is the compound expected to be a chemical of concern? Does the reporting limit exceed Ecology standards? Was the compound detected at adjacent sample locations? If the compound is not an expected chemical of concern or detected in the sample, the

compound will be considered non-detect. If the compound is considered a chemical of concern and/or was detected at adjacent locations, the compound will be evaluated for risk purposes using half the laboratory reporting limit.

Table 2 present the laboratory reporting limits.

1.6 DOCUMENTATION RECORDS

Project documentation records will include field forms, field books, laboratory data sheets, COC forms, and technical papers. Stantec, GeoEngineers and the City will retain the records generated during this project for a minimum of five years following the completion of this project.

At a minimum, the ~~draft and final~~ remedial action report submittal package will include the following:

- Text describing field-sampling methodologies, analytical results, conclusions, and recommendations.
- Figures showing property location, property boundaries, sampling locations and summaries of impacted areas for each of the Properties.
- Tables comparing laboratory data to the applicable standards.
- Tables summarizing QA/QC analytical results.
- Complete laboratory data reports, including copies of all COC records.
- Copies of soil boring logs.
- Other relevant material needed to support property redevelopment including areas where impacted or contaminated soils were left in place on contained within a repository;
- Data Assessment Report which discusses and compares overall field duplicate precision data from multiple data sets collected for each matrix, analytical parameter, and concentration level.

2.0 DATA GENERATION AND ACQUISITION

The purpose of the QAPP is to provide procedures that will be used to produce reliable data throughout the project by:

- Generating valid and high integrity data;
- Providing mechanisms for ongoing control of data quality;
- Evaluating data quality in terms of PARCCS; and
- Providing usable, quantitative data for analysis, interpretation, and decision making.

2.1 SAMPLING PROCESS DESIGN

Sample locations, analytical parameters, and frequency of sampling will be based on the construction work being performed and the intended reuse or disposal of the soil. Laboratory test parameters for the sampling program will include analysis for one or more of the parameters listed in the Laboratory Analyses Table (**Table 1**). The laboratory SOPs for these analytical parameters are presented in **Appendix D**.

Analytical parameters will be chosen based on information known regarding the representative contaminants most commonly associated with the former activities and/or identified areas at each property.

Sampling will occur in a stepwise process. During initial sampling activities, it is expected that a variety of chemicals of concern will be analyzed. The initial results may indicate that only certain chemicals of concern are present. Therefore, later rounds of sampling will include only those specific compounds or class of compounds present in the initial sampling events.

QA/QC samples will be submitted in accordance with the QAPP protocols presented in the following sections. Requirements for QA/QC samples are presented in **Table 3**.

2.2 ANALYTICAL METHODS REQUIREMENTS

To preserve the integrity of samples both before and during analyses, specific analytical methods and requirements for those methods will be followed. Samples will be collected, prepared, and analyzed in accordance with the analytical methods outlined in individual laboratory SOPs (**Appendix D**). The specific analytical methods and laboratory reporting limits for each parameter are presented on **Table 2**. Preparatory methods for analytical parameters are discussed in the laboratory SOPs included in **Appendix D**.

Proper sample containers, preservation, holding times, and volumes for each analytical parameter are outlined in **Table 4**. The laboratory will provide all sample containers and preservatives for soil samples collected for this project. Soil samples to be analyzed for VOCs

(including petroleum-related VOCs) or gasoline-range petroleum hydrocarbons organics will be collected, in accordance with U.S. EPA Method 5035A, using pre-cleaned, disposable, small-diameter TerraCore® or EnCore® samplers provided by the laboratory. The samplers produce soil plugs weighing approximately 5-grams. For soil samples to be analyzed by TestAmerica, the samplers will be used to fill one 40-millileter (mL) pre-tared amber glass volatile organic analyte (VOA) vial pre-preserved with 10 mL of methanol (samples for low-level VOCs will be placed in unpreserved pre-tared 40 mL VOA vials with a stir bar). Two plugs of soil (weighing a combined total of approximately 10 grams) will be added to each vial. If a larger volume of soil is required for analysis, a larger TerraCore® sampler will be obtained to eliminate the need to collect multiple smaller volume soil plugs. Low-level VOC sampling using sodium bisulfate as a preservative will not be conducted as part of this project.

All sample containers supplied by the laboratory will be cleaned according to U.S. EPA standards. QC documentation will be supplied with the sample containers and preservatives in order to verify their purity. The containers and preservatives can be traced back to their certificate of analysis by lot number. The QC documentation/certificate of analysis shall be maintained on file with the project laboratory. Additionally, the project laboratory shall provide the field team with trip blanks for any VOC analyses and laboratory-grade deionized water for rinsing field equipment and instruments.

2.3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Proper sample handling and custody procedures are crucial to achieving the required quality and validity of data obtained through field and laboratory analyses. For example, the admissibility of environmental data as evidence in a court of law is dependent upon the custody of the data. Custody procedures will be used to document the authenticity of data collected during the project. The data which require custody procedures include field samples and data files which may include field books, logs, and laboratory reports. An item is considered "in custody" if it is:

- In a person's possession;
- In view of the person after being in their possession;
- Sealed in such a manner that it cannot be tampered with after having been in physical possession; or
- In a secure area restricted to authorized personnel.

2.3.1 Sample Collection Documentation

Sample-handling procedures include field documentation, COC documentation, sample shipment, and laboratory sample tracking. Various aspects of sample handling and shipment, as well as the proposed sample identification system and documentation, are discussed in the following sections.

2.3.1.1 Field Books

Detailed records of field activities will be maintained in field books dedicated to the project. Entries will be dated and signed by personnel recording the data. The entries will be made in ink. Each field book will have a unique numerical identifier permanently attached, and each page will be numbered, permitting indexing of key data. At a minimum, information recorded in the field books will include documentation of sample locations, sampling times, types of samples collected, weather conditions, and any other information pertinent to the assessment or monitoring activity.

2.3.1.2 Field Identification System

Each sample collected during monitoring activities will be given a unique identification code. Each unique sample identification will consist of the following:

- *Project Identification Code*. A two- or four- digit designation will be used to identify the property from which the sample was collected. Examples of this include the following:

  CI – Canada Island

- *Sample Matrix Code*. Trip and equipment blanks will be further identified by a code corresponding to the sample matrix and the sample date:

  TB – trip blank sample
  EB – equipment blank sample

- *Location Code*. Lastly, each sample will be identified by a location code and interval as follows:

  DP-## - location of Geoprobe® or other direct-push boring

  TP-## - location of test pit

  HSA-## - location of hollow stem auger boring

  AR-## - location of air rotary boring

  The sample depths in feet below the ground surface will also be recorded and part of the sample identification code for soil samples. Either the sampling depth as an interval (for samples collected during drilling), or a single recorded depth (for discrete grab samples).

Examples:

CI:DP-01(5-10) = soil sample collected from direct push boring DP-01 at a depth interval of 5 to 10 feet bgs from the Canada Island area of the Properties-

TB1-02152018 = trip blank to be submitted with samples to be analyzed for VOCs on February 15, 2018

Note that field duplicate samples will be submitted "blind" to the laboratory, so that the sample cannot be identified with the location code. A unique location code will be used for duplicate samples.

Sample bottle labels appropriate for the size and type of containers shall be provided by each laboratory. The sample containers will be labeled at the time of sample collection but prior to being filled. Each label will indicate at a minimum:

- Sample identification
- Date/time of sample collection
- Sampler's initials
- Required analyses
- Type of preservative

All labels will be completed in waterproof ink. An example of a sample label is included in **Appendix E**.

2.3.1.3 Field Sample Handling

The possession and handling of samples will be documented from the time of collection until delivery to the laboratory. Stantec and GeoEngineers field personnel are responsible for adherence to COC procedures. Field personnel will maintain custody of all samples until they are relinquished to another custodian, the laboratory, or the freight shipper.

All samples to be submitted for laboratory analysis must be catalogued on a COC form using sample identification codes. A copy of the COC form is included in **Appendix E**. The date and time of collection will be recorded on the form, as well as the number of each type of sample, the method of preservation, and the type of analysis. The Stantec SOP for COC procedures is presented in **Appendix FE**.

2.3.1.4 Field Sample Packaging and Shipping

Samples will be packaged and transported in a manner which maintains integrity of the samples and permits the subsequent analyses to be performed within the prescribed holding times. Prior

to shipment, each sample container will be inspected for a label with the proper sample identification code.

Samples will be couriered or shipped via overnight mail to the laboratory. The laboratory will be contacted in advance to expect shipment so that sample holding times will be conserved. The COC forms will be sealed in a plastic bag and transported inside the sample cooler. Samples will be packed in the cooler using bubble-wrap packing materials and ice will be sealed in a Ziploc□-type bag. Any suspected highly contaminated samples will be physically isolated by sealing in a Ziploc□-type bag and if possible, a separate cooler. The cooler will be taped closed and custody seals provided by the laboratory will be attached to prevent tampering during transport, and to facilitate the detection of possible tampering (if the seals are broken). Upon relinquishing the sample cooler to the project laboratory, Stantec field personnel will assign custody of the samples to the laboratory by signing and dating the bottom of the COC form. One copy of the COC documentation will be retained by the Stantec data manager, and a second copy will be retained by the laboratory. Shipping labels/receipts will be retained by the Stantec data manager with the COC form. The integrity of the custody seals shall be noted by the laboratory on the COC form upon arrival.

2.3.1.5 Field Documentation

Field COC procedures will document the proper handling of each sample from collection in the field to delivery at the laboratory. Custody of samples shall be maintained and documented at all times. The documentation for each sample will include the following information:

- COC form
- Sample label with sample identification code
- Shipping documents

This documentation will allow for proper identification and verification of all samples upon arrival at the project laboratory.

2.3.2 Laboratory Chain of Custody

The project laboratory will perform laboratory custody procedures for sample receiving and log-in, sample storage, tracking during sample preparation and analysis, and storage of data in accordance with their SOPs. The laboratory project manager will be responsible for maintaining laboratory custody protocol. The laboratory procedures related to sample custody are presented in the QA Manuals for the laboratory **(Appendix D)**.

2.3.3 Final Evidence Files Custody Procedure

Stantec will be responsible for the custody of evidence files and will maintain and update contents of the files during the project. The evidence files will include all records relevant to sampling and

analysis activities such as field books, photographs, subcontractor reports, laboratory data deliverables, COC forms, and data reviews. Stantec will retain this file for a period of at least five years following the formal project completion date.

2.4 QUALITY CONTROL REQUIREMENTS

The quality control procedures provided in this QAPP require that the environmental data collected are of the highest standard feasible, as appropriate for the intended application. Facets of the quality control requirements are provided in the following sections.

2.4.1 Field Quality Control Requirements

Where applicable, QC checks will be strictly followed during the assessment through use of replicate measurements, equipment calibration checks, and data verification by Stantec field personnel. Field-sampling precision and data quality will be evaluated through use of sample duplicates, equipment blanks, and trip blanks. Sample duplicates provide precision information regarding homogeneity, handling, transportation, storage, and analysis. Equipment blanks will be used to demonstrate that proper decontamination procedures have been performed, and that no cross contamination has occurred during sampling or transportation. Trip blanks will be used with VOCs only, to better assess whether samples have been inadvertently exposed to sources of contamination during transport to the laboratory. If there is any discrepancy in the sample data, the Stantec project manager will be notified and, if deemed necessary, resampling of the questionable point scheduled. Requirements for field QA/QC samples are listed in **Table 3**.

2.4.2 Laboratory QC Requirements

The laboratory QA manager will be responsible for maintaining each laboratory's data precision and accuracy in accordance with state and federal specifications. Internal laboratory duplicates and calibration checks are performed on one of every twenty samples submitted for analysis. Other internal laboratory QA/QC is performed according to the laboratory SOPs. An additional set of samples will be collected for soil and submitted for laboratory MS/MSD analyses. Typically, the laboratory requires two to three sample containers for each sample location, therefore, four to six sample containers will be collected for laboratory MS/MSD analyses (i.e., six TerraCore® or EnCore® sample tubes). In the case of VOCs, twice the amount will be collected. If soil samples to be analyzed for VOCs are preserved in the field with methanol, additional sample volume is still required for the MS/MSD analyses (twice the amount).

2.5 INSTRUMENT CALIBRATION AND FREQUENCY

Calibration procedures for field and laboratory instruments are referenced in this section. Measuring and test equipment used in the field and laboratory will be subject to a formal calibration program. The program will require equipment of proper type, range, accuracy, and precision to provide data compatible with the specified requirements and the desired results. Calibration of measuring and test equipment may be performed internally using in-house reference standards, or externally by agencies or manufacturers.

The laboratories will be responsible for the calibration of their laboratory equipment. Stantec field personnel are responsible for calibration of Stantec field equipment, rented field equipment provided by vendors or subcontractors. Subconsultants conducting field work will be responsible for calibrating the equipment they use for this project.

Documented and approved procedures will be used to calibrate measurement and testing equipment. Widely accepted procedures, such as those published by U.S. EPA and the American Society for Testing and Materials (ASTM), or procedures provided by manufacturers in equipment manuals, will be adopted.

Calibrated equipment will be uniquely identified by the manufacturer's serial number, a Stantec equipment identification number, or by other means. These identification numbers will be attached to the equipment, along with a label indicating when the next calibration is due (only for equipment which does not require daily calibration). If this is not possible, records traceable to the equipment will be readily available for reference. It will be the responsibility of equipment operators to check the calibration status per the due date labels or records prior to using the equipment.

Measurement and testing equipment will be calibrated at prescribed intervals and/or as part of operational use. Frequency will be based on the type of equipment, inherent stability, manufacturer's recommendations, values given in national standards, intended use, and experience. Whenever possible, equipment will be calibrated using reference standards associated with nationally recognized standards or accepted values of physical constants. If national standards do not exist, the basis for calibration will be documented.

Physical and chemical reference standards will be used only for calibration. Equipment that fails calibration or becomes inoperable during use will be removed from service, segregated to prevent inadvertent use, and tagged to indicate the fault. Such equipment will be recalibrated and repaired to the satisfaction of the laboratory personnel or Stantec field personnel, as applicable. Equipment that cannot be repaired will be replaced.

Records will be prepared and maintained for each piece of calibrated measuring, and test equipment to document that established calibration procedures have been followed. Records

for rented field equipment and Stantec equipment, used only for this project, will be kept in the project files. The project laboratory will maintain individual laboratory calibration records.

2.5.1 Field Instrument Calibration

Instruments used to gather, generate, or measure field environmental data will be calibrated with sufficient frequency, and in such manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications. Field measurement instruments may include, but are not limited to, PID units used to detect VOCs. As applicable, field instruments will be calibrated daily prior to use. The calibration will be consistent with the standard procedure. The field calibration procedures are presented in the field SOPs located in **Appendix F**.

Calibration procedures will be documented in the field logbook and field sampling sheets. Documentation will include the following:

- Date and time of calibration
- Identity of the person performing the calibration
- Reference standard used, if applicable
- Reading taken and adjustments to attain proper reading
- Any corrective action

Trained personnel will operate field measurement equipment in accordance with the appropriate standard procedures or manufacturer's specifications. Stantec and GeoEngineers field technical staff members will examine field measurement equipment used during field sampling to verify operating condition. The Stantec field team liaison or GeoEngineers field team leader will periodically audit the calibration and field performance of the field equipment to demonstrate that the system of field calibration meets the manufacturer's specifications.

2.6 DATA MANAGEMENT

Stantec and GeoEngineers field technical staff members will manage raw data during field activities. Data such as geologic profiles will be recorded on the appropriate field forms or in field logbooks. The Stantec data manager will periodically collect data gathered during assessment activities, and as appropriate, will coordinate transfer of raw data to computer formats such as Microsoft® Excel or Microsoft® Access to better organize and track incoming data. This will enable the Stantec data manager to identify any data gaps. Any flaws in field QA/QC will be brought to the attention of the Stantec QA manager.

The laboratory project managers will be responsible for laboratory data management. Procedures for data review and data reporting are discussed in the laboratory QA Manuals, located in

Appendix D. Laboratory generated analytical data reports will present all sample results, including all QA/QC samples.

The data reports with Level II (lab QC) and will include:

- A laboratory narrative for the data set describing any out of control analyses and their effect on sample results.
- All sample results including the % moisture content for soil samples.
- An explanation of all laboratory applied data qualifiers.
- The MS/MSD results including the % recoveries and RPDs.
- Method blank results.
- LCS and LCS duplicate (LCSD) results including the % recoveries and RPDs.
- Laboratory duplicate results including RPDs.
- Surrogate results including % recoveries (as applicable per analysis).

The following data must be available upon request from the laboratory, on a case by case basis, should data issues arise:

- Summaries of daily calibration check samples (including notation of any outliers).
- Calibration blank results.

Soil results will be reported on a dry weight basis. All data, including QA/QC results, will become part of the project files, and will be maintained by the Stantec data manager. Upon report delivery, Stantec personnel will evaluate laboratory data in accordance with accepted statistical methodologies, supervised by the Stantec data manager.

3.0 ASSESSMENT AND OVERSIGHT

Performance and system audits will be completed to demonstrate that field sampling activities and laboratory analyses are performed in accordance with procedures established in this QAPP, including the attached SOPs. The audits may be both internal and external, as further described below.

3.1 TECHNICAL SYSTEMS AUDITS

Generally, system audits are a qualitative measure of adherence to overall sampling QA measures, including sample collection handling, decontamination procedures, COC, and recording requirements in the field, as well as sample receiving, log-in, and instrument operating records in the laboratory.

3.1.1 Field Data

A GeoEngineers and/or Stantec field technical staff member (most of whom are trained geologists, hydrogeologists or engineers) will be present at the site during sampling activities. The field technical staff member will provide the on-site supervision required during the project. The field technical staff member will be in daily contact with the GeoEngineers field team leader or Stantec field team liaison, who will then review compliance with the project objectives and sampling protocol outlined in this QAPP. Any anticipated modifications to the sampling or measuring procedures will be reported to the Project Manager and U.S. EPA Project Manager. GeoEngineers and Stantec field technical staff members will report modifications to the Stantec project manager and document the modification in the field logbook.

Sample data precision will be determined by the collection and subsequent analysis of sample duplicates, equipment blanks, and trip blanks to verify reproducibility.

3.1.2 Field Screening Instruments

GeoEngineers and Stantec field technical staff members will audit and maintain performance of field-screening instruments. Instruments will be calibrated according to the standard procedures located in **Appendix F**, and regular preventive maintenance will be performed as described in **Table 6**.

3.1.3 Report Preparation

Prior to submittal to the City and U.S. EPA, all reports will undergo both a peer and technical review conducted separately by Stantec project team members. Report components will be checked and initialed by a designated team member. The City will also review all reports prior to submittal to U.S. EPA.

3.1.4 Laboratory Data

Laboratory results will be reviewed for compliance against the DQO criteria for the level of reporting required.

3.2 PERFORMANCE EVALUATION AUDITS

Generally, performance audits are a quantitative measure of field sample collection and laboratory analyses quality.

3.2.1 Field Audits

The Stantec QA manager will conduct audits of field activities. U.S. EPA may also conduct an independent field audit. At least one field audit will be completed near the beginning of the sample collection activities. If a gap in field data collection activities of more than six months occurs during implementation of the grant, a second field audit will be completed. Field audits may also be utilized when staff new to the project, are performing initial field investigation activities.

The field audit will include the following checklist:

Item	Description of Field Audit Activities	QA Manager Initials
1.	Review of field-sampling records	
2.	Review of field-measurement procedures	
3.	Examination of the application of sample identifications following the specified protocol	
4.	Review of field instrument calibration records and procedures	
5.	Recalibration of field instruments to verify calibration to the manufacturer's specifications	
6.	Review of the sample handling and packaging procedures	
7.	Review of COC procedures	

Any deficiencies observed during the audit shall be noted in writing. A follow-up audit may be completed if deemed necessary by the project QA manager. Corrective action procedures may be implemented. Such actions will be documented in the field logbook.

3.2.2 Laboratory Audits

One of two laboratories will be utilized to perform analytical services required during the assessments. As discussed in Section 1.4.1.2, the laboratory is State of Washington-certified or National Voluntary Laboratory Accreditation Program (NVLAP)-certified. Documentation is presented in **Appendix C**. The laboratory QA manager will be responsible for ensuring that laboratory data precision and accuracy are maintained in accordance with specifications and laboratory SOPs.

3.3 REPORTS TO MANAGEMENT

For the duration of the project, quarterly financial and progress reports will be prepared by the Grantee project manager with assistance from the Stantec project manager and submitted to the U.S. EPA project manager. These reports will serve to U.S. EPA of project progress and any significant interim findings identified. This will streamline the process, addressing issues as they arise and adjusting the program to better define environmental concerns.

4.0 DATA VALIDATION AND USABILITY

This section describes the QA activities which will be performed to demonstrate that collected data are scientifically defensible, properly documented, of known quality, and meet project objectives. All analytical data collected for the project will be validated.

The following three steps will be followed to demonstrate that project data quality needs are met.

1. **Data Verification** – Data verification is a process of evaluating the completeness, correctness, and contractual compliance of a data set against the method standard, SOP, or contract requirements. Data verification will be performed internally by the analytical group or laboratory generating the data. Additionally, data may be checked by an external entity. Data verification may result in accepted, qualified, or rejected data.
2. **Data Validation** – Data validation is an analyte- and sample-specific process that extends the qualification of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine the analytical quality of specific data sets. Data validation criteria are based on the measurement performance criteria of the project QAPP. Data validation results are accepted, qualified, or rejected data.
3. **Data Usability Assessment** – Data usability assessment is the process of evaluating validated data to determine if the data can be used for the purpose of the project (i.e., to answer the environmental questions regarding the project results and/or to make environmental decisions). Data usability will include the following sequence of evaluation:
    - First, individual data sets will be evaluated to identify measurement performance/usability issues or problems affecting the ultimate achievement of project DQOs.
    - Second, an overall evaluation of all data generated for the project will be performed.
    - Finally, the project-specific measurement performance criteria and data validation criteria will be evaluated to determine if they were appropriate for meeting project DQOs.

In order to perform the data evaluation steps above, reported data will be supported by complete laboratory data packages, which include sample receipt and tracking information, COC records, tabulated data summary forms, and raw analytical data for analyzed field samples, standards, QC checks and QC samples, and all other project-specific documents generated.

4.1 INSTRUCTIONS FOR DATA REVIEW, VALIDATION AND VERIFICATION REQUIREMENTS

Stantec will estimate the potential effect each deviation from this QAPP may have on usability of associated data items, quality of reduced and analyzed data, and effects on the decision process.

The following procedures will be implemented to verify and validate data collected:

- *Sampling Design* – How closely a measurement represents the actual environment at a given time and location is a complex issue. Each sample will be checked for compliance with specifications, including type and location. Stantec will note deviations from the specifications, and discuss them with the U.S. EPA project manager.
- *Sample Collection Procedures* – Sample collection procedures identified in this QAPP will be followed. If field conditions require deviations, they will be discussed with the U.S. EPA project manager.
- *Sample Handling* – Deviations from the planned sample handling procedures will be noted on the COC forms and in the field logbooks.

GeoEngineers and Stantec field technical staff members will evaluate sample containers and preservation methods used to demonstrate they are in accordance with **Table 4**.

- *Analytical Procedures* – Each sample result will be reviewed to verify that the appropriate analytical procedures were used to generate the data. Data validation will include an assessment of how seriously a sample deviated beyond the acceptance limit so that potential effects of the deviation can be evaluated.
- *Quality Control* – QC checks to be performed during sample collection, handling, and analysis are specified in an earlier section of this QAPP. For each specified QC check, the procedures, acceptance criteria, and corrective action will be specified. During data validation, the corrective actions taken, affected samples, and potential effect of actions on the validity of data will be documented.
- *Calibration* – Field and laboratory instrument calibrations will be documented to demonstrate that calibrations:
    - Were performed within an acceptable time frame prior to generation of measurement data;
    - Were performed in proper sequence;
    - Included the proper number of calibration points;
    - Were performed using a standard that bracketed the range of reported measurement results;

- Had acceptable linearity checks and other checks and that the measurement system was stable when calibration was performed.

When calibration problems are identified, any data produced between the suspect calibration event, and any subsequent recalibration will be flagged to alert data users.

- *Data Reduction and Processing* – Data integrity checks will be performed to evaluate accuracy of raw data and compare important events and duplicate rekeying of data in order to identify data entry errors. The laboratory QA Manual (**Appendix D**) discusses data processing procedures.

4.2 INSTRUCTIONS FOR VALIDATION AND VERIFICATION OF METHODS

This section describes the process which will be followed to verify and validate the project data.

4.2.1 Verification

Field data will be verified by the Stantec QA manager or Stantec data manager, who will review field documentation and COC records. Data from direct-reading instruments, such as a PID, will be verified by the field team lead or liaison by review of calibration and operating records. The laboratory data will be verified with respect to COC, units of measure, and citation of analytical methods. Data verification procedures will include reviewing and documenting sample receipt, sample preparation, sample analysis (including internal QC checks), data reduction, and reporting. Any deviations from acceptance criteria, corrective actions, and data determined to be of limited usability (i.e., laboratory-qualified data) will be noted in the case narrative of the laboratory report. The QA manager or data manager will also verify use of blanks and duplicates. All applicable reference and identification codes and numbers will be reviewed as part of the documentation.

4.2.2 Validation

Stantec will conduct data validation consistent with the procedure identified in Section 1.5 of this QAPP. The data verification/validation procedure will identify data as acceptable, of limited usability, qualified or estimated, or rejected. Conditions which will result in data being qualified or estimated or rejected are identified in Section 1.5 of this QAPP. Data verification/validation results will be provided in data validation memoranda which will be provided to Stantec's project manager and included with the remedial action report documents. All sampling, handling, field analytical data, and laboratory data will be validated by entities external to the data generator. The validation procedure will specify the verification process of the QC measures used in the field and laboratory. Laboratory data validation procedures are discussed in the QA Manual (**Appendix D**).

Each analytical report will be reviewed for compliance with the applicable method and quality of the data reported.

If data are determined to be unusable, corrective action may be taken. Potential corrective actions may include resampling by the field team or laboratory reanalysis of the samples. Corrective actions will depend on ability to mobilize the field team, and whether data are critical to project DQOs. Should Stantec's QA manager identify a situation requiring corrective action during data verification/validation, Stantec's project manager will be responsible for approving implementation of the corrective action.

4.3 INSTRUCTION FOR RECONCILIATION WITH DATA QUALITY OBJECTIVES

This section describes scientific and statistical procedures/methods which will be used to determine whether data are of the right type, quality, and quantity to support environmental decision-making for the project.

The Data Quality Assessment (DQA) process is described in *Guidance for the Data Quality Assessment Process: Practical Methods for Data Analysis*, EPA QA/G-9, July 1996 (U.S. EPA, 1996). EPA QA/G-9 will guide data assessment for this project. The DQA process will consist of five steps:

1. Review DQOs and sampling design
2. Conduct preliminary data review
3. Select statistical test
4. Verify assumptions
5. Draw conclusions from the data

While the formal DQA process presented in the guidance may not be followed in its entirety, a systematic assessment of data quality will be performed. This process will include a preliminary data review. Data will be presented in tables and figures to identify trends, relationships, and anomalies.

The overall usability of data will be assessed by evaluating the PARCCS of the data set to the measurement performance criteria in Section 1.5 of this QAPP using statistical quantities as applicable. The procedures and statistical formulas to be used for these evaluations are presented in the following sections.

4.3.1 Precision

In order to meet the needs of the project, data must meet the measurement performance criteria for precision. Project precision will be evaluated by assessing the RPD data from the field

duplicate samples. Analytical precision will be evaluated by assessing the RPD data from either duplicate spiked sample analyses or duplicate sample analyses. The RPD between two measurements is calculated using the following simplified formula:

$$RPD = \frac{|R_1 - R_2|}{(R_1 + R_2)/2} \quad X\ 100$$

where: R_1 = value of first result
R_2 = value of second result

Overall precision for the sampling programs will be determined by calculating the mean RPD for all field duplicates in a given sampling program. This will provide an evaluation of the overall variability attributable to the sampling procedure, sample matrix, and laboratory procedures in each sampling program.

The overall precision requirement will be the same as the project precision. It should be noted that the RPD of two measurements can be very high when the data approach the quantitation limit of an analysis. The calculation of the mean RPD will include only the RPD values for field duplicate sample analyte data that are greater than or equal to five times the quantitation limit for an analysis.

Poor overall precision may be the result of one or more of the following:

- Field instrument variation
- Analytical measurement variation
- Poor sampling technique
- Sample transport problems
- Heterogeneous matrices

In order to identify the cause of imprecision, the field-sampling design rationale and sampling techniques should be evaluated by the reviewer, and both field and analytical duplicate/replicate sample results should be reviewed. If poor precision is indicated in both the field and analytical duplicates/replicates, then the laboratory may be the source of error. If poor precision is limited to the field duplicate/replicate results, then the sampling technique, field instrument variation, sample transport, or heterogeneous sample matrices may be the source of error.

If the QA/QC report supplied by the analytical laboratory or the data validation process indicates that analytical imprecision exists for a particular data set, then the impact of that imprecision on data usability must be discussed in a Data Assessment Report. The Data Assessment Report will be prepared by Stantec and submitted as part of the remedial action report document.

When project-required precision is not achieved, and project data are not usable to adequately address environmental questions and to support project decision making, the Data Assessment Report will address how this problem will be resolved and discuss need for resampling.

4.3.2 Accuracy and Bias

In order to meet the needs of data users, project data will follow the measurement performance criteria for accuracy and bias as described in Section 1.5.2.

4.3.2.1 Sample Contamination

Data for QC check samples will be reviewed to evaluate accuracy and potential bias of sample results. If the data indicate that contamination not related to project environmental concentrations was introduced into a field sample due to sample collection or handling methodologies, the impact of that contamination on data usability will be discussed in the Data Assessment Report, and the Stantec project manager and field team leader will be notified. Stantec will use the data to differentiate possible contamination introduced as a result of field sample collection, and transport methods and contamination introduced in the laboratory at the time of sample preparation and analysis. It should be noted that sample contamination may result in either a negative or a positive bias. For example, improperly cleaned sample containers for metals analysis may result in retention of metals on interior container walls. This will result in lower metals concentrations reported than are actually present in the environmental sample, which is a negative bias. A positive bias will occur when sample container contamination results in an additive effect, where reported analyte concentrations are higher than the true sample concentrations for that analyte.

4.3.2.2 Overall Accuracy/Bias

Data from method/preparation blank samples provide an indication of laboratory contamination, which may result in sample data bias. Sample data associated with method/preparation blank contamination will be identified during the data verification/validation process. Sample data associated with method/preparation blank contamination are evaluated during the data validation procedure to determine if analytes detected in the samples, and the associated method/preparation blanks are "real" or are the result of laboratory contamination. The procedure for this evaluation involves comparing the concentration of the analyte in the sample to the concentration of the method/preparation blank, taking into account adjustments for sample dilution and dry-weight reporting. In general, the sample data are qualified as not detected if the sample concentration is less than five times (ten times for common laboratory contaminants) the method/preparation blank concentration. Typically, the common quantitation limit for the affected analyte is elevated to the concentration detected in the sample.

Data from field blanks and trip blanks provide an indication of field and transportation conditions, which may result in bias of sample data. Sample data associated with contaminated field and

trip blank samples are identified during the data verification/validation process. The evaluation procedure and qualification of sample data associated with field blank and trip blank contamination is performed in the same manner as the evaluation procedure for method blank sample contamination.

Surrogate spike recoveries provide information regarding the accuracy/bias of the organic analyses on an individual sample bias. Surrogate compounds are not expected to be found in the samples and are added to every sample prior to sample preparation/purging. The percent recovery data provide an indication of the effect of the sample matrix on the preparation and analysis procedure. Sample data exhibiting matrix effects will be identified during data verification/validation process.

Matrix spike sample data can provide information regarding the accuracy/bias of the analytical methods relative to the sample matrix. Matrix spike samples are field samples that have been fortified with target analytes prior to sample preparation and analysis. The percent recovery data provide an indication of the effect of the sample matrix on the preparation and analysis procedure. Sample data exhibiting matrix effects will be identified during data verification/validation process.

Analytical accuracy/bias will be determined by evaluating the percent recovery data of LCSs. LCSs are artificial samples prepared in the laboratory using a blank matrix that is fortified with analytes from a standard reference material that is independent of the calibration standards. LCSs are prepared and analyzed in the same manner as the field samples. The data from LCS analyses will provide an indication of the accuracy and bias of the analytical method for each target analyte.

Percent recovery is calculated using the following formula:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \quad X \ 100$$

where: SSR = Spiked Sample Result

SR = Sample Result or Background

SA = Spike Added

The percent recovery of a LCS is determined by dividing the measured value by the true value and multiplying by 100.

Overall accuracy/bias for the sampling events will be determined by calculating the percent accuracy measurements that meet the measurement performance criteria specified in Section 1.5.2 of this QAPP. Overall accuracy will be considered acceptable if the surrogate percent

recoveries are met for at least 75 percent of the samples, the LCS percent recoveries are met for all samples, and the MS/MSD percent recoveries are met for at least 75 percent of the samples.

For accuracy/bias, the Data Assessment Report will: 1) discuss and compare overall contamination and accuracy/bias data from multiple data sets collected for each matrix, analytical parameter, and concentration level, 2) describe limitations on the use of project data if extensive contamination and/or inaccuracy/bias exist, or when it is limited to a specific sampling or laboratory analytical group, data set, analytical parameter, or concentration level, 3) identify qualitative and/or quantitative bias trends in multiple performance evaluation sample results for each matrix, analytical parameter, and concentration level, 4) discuss the impact of any qualitative and/or quantitative trends in bias on the sample data, and 5) report any performance evaluation samples that have false positive and/or false negative results 6) discuss the impact of these results on data usability, clearly differentiate between usable and unusable data for the users, if unusable data are identified..

When project-required accuracy/bias is not achieved, and project data are not usable to adequately address environmental questions and to support project decision making, the Data Assessment Report will address how this problem will be resolved and discuss potential need for resampling.

4.3.3 Sample Representativeness

In order to meet the needs of the data users, project data must meet the measurement performance criteria to sample representativeness specified in Section 1.5.3.

Representativeness of samples will be assessed by reviewing results of field audits and data from field duplicate samples. If field duplicate precision checks indicate potential spatial variability, additional scoping discussions and subsequent resampling may be necessary in order to collect more representative data that reflects heterogeneous site conditions. Overall sample representativeness will be determined by calculating the percent of field duplicate sample data which achieved the RPD criteria specified in Section 1.5.3 of this QAPP. Overall sample representativeness will be considered acceptable if results of field audits indicate that the approved sampling methods or alternate acceptable sampling methods were used to collect the samples, and field duplicates RPD data are acceptable for at least 75 percent of samples.

For representativeness, the Data Assessment Report will: 1) discuss and compare overall representativeness for each matrix, parameter, and concentration level, 2)describe limitations on use of project data when overall non-representative sampling has occurred or when non-representative sampling is limited to a specific sampling group, data set, matrix, analytical parameter, or concentration level, 3) address how data representativeness issues will be resolved and discuss the need for resampling if project data do not adequately address environmental questions and support project decision making, and 4) clearly differentiate between usable and unusable data for the users, if unusable data are identified.

4.3.4 Sensitivity and Quantitation Limits

In order to meet the needs of the data user, project data must meet the measurement performance criteria for sensitivity as specified. Low point calibration standards should produce a signal at least ten times the background noise levels and should be part of a linear calibration curve.

The quantitation limits (QLs) for the sample data will be reviewed so that the sensitivity of the analyses is sufficient to achieve any applicable State of Washington or Ecology standards. The method/preparation blank sample data and LCS percent recovery data will be reviewed to assess compliance with the measurement performance criteria specified in Section 1.5.6 of this QAPP.

Overall sensitivity will be assessed by comparing the sensitivity for each monitoring program to the detectability requirements for the analyses. Overall sensitivity will be considered acceptable if QLs for samples are less than the acceptable evaluation criteria.

It should be noted that QLs may be elevated as a result of high concentrations of target compounds, non-target compounds, and matrix interferences (collectively known as sample matrix effects). In these cases, the sensitivity of the analyses will be evaluated on an individual sample basis relative to the applicable evaluation criteria. The need to investigate the use of alternate analytical methods may be required if the sensitivity of the analytical methods identified in this QAPP cannot achieve the evaluation criteria because of sample matrix interference.

With regard to sensitivity and QLs, the Data Assessment Report will: 1) discuss and compare overall sensitivity and QLs from multiple data sets collected for the project for each matrix, analytical parameter, and concentration level, 2) describe limitations on use of project data if project-required sensitivity and QLs were not achieved for all project data or when it is limited to a specific sampling or laboratory/analytical group, data set, matrix, analytical parameter, or concentration level, 3) discuss impact on data usability if the laboratory QA/QC reports indicate that sensitivity and/or QLs were not achieved, 4) address how data usability issues will be resolved and discuss the need for resampling if project data do not adequately address environmental questions and support project decision making, and 5) clearly differentiate between usable and unusable data for the users, if unusable data are identified.

4.3.5 Completeness

In order to meet the needs of the data users, project data will follow the measurement performance criteria for data completeness outlined in Section 1.5.4.

Completeness will be assessed by comparing the number of valid (usable) sample results to the total possible number of results within a specific sample matrix and/or analysis. Percent completeness will be calculated using the following formula:

$$\% \text{ Completeness} = \frac{\text{Number of Valid (usable) measurements}}{\text{Number of Measurements Planned}} \text{ X } 100$$

Overall completeness will be assessed by calculating the mean percent completeness for the entire set of data obtained for each sampling program. The overall completeness for the project will be calculated when all sampling and analysis is concluded. Overall completeness will be considered acceptable if at least 90 percent of the data are determined valid.

For completeness, the Data Assessment Report will: 1) discuss and compare overall completeness of multiple data sets collected for each matrix, analytical parameter, and concentration level, 2) describe the limitation on use of project data if project-required completeness was not achieved for the overall project or when it is limited to a specific sampling or laboratory/analytical group, data set, analytical parameter, or concentration level, and 3) address how data completeness issues will be resolved and discuss the need for resampling if project data do not adequately address environmental questions and support project decision making.

4.3.6 Comparability

In order to meet the needs of the data users, project data will follow the measurement performance criteria for comparability outlined in Section 1.5.5.

The comparability of data sets will be evaluated by reviewing the sampling and analysis methods used to generate the data for each data set. Project comparability will be deemed acceptable if the sampling and analysis methods specified in this QAPP, and any approved QAPP revisions or amendments are used for generating data for any media sampled during the assessments.

For long-term monitoring projects, data comparability is extremely important. For these projects, data comparability will be assessed by comparing project data with previously generated data to determine the possibility of false positives and/or false negatives. Data variations may reflect a changing environment or indicate sampling and/or analytical error. Comparability criteria will be established to evaluate these data sets in order to identify statistical outliers to trigger resampling as verified. Also, overall data comparability for long-term monitoring projects will be assessed by evaluating analyte concentrations over time. The data from monitoring events will be evaluated for trends, if necessary, using the Mann-Kendall test described in Section 4.3.4.1 of EPA QA/G-9. Suspected outliers will be assessed using the Extreme Value Test described in Section 4.4.3 of EPA QA/G-9. As the monitoring database becomes larger, it may be necessary to use different statistical methods to determine trends and outliers. Any changes to the statistical methods used for this project will be communicated to the U.S. EPA prior to initiating the change.

Overall comparability of data from split samples (samples that are collected at the same time from the same location and split equally between two parties using sample containers from the same source or vendor) will be evaluated by determining the RPD of detected analytes in both samples following data verification/validation. Analytes that are detected in only one of the two

samples will be assessed by reviewing the data verification/validation reports for both data sets and determining the cause of the discrepancy. Overall comparability of split sample data will be considered acceptable if the RPD for detected analytes, with concentrations greater than or equal to five times their respective quantitation limits, does not exceed RPD acceptance criteria for field duplicate samples.

For data comparability, the Data Assessment Report will: 1) discuss and compare overall comparability between multiple data sets collected for each matrix, analytical parameter, and concentration level, 2) describe the limitation on use of project data when project-required data comparability is not achieved for the overall project or when it is limited to a specific sampling or laboratory/analytical group, data set, matrix, analytical parameter, or concentration level, 3) discuss the effect on data usability if it is determined that long-term monitoring data are not comparable and address whether the data indicate a changing environment or the anomalies are a result of sampling and/or analytical error, 4) discuss the effect on data usability, if screen/confirmatory comparability criteria and/or oversight split-sampling comparability criteria are not met, 5) address how data comparability issues will be resolved and discuss the need for resampling if project data do not adequately address environmental questions and support project decision making, and 6) clearly differentiate between usable and unusable data for the users, if unusable data are identified.

4.3.7 Data Limitations and Actions

Sources of sampling and analytical error will be identified and corrected as early as possible. An ongoing data assessment process will be incorporated throughout the project, rather than as a final step, to facilitate early detection and correction of problems, so that project quality objectives are met.

Data that do not meet the measurement performance criteria specified in this QAPP will be identified, and impact on project quality objectives will be assessed and discussed within the final project report. Specific actions for data that do not meet measurement performance criteria will depend on the use of data and may require that additional samples be collected or use of the data be restricted.

5.0 REFERENCES

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U.S. EPA. 2016. *National Functional Guideline for Superfund Organic Methods Data Review*. EPA-540-R-2016-002. Office of Superfund Remediation and Technology Innovation (OSRTI).

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TABLES

Table 1
Analytical Methods

Laboratory Name	Analyte Type and Analytical Method
	SOIL
TestAmerica Randee Arrington, Lab Manager 11922 E. 1st Avenue Spokane, WA 99206 Phone: (425) 883-3881 Email: Randee.Arrington@testamerica.com	VOCs (EPA 8260C) SVOCs (EPA 8270D) PAHs (EPA 8270D SIM) Pesticides - Organophosphorus (EPA 8241B) Pesticides - Organochlorine (8081B) Herbicides (EPA 8151A) PCBs (EPA 8082A) GRO (NWTPH-GX) DRO and RRO (NWTPH-DX) ICP Metals (EPA 200.7/6010C) ICP-MS Metals (EPA 200.8/6020C) Mercury (EPA 7470A/7471B) Hexavalent Chromium (EPA 7196A) Oil & Grease (EPA 1664A) Total Organic Carbon (EPA 9060A-Mod)

EPA = Environmental Protection Agency
DRO = diesel range organics
GRO = gasoline range organics
ICP = inductively coupled plasma
PAH = polycyclic aromatic hydrocarbons
PCB = polychlorinated biphenyls
SVOC = semivolatile organic compound
VOC = volatile organic compound

Table 2
Analytical Parameters, Reporting Limits, Precision and Accuracy
TestAmerica - Soil and Bulk Samples

Laboratory	Analyte Group	Analyte	CAS #	Matrix	Analytical Method	Prep Method	DL/MDL	LOQ/PQL	Units	LCL % Recovery	UCL % Recovery	RPDL (%)	Comments
TestAmerica	VOCs	1,1,1,2-Tetrachloroethane	630-20-6	Soil	SW8260C	5035A	0.24	1	ug/Kg	79	128	11	
TestAmerica	VOCs	1,1,1-Trichloroethane	71-55-6	Soil	SW8260C	5035A	0.3	2	ug/Kg	78	150	14	
TestAmerica	VOCs	1,1,2,2-Tetrachloroethane	79-34-5	Soil	SW8260C	5035A	0.9	4	ug/Kg	57	127	18	
TestAmerica	VOCs	1,1,2-Trichloroethane	79-00-5	Soil	SW8260C	5035A	0.25	2	ug/Kg	73	123	15	
TestAmerica	VOCs	1,1,2-Trichlorotrifluoroethane	76-13-1	Soil	SW8260C	5035A	0.52	3	ug/Kg	70	145	17	
TestAmerica	VOCs	1,1-Dichloroethane	75-34-3	Soil	SW8260C	5035A	0.19	1	ug/Kg	70	141	30	
TestAmerica	VOCs	1,1-Dichloroethene	75-35-4	Soil	SW8260C	5035A	0.5	5	ug/Kg	77	137	23	
TestAmerica	VOCs	1,1-Dichloropropene	563-58-6	Soil	SW8260C	5035A	0.3	2	ug/Kg	76	150	11	
TestAmerica	VOCs	1,2,3-Trichlorobenzene	87-61-6	Soil	SW8260C	5035A	0.6	3	ug/Kg	60	129	18	
TestAmerica	VOCs	1,2,3-Trichloropropane	96-18-4	Soil	SW8260C	5035A	0.3	2	ug/Kg	59	127	16	
TestAmerica	VOCs	1,2,4-Trichlorobenzene	120-82-1	Soil	SW8260C	5035A	0.4	2	ug/Kg	68	131	16	
TestAmerica	VOCs	1,2,4-Trimethylbenzene	95-63-6	Soil	SW8260C	5035A	0.16	2	ug/Kg	73	127	12	
TestAmerica	VOCs	1,2-Dibromo-3-Chloropropane	96-12-8	Soil	SW8260C	5035A	1.6	10	ug/Kg	53	129	20	
TestAmerica	VOCs	1,2-Dibromoethane	106-93-4	Soil	SW8260C	5035A	0.2	1	ug/Kg	77	123	18	
TestAmerica	VOCs	1,2-Dichlorobenzene	95-50-1	Soil	SW8260C	5035A	0.31	2	ug/Kg	67	126	12	
TestAmerica	VOCs	1,2-Dichloroethane	107-06-2	Soil	SW8260C	5035A	0.15	1	ug/Kg	68	150	17	
TestAmerica	VOCs	1,2-Dichloropropane	78-87-5	Soil	SW8260C	5035A	0.4	2	ug/Kg	75	136	10	
TestAmerica	VOCs	1,3,5-Trimethylbenzene	108-67-8	Soil	SW8260C	5035A	0.17	5	ug/Kg	72	128	16	
TestAmerica	VOCs	1,3-Dichlorobenzene	541-73-1	Soil	SW8260C	5035A	0.26	2	ug/Kg	52	150	12	
TestAmerica	VOCs	1,3-Dichloropropane	142-28-9	Soil	SW8260C	5035A	0.23	2	ug/Kg	75	120	18	
TestAmerica	VOCs	1,4-Dichlorobenzene	106-46-7	Soil	SW8260C	5035A	0.2	1	ug/Kg	71	123	12	
TestAmerica	VOCs	2,2-Dichloropropane	594-20-7	Soil	SW8260C	5035A	0.9	5	ug/Kg	54	150	28	
TestAmerica	VOCs	2-Butanone	78-93-3	Soil	SW8260C	5035A	8.9	40	ug/Kg	51	146	31	
TestAmerica	VOCs	2-Chlorotoluene	95-49-8	Soil	SW8260C	5035A	0.17	2	ug/Kg	71	127	16	
TestAmerica	VOCs	4-Chlorotoluene	106-43-4	Soil	SW8260C	5035A	0.2	2	ug/Kg	68	126	16	
TestAmerica	VOCs	4-Methyl-2-pentanone	108-10-1	Soil	SW8260C	5035A	1.5	10	ug/Kg	64	125	27	
TestAmerica	VOCs	Acetone	67-64-1	Soil	SW8260C	5035A	2.4	15	ug/Kg	48	150	40	
TestAmerica	VOCs	Benzene	71-43-2	Soil	SW8260C	5035A	0.3	2	ug/Kg	79	135	10	
TestAmerica	VOCs	Bromobenzene	108-86-1	Soil	SW8260C	5035A	2.3	10	ug/Kg	68	126	19	
TestAmerica	VOCs	Bromochloromethane	74-97-5	Soil	SW8260C	5035A	0.25	2	ug/Kg	76	150	15	
TestAmerica	VOCs	Bromodichloromethane	75-27-4	Soil	SW8260C	5035A	0.18	1	ug/Kg	79	132	10	
TestAmerica	VOCs	Bromoform	75-25-2	Soil	SW8260C	5035A	0.3	2	ug/Kg	65	134	17	
TestAmerica	VOCs	Bromomethane	74-83-9	Soil	SW8260C	5035A	0.21	1	ug/Kg	57	146	38	
TestAmerica	VOCs	Carbon disulfide	75-15-0	Soil	SW8260C	5035A	0.2	1	ug/Kg	68	150	30	
TestAmerica	VOCs	Carbon tetrachloride	56-23-5	Soil	SW8260C	5035A	0.3	2	ug/Kg	77	150	12	
TestAmerica	VOCs	Chlorobenzene	108-90-7	Soil	SW8260C	5035A	0.4	2	ug/Kg	80	123	10	
TestAmerica	VOCs	Chloroethane	75-00-3	Soil	SW8260C	5035A	0.2	2	ug/Kg	55	150	40	
TestAmerica	VOCs	Chloroform	67-66-3	Soil	SW8260C	5035A	0.3	2	ug/Kg	80	133	13	
TestAmerica	VOCs	Chloromethane	74-87-3	Soil	SW8260C	5035A	0.14	1	ug/Kg	53	145	28	
TestAmerica	VOCs	cis-1,2-Dichloroethene	156-59-2	Soil	SW8260C	5035A	0.3	2	ug/Kg	74	138	14	
TestAmerica	VOCs	cis-1,3-Dichloropropene	10061-01-5	Soil	SW8260C	5035A	0.2	1	ug/Kg	70	122	16	
TestAmerica	VOCs	Dibromochloromethane	124-48-1	Soil	SW8260C	5035A	0.27	2	ug/Kg	75	125	17	
TestAmerica	VOCs	Dibromomethane	74-95-3	Soil	SW8260C	5035A	0.17	1	ug/Kg	72	150	14	

Table 2
Analytical Parameters, Reporting Limits, Precision and Accuracy
TestAmerica - Soil and Bulk Samples

Laboratory	Analyte Group	Analyte	CAS #	Matrix	Analytical Method	Prep Method	DL/MDL	LOQ/PQL	Units	LCL % Recovery	UCL % Recovery	RPDL (%)	Comments
TestAmerica	VOCs	Dichlorodifluoromethane	75-71-8	Soil	SW8260C	5035A	0.49	2	ug/Kg	33	137	30	
TestAmerica	VOCs	Dichlorofluoromethane	75-43-4	Soil	SW8260C	5035A	0.3	2	ug/Kg	61	150	37	
TestAmerica	VOCs	Ethylbenzene	100-41-4	Soil	SW8260C	5035A	0.4	2	ug/Kg	80	127	10	
TestAmerica	VOCs	Hexachlorobutadiene	87-68-3	Soil	SW8260C	5035A	0.6	3	ug/Kg	65	136	19	
TestAmerica	VOCs	Hexane	110-54-3	Soil	SW8260C	5035A	0.75	5	ug/Kg	65	150	19	
TestAmerica	VOCs	Isopropylbenzene	98-82-8	Soil	SW8260C	5035A	0.2	2	ug/Kg	80	128	17	
TestAmerica	VOCs	Methyl tert-butyl ether	1634-04-4	Soil	SW8260C	5035A	0.3	2	ug/Kg	69	150	30	
TestAmerica	VOCs	Methylene Chloride	75-09-2	Soil	SW8260C	5035A	0.24	15	ug/Kg	66	150	40	
TestAmerica	VOCs	m-Xylene & p-Xylene	179601-23-1	Soil	SW8260C	5035A	0.2	2	ug/Kg	80	128	13	
TestAmerica	VOCs	Naphthalene	91-20-3	Soil	SW8260C	5035A	1.8	10	ug/Kg	61	124	17	
TestAmerica	VOCs	n-Butylbenzene	104-51-8	Soil	SW8260C	5035A	0.2	2	ug/Kg	71	130	12	
TestAmerica	VOCs	N-Propylbenzene	103-65-1	Soil	SW8260C	5035A	0.32	2	ug/Kg	74	127	17	
TestAmerica	VOCs	o-Xylene	95-47-6	Soil	SW8260C	5035A	0.26	2	ug/Kg	80	125	14	
TestAmerica	VOCs	p-Isopropyltoluene	99-87-6	Soil	SW8260C	5035A	0.4	2	ug/Kg	71	129	11	
TestAmerica	VOCs	sec-Butylbenzene	135-98-8	Soil	SW8260C	5035A	0.25	2	ug/Kg	70	129	12	
TestAmerica	VOCs	Styrene	100-42-5	Soil	SW8260C	5035A	0.2	2	ug/Kg	79	129	15	
TestAmerica	VOCs	t-Butylbenzene	98-06-6	Soil	SW8260C	5035A	0.2	2	ug/Kg	71	127	13	
TestAmerica	VOCs	Tetrachloroethene	127-18-4	Soil	SW8260C	5035A	0.4	2	ug/Kg	61	150	16	
TestAmerica	VOCs	Toluene	108-88-3	Soil	SW8260C	5035A	0.3	2	ug/Kg	80	125	16	
TestAmerica	VOCs	trans-1,2-Dichloroethene	156-60-5	Soil	SW8260C	5035A	0.4	2	ug/Kg	71	150	22	
TestAmerica	VOCs	trans-1,3-Dichloropropene	10061-02-6	Soil	SW8260C	5035A	1.4	10	ug/Kg	75	121	17	
TestAmerica	VOCs	Trichloroethene	79-01-6	Soil	SW8260C	5035A	0.3	2	ug/Kg	80	144	10	
TestAmerica	VOCs	Trichlorofluoromethane	75-69-4	Soil	SW8260C	5035A	0.3	2	ug/Kg	73	143	26	
TestAmerica	VOCs	Vinyl chloride	75-01-4	Soil	SW8260C	5035A	0.3	2	ug/Kg	28	150	29	
TestAmerica	VOCs	Xylenes, Total	1330-20-7	Soil	SW8260C	5035A	0.26	2	ug/Kg	80	126	13	
TestAmerica	SVOCs	1,2,4-Trichlorobenzene	120-82-1	Soil	SW8270D	3550B	6	50	ug/Kg	66	120	10	
TestAmerica	SVOCs	1,2-Dichlorobenzene	95-50-1	Soil	SW8270D	3550B	12	50	ug/Kg	73	120	10	
TestAmerica	SVOCs	1,3-Dichlorobenzene	541-73-1	Soil	SW8270D	3550B	4.8	50	ug/Kg	72	120	10	
TestAmerica	SVOCs	1,4-Dichlorobenzene	106-46-7	Soil	SW8270D	3550B	8.3	50	ug/Kg	70	120	10	
TestAmerica	SVOCs	1-Methylnaphthalene	90-12-0	Soil	SW8270D	3550B	5	30	ug/Kg	76	120	10	
TestAmerica	SVOCs	2,4,5-Trichlorophenol	95-95-4	Soil	SW8270D	3550B	45	200	ug/Kg	64	120	16	
TestAmerica	SVOCs	2,4,6-Trichlorophenol	88-06-2	Soil	SW8270D	3550B	36	150	ug/Kg	65	120	10	
TestAmerica	SVOCs	2,4-Dichlorophenol	120-83-2	Soil	SW8270D	3550B	15	100	ug/Kg	69	121	10	
TestAmerica	SVOCs	2,4-Dimethylphenol	105-67-9	Soil	SW8270D	3550B	15	100	ug/Kg	64	120	10	
TestAmerica	SVOCs	2,4-Dinitrophenol	51-28-5	Soil	SW8270D	3550B	200	1000	ug/Kg	10	120	37	
TestAmerica	SVOCs	2,4-Dinitrotoluene	121-14-2	Soil	SW8270D	3550B	43	200	ug/Kg	71	125	10	
TestAmerica	SVOCs	2,6-Dinitrotoluene	606-20-2	Soil	SW8270D	3550B	34	150	ug/Kg	63	129	13	
TestAmerica	SVOCs	2-Chloronaphthalene	91-58-7	Soil	SW8270D	3550B	5	25	ug/Kg	73	120	10	
TestAmerica	SVOCs	2-Chlorophenol	95-57-8	Soil	SW8270D	3550B	42	200	ug/Kg	78	120	10	
TestAmerica	SVOCs	2-Methylnaphthalene	91-57-6	Soil	SW8270D	3550B	8.8	50	ug/Kg	71	120	10	
TestAmerica	SVOCs	2-Methylphenol	95-48-7	Soil	SW8270D	3550B	37	150	ug/Kg	70	120	15	
TestAmerica	SVOCs	2-Nitroaniline	88-74-4	Soil	SW8270D	3550B	15	100	ug/Kg	63	122	10	
TestAmerica	SVOCs	2-Nitrophenol	88-75-5	Soil	SW8270D	3550B	46	200	ug/Kg	67	120	10	

Table 2
Analytical Parameters, Reporting Limits, Precision and Accuracy
TestAmerica - Soil and Bulk Samples

Laboratory	Analyte Group	Analyte	CAS #	Matrix	Analytical Method	Prep Method	DL/MDL	LOQ/PQL	Units	LCL % Recovery	UCL % Recovery	RPDL (%)	Comments
TestAmerica	SVOCs	3 & 4 Methylphenol	15831-10-4	Soil	SW8270D	3550B	15	200	ug/Kg	70	120	10	
TestAmerica	SVOCs	3,3'-Dichlorobenzidine	91-94-1	Soil	SW8270D	3550B	100	400	ug/Kg	35	135	15	
TestAmerica	SVOCs	3-Nitroaniline	99-09-2	Soil	SW8270D	3550B	40	200	ug/Kg	21	120	11	
TestAmerica	SVOCs	4,6-Dinitro-2-methylphenol	534-52-1	Soil	SW8270D	3550B	100	1000	ug/Kg	16	134	17	
TestAmerica	SVOCs	4-Bromophenyl phenyl ether	101-55-3	Soil	SW8270D	3550B	41	200	ug/Kg	74	120	10	
TestAmerica	SVOCs	4-Chloro-3-methylphenol	59-50-7	Soil	SW8270D	3550B	33	150	ug/Kg	69	120	10	
TestAmerica	SVOCs	4-Chloroaniline	106-47-8	Soil	SW8270D	3550B	400	1500	ug/Kg	10	120	40	
TestAmerica	SVOCs	4-Chlorophenyl phenyl ether	7005-72-3	Soil	SW8270D	3550B	41	200	ug/Kg	75	120	10	
TestAmerica	SVOCs	4-Nitroaniline	100-01-6	Soil	SW8270D	3550B	20	100	ug/Kg	63	120	40	
TestAmerica	SVOCs	4-Nitrophenol	100-02-7	Soil	SW8270D	3550B	368	1500	ug/Kg	21	134	10	
TestAmerica	SVOCs	Acenaphthene	83-32-9	Soil	SW8270D	3550B	5	25	ug/Kg	71	120	10	
TestAmerica	SVOCs	Acenaphthylene	208-96-8	Soil	SW8270D	3550B	5	25	ug/Kg	73	128	10	
TestAmerica	SVOCs	Anthracene	120-12-7	Soil	SW8270D	3550B	5	25	ug/Kg	74	120	10	
TestAmerica	SVOCs	Benzo[a]anthracene	56-55-3	Soil	SW8270D	3550B	5	25	ug/Kg	73	120	10	
TestAmerica	SVOCs	Benzo[a]pyrene	50-32-8	Soil	SW8270D	3550B	13	60	ug/Kg	72	121	10	
TestAmerica	SVOCs	Benzo[b]fluoranthene	205-99-2	Soil	SW8270D	3550B	5	25	ug/Kg	71	124	10	
TestAmerica	SVOCs	Benzo[g,h,i]perylene	191-24-2	Soil	SW8270D	3550B	15	60	ug/Kg	75	122	10	
TestAmerica	SVOCs	Benzo[k]fluoranthene	207-08-9	Soil	SW8270D	3550B	14	60	ug/Kg	68	123	10	
TestAmerica	SVOCs	Benzoic acid	65-85-0	Soil	SW8270D	3550B	1060	2500	ug/Kg	10	141	10	
TestAmerica	SVOCs	Benzyl alcohol	100-51-6	Soil	SW8270D	3550B	37	4000	ug/Kg	60	120	10	
TestAmerica	SVOCs	Bis(2-chloroethoxy)methane	111-91-1	Soil	SW8270D	3550B	41	200	ug/Kg	74	120	10	
TestAmerica	SVOCs	Bis(2-chloroethyl)ether	111-44-4	Soil	SW8270D	3550B	40	200	ug/Kg	70	120	17	
TestAmerica	SVOCs	Bis(2-ethylhexyl) phthalate	117-81-7	Soil	SW8270D	3550B	136	600	ug/Kg	66	130	10	
TestAmerica	SVOCs	bis(chloroisopropyl) ether	108-60-1	Soil	SW8270D	3550B	37	250	ug/Kg	64	121	11	
TestAmerica	SVOCs	Butyl benzyl phthalate	85-68-7	Soil	SW8270D	3550B	50	200	ug/Kg	67	135	10	
TestAmerica	SVOCs	Carbazole	86-74-8	Soil	SW8270D	3550B	31	150	ug/Kg	80	131	10	
TestAmerica	SVOCs	Chrysene	218-01-9	Soil	SW8270D	3550B	13	60	ug/Kg	71	120	10	
TestAmerica	SVOCs	Dibenz(a,h)anthracene	53-70-3	Soil	SW8270D	3550B	12	50	ug/Kg	71	120	40	
TestAmerica	SVOCs	Dibenzofuran	132-64-9	Soil	SW8270D	3550B	36	150	ug/Kg	77	120	10	
TestAmerica	SVOCs	Diethyl phthalate	84-66-2	Soil	SW8270D	3550B	132	550	ug/Kg	71	120	10	
TestAmerica	SVOCs	Dimethyl phthalate	131-11-3	Soil	SW8270D	3550B	33	150	ug/Kg	77	120	10	
TestAmerica	SVOCs	Di-n-butyl phthalate	84-74-2	Soil	SW8270D	3550B	57	500	ug/Kg	68	129	10	
TestAmerica	SVOCs	Di-n-octyl phthalate	117-84-0	Soil	SW8270D	3550B	222	1000	ug/Kg	68	124	10	
TestAmerica	SVOCs	Fluoranthene	206-44-0	Soil	SW8270D	3550B	5	25	ug/Kg	75	120	10	
TestAmerica	SVOCs	Fluorene	86-73-7	Soil	SW8270D	3550B	5	25	ug/Kg	68	121	10	
TestAmerica	SVOCs	Hexachlorobenzene	118-74-1	Soil	SW8270D	3550B	5	50	ug/Kg	70	120	10	
TestAmerica	SVOCs	Hexachlorobutadiene	87-68-3	Soil	SW8270D	3550B	15	50	ug/Kg	71	120	11	
TestAmerica	SVOCs	Hexachlorocyclopentadiene	77-47-4	Soil	SW8270D	3550B	26	100	ug/Kg	63	131	15	
TestAmerica	SVOCs	Hexachloroethane	67-72-1	Soil	SW8270D	3550B	38	150	ug/Kg	72	120	10	
TestAmerica	SVOCs	Indeno[1,2,3-cd]pyrene	193-39-5	Soil	SW8270D	3550B	5	40	ug/Kg	75	120	17	
TestAmerica	SVOCs	Isophorone	78-59-1	Soil	SW8270D	3550B	37	150	ug/Kg	78	120	10	
TestAmerica	SVOCs	Naphthalene	91-20-3	Soil	SW8270D	3550B	5	25	ug/Kg	75	120	10	
TestAmerica	SVOCs	Nitrobenzene	98-95-3	Soil	SW8270D	3550B	42	200	ug/Kg	70	120	10	

Table 2
Analytical Parameters, Reporting Limits, Precision and Accuracy
TestAmerica - Soil and Bulk Samples

Laboratory	Analyte Group	Analyte	CAS #	Matrix	Analytical Method	Prep Method	DL/MDL	LOQ/PQL	Units	LCL % Recovery	UCL % Recovery	RPDL (%)	Comments
TestAmerica	SVOCs	N-Nitrosodi-n-propylamine	621-64-7	Soil	SW8270D	3550B	44	200	ug/Kg	62	120	10	
TestAmerica	SVOCs	N-Nitrosodiphenylamine	86-30-6	Soil	SW8270D	3550B	15	60	ug/Kg	73	127	10	
TestAmerica	SVOCs	Pentachlorophenol	87-86-5	Soil	SW8270D	3550B	91	400	ug/Kg	36	120	24	
TestAmerica	SVOCs	Phenanthrene	85-01-8	Soil	SW8270D	3550B	12	60	ug/Kg	73	120	11	
TestAmerica	SVOCs	Phenol	108-95-2	Soil	SW8270D	3550B	38	150	ug/Kg	65	120	10	
TestAmerica	SVOCs	Pyrene	129-00-0	Soil	SW8270D	3550B	15	60	ug/Kg	73	120	10	
TestAmerica	PAHs	1-Methylnaphthalene	90-12-0	Soil	8270D-SIM	3550C	2.22	10	ug/Kg	46	131	35	
TestAmerica	PAHs	2-Methylnaphthalene	91-57-6	Soil	8270D-SIM	3550C	1.45	10	ug/Kg	39	132	35	
TestAmerica	PAHs	Acenaphthene	83-32-9	Soil	8270D-SIM	3550C	2.53	10	ug/Kg	43	140	35	
TestAmerica	PAHs	Acenaphthylene	208-96-8	Soil	8270D-SIM	3550C	3.32	10	ug/Kg	56	123	35	
TestAmerica	PAHs	Anthracene	120-12-7	Soil	8270D-SIM	3550C	1.24	10	ug/Kg	60	129	35	
TestAmerica	PAHs	Benzo[a]anthracene	56-55-3	Soil	8270D-SIM	3550C	1.23	10	ug/Kg	61	136	35	
TestAmerica	PAHs	Benzo[a]pyrene	50-32-8	Soil	8270D-SIM	3550C	2	10	ug/Kg	60	133	35	
TestAmerica	PAHs	Benzo[b]fluoranthene	205-99-2	Soil	8270D-SIM	3550C	2.28	10	ug/Kg	66	141	35	
TestAmerica	PAHs	Benzo[g,h,i]perylene	191-24-2	Soil	8270D-SIM	3550C	2.11	10	ug/Kg	58	147	35	
TestAmerica	PAHs	Benzo[k]fluoranthene	207-08-9	Soil	8270D-SIM	3550C	2.5	10	ug/Kg	63	150	35	
TestAmerica	PAHs	Chrysene	218-01-9	Soil	8270D-SIM	3550C	1.52	10	ug/Kg	57	144	35	
TestAmerica	PAHs	Dibenz(a,h)anthracene	53-70-3	Soil	8270D-SIM	3550C	2.41	10	ug/Kg	60	150	35	
TestAmerica	PAHs	Fluoranthene	206-44-0	Soil	8270D-SIM	3550C	2.29	10	ug/Kg	63	141	35	
TestAmerica	PAHs	Fluorene	86-73-7	Soil	8270D-SIM	3550C	2.21	10	ug/Kg	54	131	35	
TestAmerica	PAHs	Indeno[1,2,3-cd]pyrene	193-39-5	Soil	8270D-SIM	3550C	1.87	10	ug/Kg	55	142	35	
TestAmerica	PAHs	Naphthalene	91-20-3	Soil	8270D-SIM	3550C	0.99	10	ug/Kg	41	121	35	
TestAmerica	PAHs	Phenanthrene	85-01-8	Soil	8270D-SIM	3550C	1.26	10	ug/Kg	55	141	35	
TestAmerica	PAHs	Pyrene	129-00-0	Soil	8270D-SIM	3550C	1.44	10	ug/Kg	62	139	35	
TestAmerica	Pesticides-OP	Atrazine	1912-24-9	Soil	8141B	3540C	12.1	67	ug/Kg	56	115	31	
TestAmerica	Pesticides-OP	Azinphos-methyl	86-50-0	Soil	8141B	3540C	3.5	13	ug/Kg	57	115	21	
TestAmerica	Pesticides-OP	Bolstar	35400-43-2	Soil	8141B	3540C	4.24	13	ug/Kg	57	115	30	
TestAmerica	Pesticides-OP	Chlorpyrifos	2921-88-2	Soil	8141B	3540C	6.46	20	ug/Kg	56	115	27	
TestAmerica	Pesticides-OP	Coumaphos	56-72-4	Soil	8141B	3540C	2.8	13	ug/Kg	57	117	26	
TestAmerica	Pesticides-OP	Demeton, Total	8065-48-3	Soil	8141B	3540C	7.52	39	ug/Kg	33	115	51	
TestAmerica	Pesticides-OP	Diazinon	333-41-5	Soil	8141B	3540C	7.27	22	ug/Kg	50	115	29	
TestAmerica	Pesticides-OP	Dichlorvos	62-73-7	Soil	8141B	3540C	7.4	23	ug/Kg	37	152	50	
TestAmerica	Pesticides-OP	Dimethoate	60-51-5	Soil	8141B	3540C	7.08	22	ug/Kg	53	115	29	
TestAmerica	Pesticides-OP	Disulfoton	298-04-4	Soil	8141B	3540C	7.73	48	ug/Kg	31	115	35	
TestAmerica	Pesticides-OP	EPN	2104-64-5	Soil	8141B	3540C	3.68	13	ug/Kg	56	115	23	
TestAmerica	Pesticides-OP	Ethoprop	13194-48-4	Soil	8141B	3540C	4.93	15	ug/Kg	51	115	34	
TestAmerica	Pesticides-OP	Ethyl Parathion	56-38-2	Soil	8141B	3540C	5.29	18	ug/Kg	57	115	23	
TestAmerica	Pesticides-OP	Famphur	52-85-7	Soil	8141B	3540C	3.22	13	ug/Kg	60	115	23	
TestAmerica	Pesticides-OP	Fensulfothion	115-90-2	Soil	8141B	3540C	8.15	25	ug/Kg	58	115	23	
TestAmerica	Pesticides-OP	Fenthion	55-38-9	Soil	8141B	3540C	8.74	33	ug/Kg	53	115	24	
TestAmerica	Pesticides-OP	Malathion	121-75-5	Soil	8141B	3540C	4.64	15	ug/Kg	49	115	23	
TestAmerica	Pesticides-OP	Merphos	150-50-5	Soil	8141B	3540C	5.14	30	ug/Kg	10	115	25	
TestAmerica	Pesticides-OP	Methyl parathion	298-00-0	Soil	8141B	3540C	6.37	20	ug/Kg	58	115	23	

Table 2
Analytical Parameters, Reporting Limits, Precision and Accuracy
TestAmerica - Soil and Bulk Samples

Laboratory	Analyte Group	Analyte	CAS #	Matrix	Analytical Method	Prep Method	DL/MDL	LOQ/PQL	Units	LCL % Recovery	UCL % Recovery	RPDL (%)	Comments
TestAmerica	Pesticides-OP	o,o',o''-Triethylphosphorothioate	126-68-1	Soil	8141B	3540C	7.85	39	ug/Kg	10	158	50	
TestAmerica	Pesticides-OP	Phorate	298-02-2	Soil	8141B	3540C	5.7	20	ug/Kg	24	115	44	
TestAmerica	Pesticides-OP	Propazine	139-40-2	Soil	8141B	3540C	8.63	67	ug/Kg	59	115	30	
TestAmerica	Pesticides-OP	Ronnel	299-84-3	Soil	8141B	3540C	15.2	46	ug/Kg	58	115	29	
TestAmerica	Pesticides-OP	Simazine	122-34-9	Soil	8141B	3540C	22.1	67	ug/Kg	48	115	43	
TestAmerica	Pesticides-OP	Sulfotepp	3689-24-5	Soil	8141B	3540C	6.26	20	ug/Kg	52	115	37	
TestAmerica	Pesticides-OP	Thionazin	297-97-2	Soil	8141B	3540C	5.57	18	ug/Kg	52	115	41	
TestAmerica	Pesticides-OP	Tokuthion	34643-46-4	Soil	8141B	3540C	3.91	20	ug/Kg	58	115	30	
TestAmerica	Pesticides-OP	Trichloronate	327-98-0	Soil	8141B	3540C	6.25	20	ug/Kg	52	115	31	
TestAmerica	Pesticides-OC	4,4'-DDD	72-54-8	Soil	8081B	3546	0.09	2	ug/Kg	68	122	35	
TestAmerica	Pesticides-OC	4,4'-DDE	72-55-9	Soil	8081B	3546	0.06	2	ug/Kg	64	121	34	
TestAmerica	Pesticides-OC	4,4'-DDT	50-29-3	Soil	8081B	3546	0.14	2	ug/Kg	49	137	32	
TestAmerica	Pesticides-OC	Aldrin	309-00-2	Soil	8081B	3546	0.09	1	ug/Kg	56	117	26	
TestAmerica	Pesticides-OC	alpha-BHC	319-84-6	Soil	8081B	3546	0.16	1	ug/Kg	62	115	15	
TestAmerica	Pesticides-OC	alpha-Chlordane	5103-71-9	Soil	8081B	3546	0.12	1	ug/Kg	62	117	31	
TestAmerica	Pesticides-OC	beta-BHC	319-85-7	Soil	8081B	3546	0.47	2	ug/Kg	62	112	19	
TestAmerica	Pesticides-OC	delta-BHC	319-86-8	Soil	8081B	3546	0.1	1	ug/Kg	63	120	23	
TestAmerica	Pesticides-OC	Dieldrin	60-57-1	Soil	8081B	3546	0.35	2	ug/Kg	63	121	26	
TestAmerica	Pesticides-OC	Endosulfan I	959-98-8	Soil	8081B	3546	0.13	1	ug/Kg	64	120	30	
TestAmerica	Pesticides-OC	Endosulfan II	33213-65-9	Soil	8081B	3546	0.05	2	ug/Kg	50	139	30	
TestAmerica	Pesticides-OC	Endosulfan sulfate	1031-07-8	Soil	8081B	3546	0.08	2	ug/Kg	63	116	27	
TestAmerica	Pesticides-OC	Endrin	72-20-8	Soil	8081B	3546	0.12	2	ug/Kg	70	127	27	
TestAmerica	Pesticides-OC	Endrin aldehyde	7421-93-4	Soil	8081B	3546	0.48	2	ug/Kg	30	143	36	
TestAmerica	Pesticides-OC	Endrin ketone	53494-70-5	Soil	8081B	3546	0.36	2	ug/Kg	56	128	24	
TestAmerica	Pesticides-OC	gamma-BHC (Lindane)	58-89-9	Soil	8081B	3546	0.03	1	ug/Kg	55	127	35	
TestAmerica	Pesticides-OC	gamma-Chlordane	5103-74-2	Soil	8081B	3546	0.19	1	ug/Kg	60	119	30	
TestAmerica	Herbicides	2,4,5-T	93-76-5	Soil	8151A	8151A	16	65	ug/Kg	46	150	40	
TestAmerica	Herbicides	2,4-D	94-75-7	Soil	8151A	8151A	14	60	ug/Kg	51	150	40	
TestAmerica	Herbicides	2,4-DB	94-82-6	Soil	8151A	8151A	10.9	50	ug/Kg	62	150	40	
TestAmerica	Herbicides	Dalapon	75-99-0	Soil	8151A	8151A	22.3	90	ug/Kg	15	110	40	
TestAmerica	Herbicides	Dicamba	1918-00-9	Soil	8151A	8151A	19.4	80	ug/Kg	30	134	40	
TestAmerica	Herbicides	Dichlorprop	120-36-5	Soil	8151A	8151A	11	50	ug/Kg	47	150	40	
TestAmerica	Herbicides	MCPA	94-74-6	Soil	8151A	8151A	10.9	50	ug/Kg	51	150	40	
TestAmerica	Herbicides	MCPP	93-65-2	Soil	8151A	8151A	20.6	90	ug/Kg	48	150	40	
TestAmerica	Herbicides	Silvex (2,4,5-TP)	93-72-1	Soil	8151A	8151A	21.2	90	ug/Kg	59	150	40	
TestAmerica	PCBs	PCB-1016	12674-11-2	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	58	150	25	
TestAmerica	PCBs	PCB-1221	11104-28-2	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	NA	NA		
TestAmerica	PCBs	PCB-1232	11141-16-5	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	NA	NA		
TestAmerica	PCBs	PCB-1242	53469-21-9	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	NA	NA		
TestAmerica	PCBs	PCB-1248	12672-29-6	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	NA	NA		
TestAmerica	PCBs	PCB-1254	11097-69-1	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	NA	NA		
TestAmerica	PCBs	PCB-1260	11096-82-5	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	52	150	25	
TestAmerica	PCBs	PCB-1262	37324-23-5	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	NA	NA		

Table 2
Analytical Parameters, Reporting Limits, Precision and Accuracy
TestAmerica - Soil and Bulk Samples

Laboratory	Analyte Group	Analyte	CAS #	Matrix	Analytical Method	Prep Method	DL/MDL	LOQ/PQL	Units	LCL % Recovery	UCL % Recovery	RPDL (%)	Comments
TestAmerica	PCBs	PCB-1268	11100-14-4	Soil	8082A	3665A/3550C	0.0022	0.01	mg/Kg	NA	NA		
TestAmerica	TPH	GRO	STL00228	Soil	NWTPH_Gx	5035A	1.8	5	mg/Kg	74.4	124	20	
TestAmerica	TPH	DRO	STL00163	Soil	NWTPH_Dx	3550C	4.19	10	mg/Kg	50	150	25	
TestAmerica	TPH	RRO	STL00299	Soil	NWTPH_Dx	3550C	2.45	25	mg/Kg	50	150	25	
TestAmerica	ICP Metals	Aluminum	7429-90-5	Soil	6010C	3050B	33.1	50	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Antimony	7440-36-0	Soil	6010C	3050B	0.904	2.5	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Arsenic	7440-38-2	Soil	6010C	3050B	0.496	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Barium	7440-39-3	Soil	6010C	3050B	0.335	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Beryllium	7440-41-7	Soil	6010C	3050B	0.202	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Cadmium	7440-43-9	Soil	6010C	3050B	0.059	1	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Calcium	7440-70-2	Soil	6010C	3050B	70.9	100	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Chromium	7440-47-3	Soil	6010C	3050B	0.177	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Cobalt	7440-48-4	Soil	6010C	3050B	0.097	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Copper	7440-50-8	Soil	6010C	3050B	1.54	4	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Iron	7439-89-6	Soil	6010C	3050B	43.2	100	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Lead	7439-92-1	Soil	6010C	3050B	1.47	3	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Manganese	7439-96-5	Soil	6010C	3050B	2.25	15	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Molybdenum	7439-98-7	Soil	6010C	3050B	0.518	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Nickel	7440-02-0	Soil	6010C	3050B	0.154	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Potassium	7440-09-7	Soil	6010C	3050B	12.5	25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Selenium	7782-49-2	Soil	6010C	3050B	3.01	5	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Silver	7440-22-4	Soil	6010C	3050B	0.134	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Sodium	7440-23-5	Soil	6010C	3050B	10.4	25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Thallium	7440-28-0	Soil	6010C	3050B	0.346	2.5	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Vanadium	7440-62-2	Soil	6010C	3050B	0.22	1.25	mg/Kg	80	120	20	
TestAmerica	ICP Metals	Zinc	7440-66-6	Soil	6010C	3050B	2.65	5	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Antimony	7440-36-0	Soil	6020B	3050B	0.068	0.2	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Arsenic	7440-38-2	Soil	6020B	3050B	0.1	0.5	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Barium	7440-39-3	Soil	6020B	3050B	0.04	0.5	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Beryllium	7440-41-7	Soil	6020B	3050B	0.015	0.2	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Cadmium	7440-43-9	Soil	6020B	3050B	0.077	0.4	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Chromium	7440-47-3	Soil	6020B	3050B	0.063	0.5	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Cobalt	7440-48-4	Soil	6020B	3050B	0.01	0.2	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Copper	7440-50-8	Soil	6020B	3050B	0.22	1	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Lead	7439-92-1	Soil	6020B	3050B	0.048	0.5	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Manganese	7439-96-5	Soil	6020B	3050B	0.453	2	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Nickel	7440-02-0	Soil	6020B	3050B	0.193	0.5	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Selenium	7782-49-2	Soil	6020B	3050B	0.218	1	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Silver	7440-22-4	Soil	6020B	3050B	0.02	0.2	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Thallium	7440-28-0	Soil	6020B	3050B	0.055	0.4	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Vanadium	7440-62-2	Soil	6020B	3050B	0.272	2	mg/Kg	80	120	20	
TestAmerica	ICP/MS Metals	Zinc	7440-66-6	Soil	6020B	3050B	1.61	5	mg/Kg	80	120	20	
TestAmerica	Misc	Mercury	7439-97-6	Soil	7471B	7471A_Prep	0.05	0.00357	mg/Kg	80	120	20	

Table 2
Analytical Parameters, Reporting Limits, Precision and Accuracy
TestAmerica - Soil and Bulk Samples

Laboratory	Analyte Group	Analyte	CAS #	Matrix	Analytical Method	Prep Method	DL/MDL	LOQ/PQL	Units	LCL % Recovery	UCL % Recovery	RPDL (%)	Comments
TestAmerica	Misc	Hexavalent Chromium	18540-29-9	Soil	7196A	3060A	2	5	mg/Kg	80	120	30	
TestAmerica	Misc	Total Organic Carbon (TOC)	7440-44-0	Soil	9060A	NA	44.4	2000	mg/Kg	68	149	32	

Notes: 1) All MDLs and control limits are subject to change as new studies are performed.
2) MDLs and control limits were provided by Randee Arrington of TestAmerica to Kim Vik of Stantec on 6/26/18.

CAS = Chemical Abstracts Service
DL = detection limit
DRO = diesel range organics
EPA = Environmental Protection Agency
F = fahrenheit
GRO = gasoline range organics
ICP = inductively coupled plasma
ICP/MS = inductively coupled plasma mass spectrometry
LCL = lower control limit (laborabory control sample)
LOQ = limit of quantitation
MDL = method detection limit
mg/kg = milligrams per kilogram
mod = modified
NA = not applicable or not available
NWTPH-Dx = Northwest Total Petroleum Hydrocarbon (diesel)
NWTPH-Gx = Northwest Total Petroleum Hydrocarbon (gasoline)
OP = organophosphorus pesticides
OC = organochlorine pesticides
PAH = polynuclear aromatic hydrocarbon
PCB = polychlorinated biphenyl
PQL = practical quantitation limit
RPDL = relative percent difference limit (laboratory control sample)
SIM = selective ion monitoring
SVOC = semi-volatile organic compound
SW = solid waste
TPH = total petroleum hydrocarbons
TOC = total organic carbon
LCL = lower control limit (laboratory control sample)
ug/kg = micrograms per kilogram
VOC = volatile organic compound

Table 3
Field & Lab Quality Assurance/Quality Control Sample Requirements
Brownfields Assessment & Area-Wide Planning Projects

	QC Sample Type	Frequency of Sample/Analysis	Details
Field Samples	Duplicate Samples	1 duplicate per 20 samples per matrix, or 1 duplicate per sample matrix if fewer than 20 samples	Duplicate sample to be collected by the same methods at the same time as the original sample. Used to verify sample and analytical reproducibility.
	Equipment/Field Blanks*	1 equipment blank per 20 samples, minimum 1 equipment blank per day per sample matrix *or* 1 field blank per bottle lot used, or 1 per site, whichever is more frequent	Distilled water placed into contact with sampling equipment. Used to assess quality of data from field sampling and decontamination procedures. ***** If all disposable equipment/single use sampling equipment is being used, then field blanks may be collected at a rate of 1 per bottle lot or per site, whichever is more frequent.
	Trip Blanks	1 trip blank per cooler containing samples for VOC analysis for water samples	Laboratory prepared organic-free blank to assess potential contamination during sample container shipment and storage, for VOCs in water only.
		1 trip blank per field sampling event, or per lot of bottles for soils, whichever is more frequent	For soil VOC samples preserved with methanol, one set of preserved vials will be included to assess potential contamination during sample container shipment and storage.
Lab Samples	Matrix Spike/ Matrix Spike Duplicate	1 MS/MSD per 20 or fewer samples per matrix in accordance with laboratory SOP	Laboratory spiked sample to evaluate matrix and measurement methodology.
	Method Blanks	1 method blank per daily run of samples prepared, or per laboratory SOP	Laboratory blank sample to assess potential for contamination from laboratory instruments or procedures.
	Laboratory Control Samples and Duplicates	Analyzed as per method requirements and laboratory SOPs	Evaluates laboratory reproducibility.

Notes:
MS/MSD = matrix spike/matrix spike duplicate
SOP(s) = standard operating procedure(s)
VOC = volatile organic compound

Table 4
Sample Container, Preservation and Holding Time Requirements for State of Washington

Analysis	Container	Preservation	Holding Time
SOIL SAMPLES			
Metals	4 oz glass/plastic jar	None: Cr(VI) Cool to </= 6° C	6 months; mercury 28 days; Cr(VI) 30 days
VOCs/PVOCs	(4) 40mL amber glass vial	Sodium bisulfite; CH_3OH, Cool to </= 6° C	14 days
SVOCs/PAHs/DRO	4 oz glass jar per two analyses	Cool to </= 6° C	14 days for extraction; 40 days for analysis
GRO	(4) 40mL amber glass vial	Sodium bisulfite; CH_3OH, Cool to </= 6° C	14 days
Pesticides, Herbicides and PCBs	4 oz glass jar	Cool to </= 6° C	14 days for extraction; 40 days for analysis; 1 year hold time (PCBs), 40 days from extraction to analysis
Reactive Cyanide/ Cyanide Total/TOC	4 oz glass jar	Cool to </= 6° C	14 days; TOC 28 days
Reactive Sulfide	4 oz glass jar	Cool to </= 6° C	28 days
% Moisture	4 oz glass jar	Cool to </= 6° C	14 days
pH	4 oz glass/plastic jar	Cool to </= 6° C	Measure as soon as possible (0 days)
Flash Point	4 oz glass jar	Cool to </= 6° C	14 days
Free Liquids - Paint Filter	4 oz glass jar	Cool to </= 6° C	14 days
WATER SAMPLES			
Metals	250 mL plastic bottle	HNO_3 to pH<2	6 months; mercury 28 days
Chromium VI	50 mL plastic vial	field filter, buffer sol'n, Cool to </= 6° C	28 days
VOCs/PVOCs/GRO	(3) 40 mL glass VOC vials, per analysis	HCl to pH <2, Cool to </= 6° C	14 days; 7 days unpreserved
Dissolved Gases (methane, ethane, ethene)	(2) 40 mL glass VOC vials	HCl to pH <2, Cool to </= 6° C	14 days
PAH/SVOCs/PCBs/ Pesticides	PAH – (2) 40 mL amber glass; (2) 100 mL amber glass per analysis	Cool to </= 6° C	7 days for extraction; 40 days for analysis; one year (PCBs)
DRO	(2) 40 mL amber glass vials	HCl to pH <2, Cool to </= 6° C	14 days for extraction; 40 days for analysis
Cyanide	250 mL amber plastic bottle	NaOH to pH>12, Cool to </= 6° C	14 days
Alkalinity	125 mL plastic bottle	Cool to </= 6° C	14 days
Nitrate	125 mL plastic bottle	Cool to </= 6° C	48 hours
Phosphorus	250 mL plastic bottle	H_2SO_4 to pH<2, Cool to </= 6° C	28 days
Sulfate	125 mL plastic bottle	Cool to </= 6° C	28 days
Oil and Grease	1 L glass bottle	HCl to pH <2, Cool to </= 6° C	28 days
TOC	250 mL narrow mouth amber glass bottle	HCl to pH<2, Cool to </= 6° C	28 days
BULK SAMPLES			
Asbestos	Resealable plastic bag or glass/plastic jar	None	180 days
PAINT CHIP SAMPLES			
Lead	Resealable plastic bag or glass/plastic jar	None	180 days
AIR SAMPLES			
TO-15 VOCs	Summa Canister/Tedlar bag	None	3 days Tedlar; 30 days Summa

Table 4
Sample Container, Preservation and Holding Time Requirements for State of Washington

Definitions:

° C	degrees Celsius
CH_3OH	Methanol
Cr(VI)	Hexavalent Chromium
DRO	Diesel Range Organics
GRO	Gasoline Range Organics
H_2SO_4	Sulfuric Acid
HCl	Hydrogen Chloride
HNO_3	Nitric Acid
L	Liter
mL	Milliliter
NaOH	Sodium Hydroxide
oz	Ounce
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PVOC	Petroleum Volatile Organic Compound
SVOC	Semi-volatile Organic Compound
TOC	Total Organic Carbon
VOC	Volatile Organic Compound

Table 5
Quality Assurance Objectives for Field Measurements

Matrix	Parameter	Method Reference	Precision[(a)]	Accuracy[(b)]	Completeness
Groundwater or Surface Water	Water levels	ASTM D5413 - 93(2007)	+/- 0.01 ft	0.005 ft	95%
	Temperature	EPA 170.1, Mercury thermometer or electronic temperature probe	±0.5° C	1.0° C	95%
	Conductivity	EPA 120.1, Electrometric	±25 µmho/cm^2	10 µmho/cm^2	95%
	pH	EPA 150.1, Electrometric	±0.1 pH units	0.05 pH units	95%
	Turbidity	EPA 180.1, Electrometric	10 NTU[(d)]	0.5 NTU[(c)]	95%
	Redox Potential	ASTM D1498-08	±10 mV	10 mV	95%
	Dissolved Oxygen	SM-A4500	±0.05 mg/L	±0.1 mg/L	95%
	Ferrous Iron	SM3500-FeD using a Hanna 96 Series Photometer	±0.01 mg/L @1.50 mg/L	±0.04 mg/L	95%

Notes:

[(a)] Expressed as the acceptable deviation from the scale.

[(b)] Expected based on equipment manufacturer specifications.

[(c)] Acceptable accuracy and precision based on the range of measurements.

ASTM = American Society for Testing and Materials (*Annual Book of ASTM Standards* , American Society of Testing and Materials, 2008)
C = centigrade
Cm = centimeter
EPA = Environmental Protection Agency
Ft = feet
mg/L = milligrams per liter
mV = millivolt
NTU = nephelometric turbidity unit.
QA = quality assurance
µmho = micromhos
SM = *Standard Methods for the Examination of Water and Wastewater, 21st ed* . (APHA, 2005).

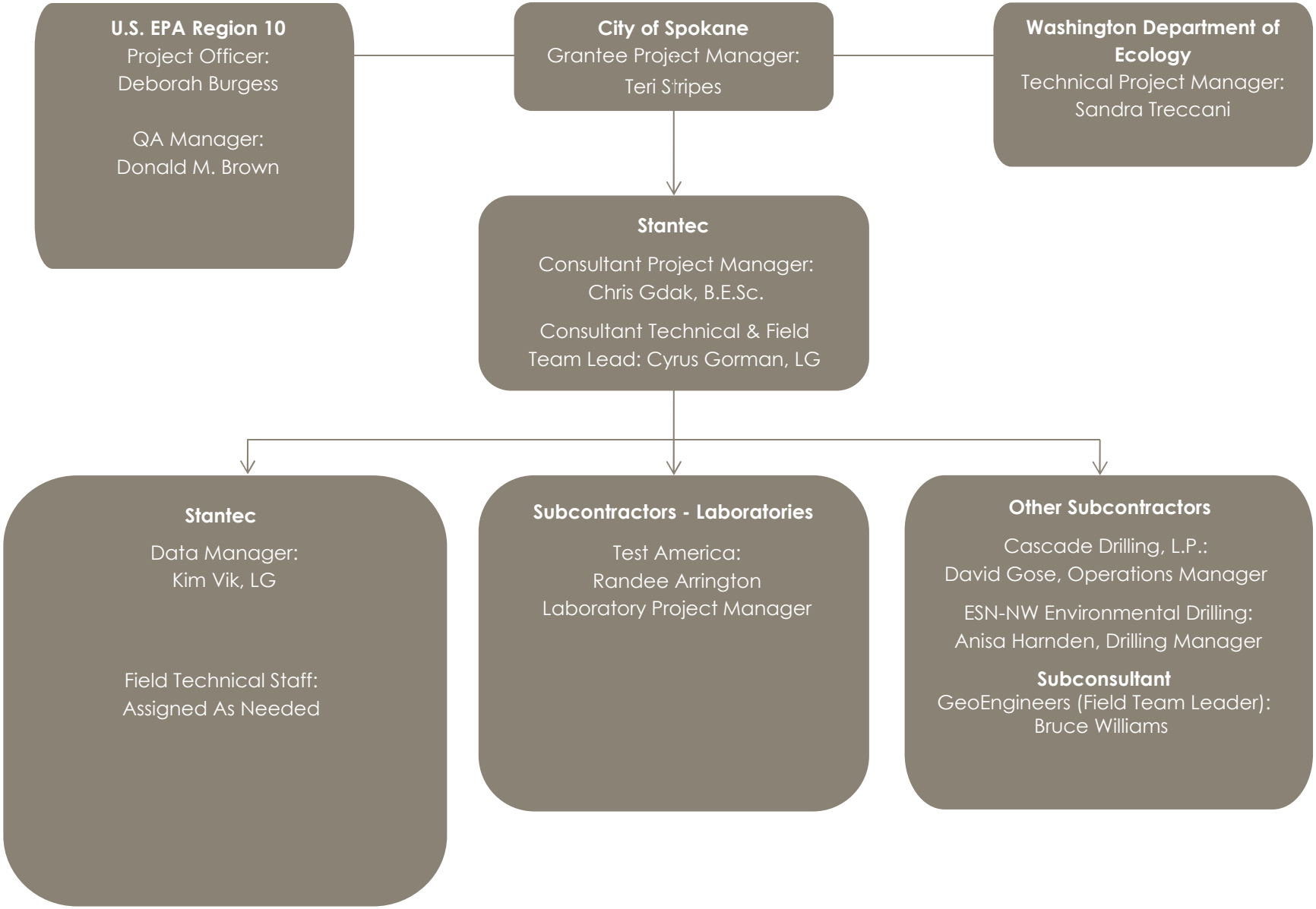
Table 6
Preventive Maintenance for Field Measurement Equipment

INSTRUMENTS	MAINTENANCE PROCEDURES/SCHEDULE	SPARE PARTS IN STOCK
ppbRae 3000 Photoionization Detector	1. Calibrate beginning and end of each day and as necessary during use. 2. Check battery, and recharge when low. 3. Clean lamp and sensor when display creeps upward, PID responds to moisture, or when movement of PID results in response on display. 4. Replace external dust filter as needed.	1. Battery charger 2. Spare lamps 3. Spare filter cartridges
Thermo Environmental Model 580B Photoionization Detector	1. Calibrate beginning and end of each day, and as necessary during use. 2. Check battery, and recharge when low. 3. Clean lamp and dust filter as needed. 4. Replace water traps if they become wet.	1. Spare lamps 2. Spare dust filters
Field Gas Chromatograph	1. Change injector septa daily. 2. Repack column when separation and linearity becomes poor. 3. Clean PID lamp before each initial calibration; change when sensitivity lost. 4. Clean injector port/liner weekly.	1. Septa 2. Empty columns & column packing 3. PID lamps 4. Injector lines
pH Meter	1. Calibrate beginning and end of each day, and as necessary during use. 2. Replace electrodes as needed.	1. pH buffers 2. Batteries 3. Spare electrodes
Conductivity Meter	1. Calibrate beginning and end of each day, and as necessary during use. 2. Check redline and replace batteries if does not calibrate.	1. Batteries
YSI 556 Multi-Meter	1. Calibrate beginning and end of each day, and as necessary during use. 2. Replace sensors per manufacturers guidelines.	1. Buffer solutions 2. Batteries
Hanna 96 Series Photometer	1. Calibrate beginning and end of each day, and as necessary during use. 2. Check redline and replace batteries if does not calibrate.	1. Reagent 2. Batteries

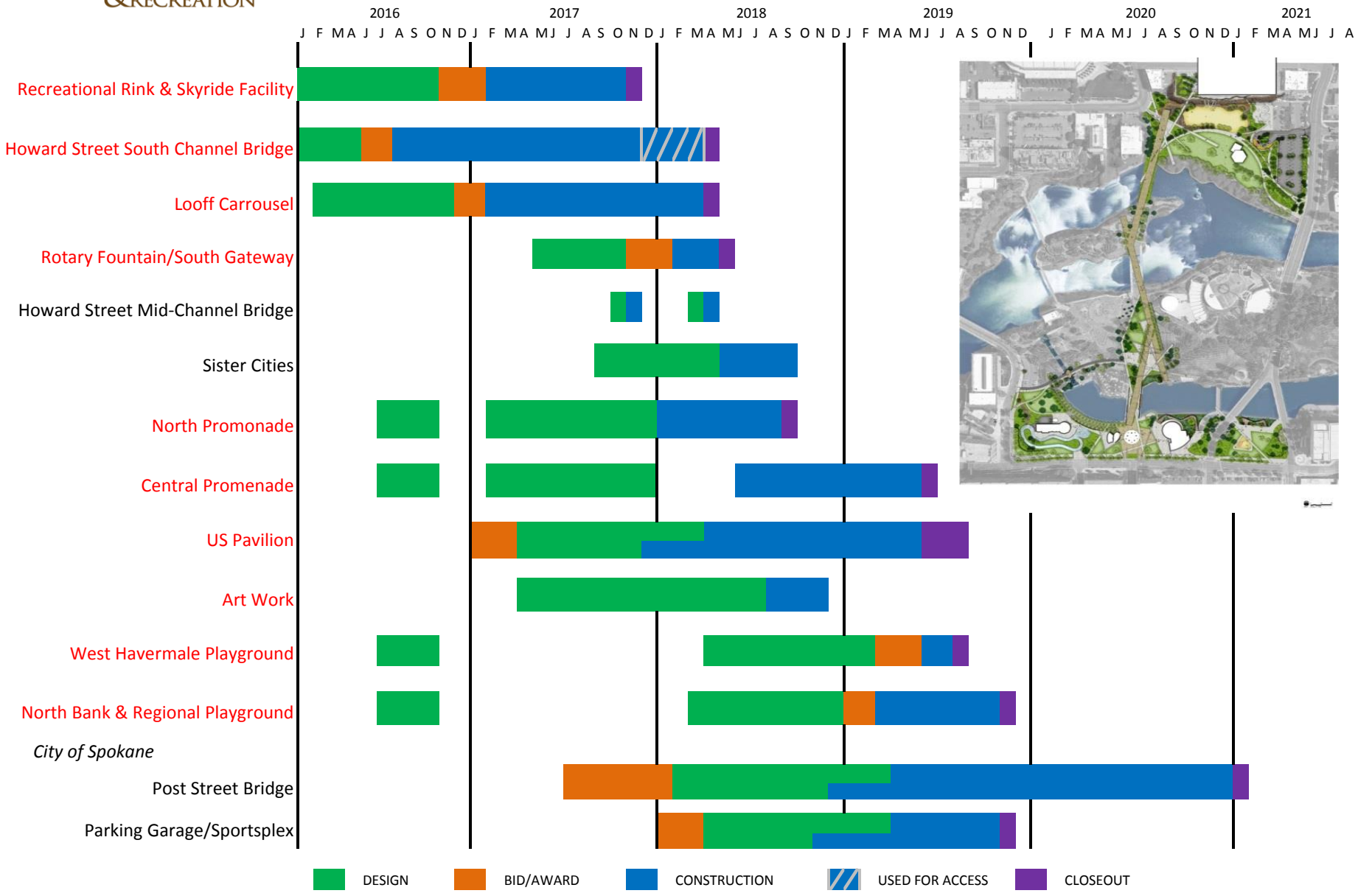
Notes:
PID = photoionization detector
UV = ultraviolet

FIGURES

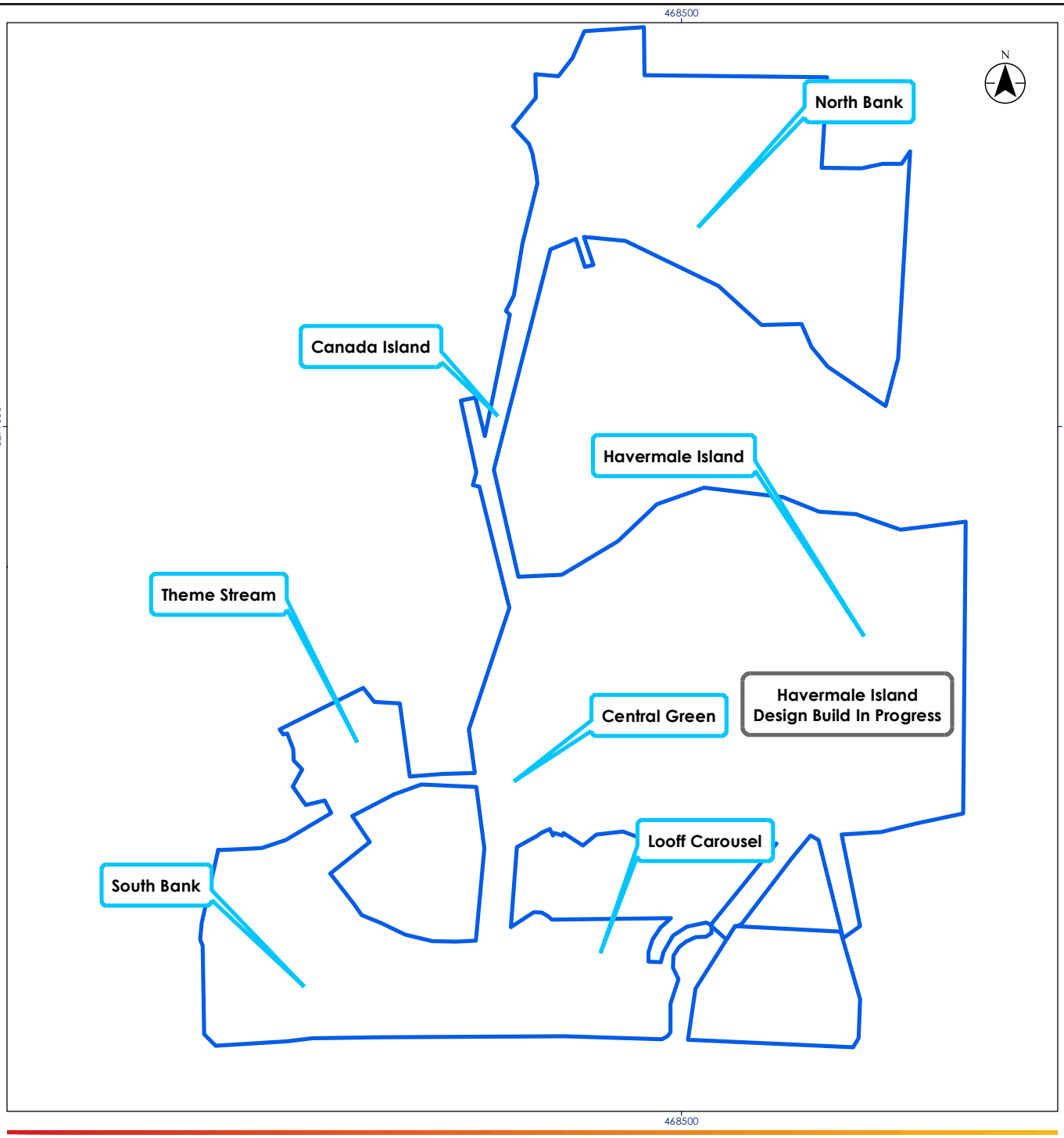
Figure 1
Project Organization Chart
Quality Assurance Project Plan
City of Spokane, Washington



RIVERFRONT PARK REDEVELOPMENT
EXECUTIVE SUMMARY SCHEDULE



11/22/2017



Planned Development Areas

0 200 400 Feet

1:3,600 (at original document size of 8.5x11)

[redacted]

Project Location
Riverfront Park
Spokane, WA

Prepared by JB on 2018-02-01
Technical Review by CG on 2018-02-01
Independent Review by CG on 2018-02-01

Client/Project
City of Spokane
Analysis of Brownfield Cleanup Alternatives

Figure No.
3

Title
Planned Development Areas

Notes
1. Coordinate System: NAD 1983 UTM Zone 11N
2. Service Layer Credits: Sources: Esri, HERE, DeLorme, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China

APPENDIX A SOIL MANAGEMENT PLAN

Soil Management Plan, Revision 1

Riverfront Park Redevelopment
Spokane, Washington

for
City of Spokane Parks and Recreation

May 4, 2017

GeoEngineers
Earth Science + Technology

Soil Management Plan, Revision 1

Riverfront Park Redevelopment
Spokane, Washington

for
City of Spokane Parks and Recreation

May 4, 2017

GeoEngineers

523 East Second Avenue
Spokane, Washington 99202
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Table of Contents

1.0 INTRODUCTION

This Soil Management Plan, Revision 1 (SMP) provides soil handling recommendations for construction and maintenance activities for redevelopment projects and maintenance in Riverfront Park in downtown Spokane, Washington (herein referred to as the "Redevelopment Project" or "subject property"). The Redevelopment Project includes multiple projects throughout the 56-acre park and maintenance is expected to occur at the park indefinitely.

The subject property is shown relative to surrounding physical features on the Vicinity Map, Figure 1. Subject property layout is shown on the Site Plan, Figure 2. Acceptable soil uses for areas disturbed during construction activities is shown on Acceptable Soil Uses, Figure 3.

This SMP provides guidance to City of Spokane (City) employees and other contractors that perform earthwork activities at the subject property. The objectives of the plan are to: (1) disclose the potential presence of potential contaminants of concern (COCs); (2) minimize risks to worker health/safety and the environment; and (3) outline general procedures for handling and disposal of contaminated soil if encountered during construction activities. This plan does not address dewatering considerations that would be associated with deep excavations encountering groundwater.

The original SMP was dated June 23, 2016. This revised plan includes modifications to Section 8.0, specifically procedures to mark and record areas where contaminated soil remains at the subject property.

2.0 BACKGROUND

The site is located at 507 North Howard Street in Spokane, Washington. The site is bounded by Spokane Falls Boulevard to the south, Post Street to the west, Washington and Division Streets to the east and the Spokane River and Mallon Avenue to the north. The property is currently owned by the City and is a public park. The site includes Havermale Island, Canada Island, and the portions of Riverfront Park on the north and south banks of the Spokane River.

Development at the subject property began in the late 1870s and primarily included mixed industrial uses and railroad activities. In 1973, the subject property underwent construction as the current park in preparation for Expo 1974. Historical records indicate that many of the historical areas were covered with fill as part of park construction and remnant impacts from industrial activities were generally unknown. Our understanding of the subject property, the comprised parcels, and historic uses of each is based on the results of our Phase I Environmental Site Assessment (ESA) for the subject property completed for the City (GeoEngineers 2014).

The Phase I ESA identified recognized environmental concerns at the subject property that may include the presence of petroleum hydrocarbons, metals, chlorinated solvents and polycyclic aromatic hydrocarbons (PAHs) in soil within the construction areas. Additionally, the Phase I ESA identified several underground storage tanks (USTs) previously in use at the subject property, some of which may remain in-place.

On April 4 and 5, 2016, GeoEngineers advanced 16 geotechnical and environmental borings to bedrock along the south bank around the Skyride Terminal and in the Gondola Meadow. Seven soil samples from

select borings were analyzed for COCs and chemical analysis indicated the presence of PAHs greater than MTCA Method A for Unrestricted Land Uses cleanup criteria (Ecology 2013) in each of the samples analyzed. In addition, lead, cadmium, arsenic and residual oil range hydrocarbons were detected above MTCA Method A for Unrestricted Land Uses cleanup criteria in boring B-13 and only lead was detected greater than MTCA Method A for Unrestricted Land Use in boring B-18. Lead, cadmium, arsenic and residual oil range hydrocarbons detected in samples from other borings above reporting limits, but below MTCA Method A Cleanup Criteria. Table 1 provides MTCA Method A Cleanup Criteria for known COCs at the subject property.

TABLE 1. MTCA METHOD A SOIL CLEANUP CRITERIA FOR UNRESTRICTED LAND USE

Parameter		MTCA Method A Unrestricted Land Use Cleanup Levels (mg/kg)
Total Petroleum Hydrocarbons	Gasoline Range Organics	100/30[1]
	Diesel Range Organics	2,000
	Heavy Oil	2,000
Metals	Arsenic	20
	Barium	NE
	Cadmium	2
	Chromium	2,000
	Lead	250
	Silver	NE
	Selenium	NE
	Mercury	2
PAHs	Benzo(a)pyrene	0.1
	Naphthalenes[2]	5
	cPAHs Toxic Equivalency[3]	0.1

Notes:

[1] Cleanup level is 100 mg/kg for gasoline mixtures without benzene and the total BTEX compounds are less than 1 percent of the total mixture. The cleanup level for all other gasoline mixtures is 30 mg/kg.

[2] Cleanup level for total naphthalenes (naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene)

[3] Toxic equivalency for carcinogenic poly aromatic hydrocarbons (cPAHs) calculated using the toxic equivalency factors found in MTCA Table 708-2.

mg/kg = milligrams per kilogram; NE = Not Established

3.0 HEALTH AND SAFETY

Excavation and other major construction activities involving suspected contaminated soil shall be conducted by Hazardous Waste Operations and Emergency Response (HAZWOPER) trained personnel with a minimum of 24-hours training. In addition to HAZWOPER training, the earthwork subcontractor shall prepare a site-specific Health and Safety Plan (HASP) describing potential COCs and exposure pathways, appropriate personal protective equipment (PPE) requirements and emergency response plans. City employees conducting regular maintenance do not require HAZWOPER training.

4.0 ENVIRONMENTAL PROFESSIONAL

For major projects, an environmental professional shall be retained to observe and document excavations. The frequency and duration of on-site observation will depend on the nature of site soils for each particular project and the planned end use of excavated soil. Regular park maintenance shall not require the observation and documentation by an environmental professional. The environmental professional shall assist the contractor and City with: identifying potentially contaminated on-site fill; collecting profile and excavation soil samples; providing soil profile documentation; and obtaining disposal approval. The environmental professional also shall document the contaminated soil excavation and handling and provide the required reports to Washington State Department of Ecology (Ecology).

5.0 DOCUMENTATION

Information regarding the location and characteristics of Contaminated Soil or Impacted Soil shall be documented in a characterization report so that future activities completed in those affected or modified areas can be appropriately planned with regard to health and safety, characterization and soil management. Reports shall include:

- Descriptions of field or construction activities;
- Exploration, excavation or sampling locations;
- Dimensions of explorations or excavations;
- A description of the soil encountered; and
- Results of field screening or laboratory chemical analysis.

Reports shall be filed with local and state agencies.

6.0 SOIL CHARACTERIZATION

In support of the redevelopment of Riverfront Park, environmental sampling shall be conducted during design studies to characterize soil that might be encountered during major construction projects. As projects are designed, exploration locations shall be identified for investigation. Ideally, environmental sampling will be combined with geotechnical investigations to reduce assessment costs by collecting both environmental and geotechnical information at the same time. Environmental-focused exploration locations shall focus on areas where soil will be excavated. Supplemental investigations shall be defined by an environmental work plan specific to each project, and the environmental work plan shall include field screening methods, sampling and analysis procedures and a health and safety plan. Representative soil samples shall be submitted for laboratory chemical analysis to characterize environmental conditions. Based on the site history, COCs throughout the park include petroleum hydrocarbons, PAHs and metals. Chemical analysis shall include:

- Total Petroleum Hydrocarbons (NWTPH-HCID);
- PAHs (EPA 8270D); and
- Metals (EPA 6010):

- Arsenic;
- Barium;
- Cadmium;
- Chromium;
- Lead;
- Mercury;
- Selenium; and
- Silver.

Additional COCs might be identified for specific projects or areas of the park based on the results of the Phase I ESA.

If total metals are detected at a concentration equal to or exceeding 20 times the Resource Conservation and Recovery Act (RCRA) maximum toxicity characteristic concentration, the samples shall be analyzed using the Toxicity Characteristic Leaching Procedure (TCLP) to determine if leachable metals exceed RCRA toxicity concentrations. Soil with leachable metals concentrations greater than the RCRA regulatory limits shall be considered hazardous. Table 2 below summarizes the RCRA toxicity characteristic regulatory levels.

TABLE 2. MAXIMUM TOXICITY CHARACTERISTIC CONTAMINANT CONCENTRATIONS

Contaminant	TCLP Regulatory Level (mg/L)	Soil Concentration Requiring TCLP Analysis, 20x Regulatory Level (mg/kg)
Arsenic	5	100
Barium	100	2,000
Cadmium	1	20
Chromium	5	100
Lead	5	100
Mercury	0.2	4
Selenium	1	20
Silver	5	100

Notes: mg/L = milligrams per liter

If petroleum hydrocarbons are detected at concentrations greater than MTCA Method A, follow up analysis shall include more precise hydrocarbon analysis methods including NWTPH-Gx and NWTPH-Dx for gasoline-, diesel- and oil-range hydrocarbons, respectively. Some site soil might contain organic matter or man-made heavy oils such as cooking grease. NWTPH-Dx with silica gel cleanup will be used as applicable to reduce the potential for biogenic interference, provided initial NWTPH-Dx analyses indicate that non-TPH hydrocarbons could be a significant component of the TPH being detected in soil; or if comparative results of NWTPH-Dx with and without silica gel cleanup on the same samples indicate biogenic interference. Additional testing might be required if petroleum hydrocarbons are detected above laboratory reporting limits in accordance with MTCA Table 830-1, Required Testing for Petroleum Releases. This includes polychlorinated biphenyls (PCBs) using EPA Method 8082 and other fuel additives and blending compounds.

If field screening indicates volatile organic compound (VOC) concentrations greater than 10 parts per million (ppm) as measured with a calibrated photoionization detector (PID), then the soil sample shall also be analyzed for VOCs using EPA method 8260. An XRF machine also can be used to field-screen soil for metals.

After review of the chemical analytical data, the soil represented by the boring shall be categorized into one of the three soil categories described in Section 7.0.

7.0 SOIL CATEGORIES AND DEFINITIONS

Three soil handling categories were developed to guide the City and contractor during major soil excavation activities. The following section (Section 8.0) discusses the specific soil excavation and handling protocols for each soil category. Use of these categories and protocols is predicated on subsurface soil within each project area being adequately characterized and extents of each soil category sufficiently delineated.

7.1. Contaminated Soil

For the purposes of soil handling for the Redevelopment Project, soil is considered "contaminated" if:

- Contaminant concentrations for any analyte exceed MTCA Method A for Unrestricted Land Use cleanup criteria;
- Contaminant concentrations meet or exceed dangerous waste and dangerous waste source criteria as defined in Washington Administrative Code (WAC) 173-303;
- TCLP results exceed RCRA regulatory levels; or
- Physical evidence of contamination (sheen, odor, staining) is observed, unless additional chemical analysis is performed to further categorize the soil.

7.2. Impacted Soil

Soil is considered "impacted" if:

- Contaminant concentrations for any analyte exceed laboratory reporting limits but are **less** than the respective MTCA Method A Cleanup Criteria for Unrestricted Land Use.

7.3. Clean Soil

Soil is considered "clean" if:

- Contaminants are not detected for any analyte at concentrations that exceed the respective method reporting limit; and
- Physical evidence of contamination (sheen, odor or staining) is **not** observed.

Method reporting limits for non-detected COCs must be less than applicable MTCA Method A cleanup levels for unrestricted land use for soil to be considered "clean".

8.0 SOIL EXCAVATION AND HANDLING RECOMMENDATIONS

Each soil category requires special handling and reuse procedures. The following sections provide additional information on handling each soil category. A flow chart is provided on Figure 3 to assist with categorizing soil and determining suitable uses and restrictions.

When excavation activities in Contaminated Soil or Impacted Soil are finished, characterization soil samples representative of soil left in place shall be collected by the environmental professional. Soil left in place includes soil under structures and soil remaining in-place after excavations. Characterization soil samples shall be submitted for chemical analysis in accordance with the test methods described in Section 6.0 or as appropriate, based on previous project testing results.

Specific on-site soil reuse areas for Contaminated Soil or Impacted Soil may be designated through the park redevelopment. If the soil is consolidated or reused onsite, limited purpose landfill regulations (WAC 173-350-400) do not apply (Ecology, 2016). Soil reuse plans should be submitted to Ecology through the Voluntary Cleanup Program opinion process to help minimize risk associated with reusing Contaminated and Impacted soil.

8.1. Contaminated Soil

Contaminated Soil includes Dangerous Waste or soil where COC concentrations were detected at concentrations **greater** than the MTCA Method A for Unrestricted Land Use cleanup criteria. Special handling and end use considerations are needed for soil categorized as contaminated. Special handling and disposal shall include the following:

- **Soil Excavation and Segregation:** The City's environmental consultant shall be on-call and on-site during applicable excavation of Contaminated Soil to field screen soil and collect characterization soil samples as needed. Field screening methods are described in Appendix A. The Contractor shall segregate Contaminated Soil from the other soil categories to prevent mingling of Contaminated Soil with other soil categories. Characterization soil samples shall be collected at the end of the excavation to represent soil left in place.
- **Loading/Transportation/Stockpiling:** Soil categorized as Dangerous Waste or Contaminated Soil can either be loaded directly into trucks and transported for off-site permitted disposal, or can be temporarily stockpiled on plastic sheeting (Visqueen) on the subject property, pending disposal or evaluation for reuse. Stockpiles shall be surrounded by sand bags and covered with plastic sheeting to minimize contaminant-impacted runoff and wind-blown dust. The sand bags shall reduce the potential for stormwater run on to, or leachate flow from the stockpiles; additionally, the sand bags may be used to anchor the plastic sheeting. Additional soil handling requirements might be provided in the approved erosion and sediment control plan.

  Contaminated Soil may be screened on site to separate grain sizes greater than 1-inch-diameter from finer material. Material greater than 1-inch-diameter may be combined with Impacted Soil for on-site reuse or disposed of as Clean Soil. The Contractor shall develop and maintain a procedure to track Contaminated Soil loads transported off site for permitted disposal. The contractor shall develop and maintain dust suppression and wash water handling procedures for screening operations.
- **Acceptable Uses of Contaminated Soil**: The acceptable use of contaminated soil depends on the COCs and the concentrations.

- Dangerous Waste shall be disposed of off-site at an approved landfill.
- Contaminated Soil not tested for VOCs or with VOCs less than reporting limits may be suitable for use under buildings, structures and roads if soil engineering properties meet geotechnical requirements for the proposed application. If soil is contaminated with VOCs at concentrations greater than MTCA Method A for Unrestricted Land Use cleanup criteria, the soil shall be disposed of off-site or an approved on-site repository. If Contaminated Soil has VOCs greater than reporting limits, but less than MTCA Method A for Unrestricted Land Use, the soil can be used in open areas under roads or walkways, but not within 20 feet of buildings and structures where vapors could accumulate within enclosed areas. Contaminated Soil identified for reuse shall be placed above the mean high groundwater table level (or above river level for the south bank) and more than 12 inches below surface grade. Characterization samples of reused soil or soil left in place should be collected and analyzed in general accordance with Section 6.0. Sample location and chemical analysis results should be entered into the project GIS database to identify locations of contaminated soil left in place and concentrations of site contaminants. Permanent stormwater infiltration infrastructure shall not be designed to allow infiltration of stormwater into and through Contaminated Soil left in place.

- **Disposal/Recycling Facilities:** Contaminated Soil can be transported to the selected disposal facility after approval is granted by the facility. Additional chemical analysis might be required by the disposal facility before material acceptance. Potential disposal/recycling facilities include the following:
  - Waste Management's Graham Road Landfill in Medical Lake, Washington.
  - Waste Management's Columbia Ridge Landfill in Arlington, Oregon for disposal of Dangerous Waste.
  - Approved on-site repository.

8.2. Impacted Soil

Impacted Soil is defined as soil with COCs concentrations **greater** than laboratory reporting limits, but **less** than MTCA Method A Unrestricted Land Use cleanup criteria. Special handling and end use considerations are needed for impacted soil. Special handling and disposal shall include the following:

- **Soil Excavation and Segregation**: The City's environmental consultant shall be on-call and on-site during applicable excavation of Impacted Soil to field screen soil and collect characterization soil samples as needed. The Contractor shall segregate Impacted Soil from soil of other categories to prevent co-mingling of soil types. Characterization soil samples shall be collected at the limits of excavations to represent soil left in place.
- **Loading/Transportation/Stockpiling:** Impacted Soil can either be loaded directly into trucks or temporarily stockpiled on plastic sheeting (Visqueen) on the subject property or other designated areas. Stockpiles shall be surrounded by sand bags and covered with plastic sheeting to minimize contaminant-impacted runoff and wind-blown dust. The sand bags shall reduce the potential for stormwater run on to, or leachate flow from the stockpiles; additionally, the sand bags may be used to anchor the plastic sheeting. Additional soil handling requirements might be provided in the approved erosion and sediment control plan.
- **Acceptable Uses of Impacted Soil**: Impacted Soil not tested for VOCs or with VOCs less than laboratory reporting limits might be suitable for use under buildings, structures, roads, under landscape areas

and within electrical and non-potable water utility corridors if soil engineering properties meet geotechnical requirements for the proposed application. If Impacted Soil has VOCs greater than reporting limits, the soil can be used in open areas under roads or walkways, but not within 20 feet of buildings and structures where vapors could accumulate in enclosed areas.

Impacted Soil shall be placed above the mean high groundwater table level (or above river level for the south bank) and more than 6 inches below surface grade. Stormwater infiltration shall not be directed towards areas of Impacted Soil left in place.

- **Disposal/Recycling Facilities:** Impacted Soil can be transported to a selected disposal facility after approval is granted by the facility, if needed. Additional chemical analysis might be required by the disposal facility before material acceptance.

8.3. Clean Soil

Clean soil includes soil where COCs are not detected or COC concentrations were detected at concentrations that represent background conditions. There are no special handling or end-use requirements for this soil. Characterization soil samples shall be collected at the limits of excavations to represent soil left in place.

8.4. Equipment

Excavation equipment used to handle contaminated soil and vehicles driven over on-site fill shall be decontaminated using a high-pressure/low-flow wash at a dedicated vehicle wash area before exiting the site. Decontamination water shall be contained onsite, sampled for the contaminants of concern (PAHs and metals), profiled and appropriately disposed. Decontamination water collected from the vehicle wash shall only be released to the municipal storm or sanitary sewers if applicable permits and approvals are obtained from Ecology and/or the City of Spokane Wastewater Management Department, as applicable. The contractor shall dedicate specific excavation equipment for handling on-site contaminated fill to reduce the required decontamination efforts and minimize decontamination water generated. Trucks used to transport contaminated soil offsite, shall be covered with tarps to minimize wind-blown loss of contaminated materials over the haul route.

8.5. Dust Control

The contractor shall minimize fugitive dust generated from on-site fill by actively suppressing dust. Dust control can include but is not limited to:

- Clearing only those areas where immediate activity will take place while maintaining original ground cover as long as practical.
- Spraying exposed surfaces with water or other suitable palliative and repeating as necessary throughout the course of construction. Water applied as dust control shall not leave the site as surface runoff.

9.0 DISCOVERY OF UNEXPECTED POTENTIALLY CONTAMINATED/IMPACTED SOIL OR USTS

The City's environmental consultant shall be on-call and available to perform field screening and characterization sampling as needed during construction activities. However; during construction activities,

it is the City's or Contractor's responsibility to identify potentially contaminated/impacted soil as described below, and to notify the City and the City's environmental consultant immediately after the discovery. Additionally, historic site uses indicate undocumented USTs may be encountered during construction activities at the subject property. It is the Contractor's responsibility to stop all work near the UST and notify the City and the City's environmental consultant immediately upon discovery.

9.1. Unexpected Potentially Contaminated or Impacted Soil

Excavated soil from a location shall be considered to be petroleum-contaminated/impacted if it exhibits one or more of the following physical characteristics:

- Staining;
- Petroleum hydrocarbon or other odors associated with VOCs;
- A moderate or heavy sheen when placed in contact with water; and/or
- Significant concentrations of organic vapors detected using headspace field screening methods.

If soil exhibiting one or more of the above characteristics is discovered that has not been previously identified and categorized, the Contractor shall notify the City immediately for characterization prior to removal and/or disposal. A "Potentially Contaminant-Impacted Soil Notification Form" is presented in Appendix B. Upon discovery of potentially contaminated/impacted soil, the Contractor shall refer to this guide for contact information of people to notify as well as information regarding the location, type and actions taken to address the potentially contaminated soil.

9.2. Undocumented UST Discovery

As described in Section 2.0 above, based on the results of our Phase I ESA, several USTs have been previously in use at the subject property, some of which might remain in-place. Additional undocumented USTs could be present beneath the subject property.

USTs encountered during construction shall be removed in accordance with the "Underground Storage Tank Regulations" ([WAC 173-360) and Ecology "Guidance for Site Checks and Site Assessments for Underground Storage Tanks" dated April 2003. A Washington State Site Assessment certified representative shall be present on the subject property during the removal of the USTs.

If a UST is discovered, the Contractor shall stop work near the UST and notify the City immediately. The Contractor also shall immediately notify Ecology and the Fire Marshall. Characterization of contents and the surrounding soil shall be performed prior to removal and/or disposal using the "Potentially Contaminant-Impacted Soil Notification Form" in Appendix B. Upon discovery of a UST and associated potentially contaminated/impacted soil adjacent to, or in the vicinity of the UST, the Contractor shall refer to this guide for contact information of people to notify as well as information regarding the actions taken to address the discovery.

If discovery of a previously unknown UST results in a release, first take steps to ensure the safety of workers at the site. The Contractor shall stop work near the UST and notify the City immediately. If safe to do so, take appropriate steps to contain the release including pumping out fluids to a different container and excavating soil where the release occurred. The City shall call environmental consultant and a licensed UST removal contractor. A tank removal and site characterization plan should be developed for the response.

10.0 CONTACT INFORMATION

If unexpected potentially contaminated soil, undocumented USTs or potentially contaminated groundwater is discovered during construction activities, the Contractor shall notify the City. As stated previously, in the event an undocumented UST is discovered, Ecology and the Fire Marshall also shall be immediately notified. Table 3 provides contact information for the program manager during construction and the Assistant Director of Park Operations at Riverfront Park for regular operation and maintenance.

TABLE 3. RELEVANT PROJECT CONTACTS

Name	Title	Phone	Email
City of Spokane Parks and Recreation – Construction Phase			
Berry Ellison	Program Manager	Office: 509.625.6276 Cell: 509.944.9932	bellison@spokanecity.org
Harvey Morrison	Construction Manager	509.981.9945	hmorrisoncm@gmail.com
City of Spokane Parks and Recreation – Riverfront Park Maintenance and Operations			
Garrett Jones	Assistant Director of Park Operations	509.363.5462	gjones@spokanecity.org
Security	NA	509.994.1424	NA
Maintenance	NA	509.879.7335	NA
Spokane Fire Department			
Michael Miller	Fire Marshall	509.625.7040	mmiller@spokanecity.org
Ecology			
Sandra Treccani	Ecology Toxics Cleanup Program Site Manager	509.329.3412	satr461@ecy.wa.gov

11.0 PARK MAINTENANCE

Regular maintenance is conducted as part of normal operations at Riverfront Park. Regular maintenance includes activities such as landscape planting, tree removal, sprinkler repair, subsurface utility replacement/repair and other ground-disturbing activities. Regular maintenance activities that result in soil disturbances shall be documented and reported to Ecology in an annual maintenance summary report. If planned maintenance activities require excavating into previously undisturbed areas or excavating soil below imported clean soil, Ecology shall be notified prior to the start of work if conditions allow. When conducting maintenance, existing caps and soil segregation infrastructure (i.e. geotextiles) shall be maintained. Maintenance activities shall be conducted in a manner to keep clean imported soil from mixing with remaining in place Contaminated or Impacted Soil. To assist Parks personnel with documenting and understanding areas of known contamination, a park-wide maintenance plan should be developed that depicts areas of known contamination. The plan should be in an electronic format such as a GIS-based platform that can be updated as additional information is gathered. The maintenance plan should be included as part of the environmental covenant. Appropriate precautions shall be made to maintain worker safety during maintenance activities. This includes training employees on potential contaminants, exposure pathways and potential effects. The importance of hygiene and using appropriate PPE when conducting maintenance activities shall also be included in the training.

Employee training shall include procedures to prevent contaminant migration and mixing during maintenance activities. This includes erosion and sediment control measures to prevent Contaminated or Impacted Soil from entering the Spokane River, storm sewer systems or locations where the public could directly contact the soil.

Soil excavated as part of maintenance activities should be reused on-site in accordance with this plan, near the area it was removed from if possible. If off-site disposal is required, the soil should be tested in accordance with this soil management plan and disposed of in accordance with local, state and federal regulations.

12.0 LIMITATIONS

We have prepared this report for the exclusive use of the City of Spokane and their authorized agents. Within the limitations of scope, schedule and budget, our services have been executed in accordance with generally accepted environmental science practices in this area at the time this report was prepared. No warranty or other conditions, express or implied, shall be understood.

Any electronic form, facsimile or hard copy of the original document (email, text, table, and/or figure), if provided, and any attachments are only a copy of the original document. The original document is stored by GeoEngineers, Inc. and will serve as the official document of record.

Please refer to Appendix C, titled "Report Limitations and Guidelines for Use," for additional information pertaining to use of this report.

13.0 REFERENCES

GeoEngineers, Inc. 2014. "Phase I Environmental Site Assessment, Riverfront Park, 610 West Spokane Falls Boulevard." GEI File No. 0110-148-00. October 07.

Washington State Department of Ecology. "Questions about Contaminated Soil Consolidation at the Riverfront Park site." Message from Sandra Treccani to Berry Ellison. December 21, 2016. E-mail.

Washington State Department of Ecology. 2013. "Model Toxics Control Act Regulation and Statute." Compiled by Washington State Department of Ecology, Toxics Cleanup Program, Publication No. 94-06. Revised 2013.

FIGURES

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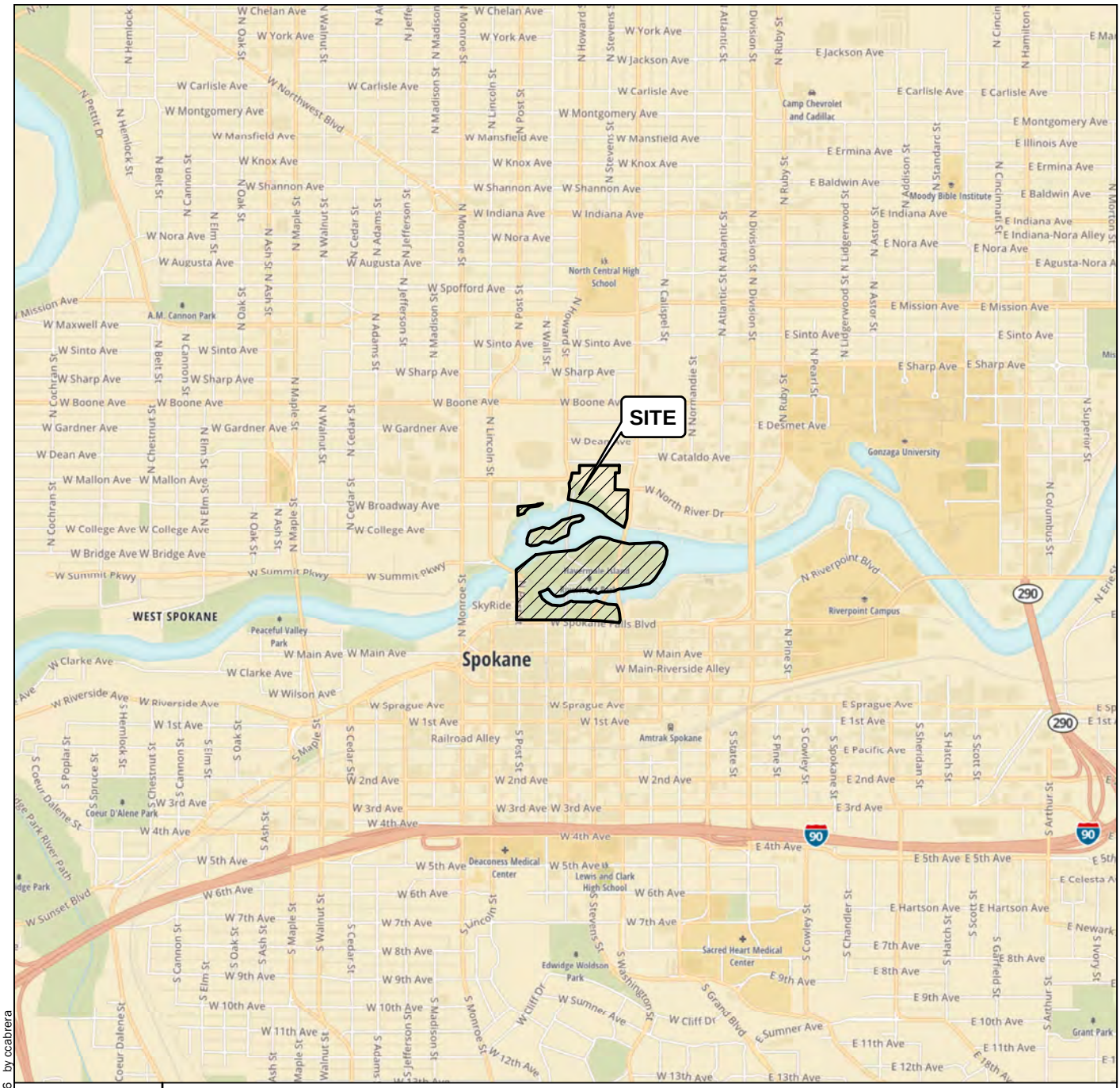


Legend

Site Boundary

N
W E
S

2,000 0 2,000

Feet

Notes:

1. The locations of all features shown are approximate.
2. This drawing is for information purposes. It is intended to assist in showing features discussed in an attached document. GeoEngineers, Inc. cannot guarantee the accuracy and content of electronic files. The master file is stored by GeoEngineers, Inc. and will serve as the official record of this communication.

Data Source: Mapbox Open Street Map, 2016

Projection: NAD 1983 UTM Zone 11N

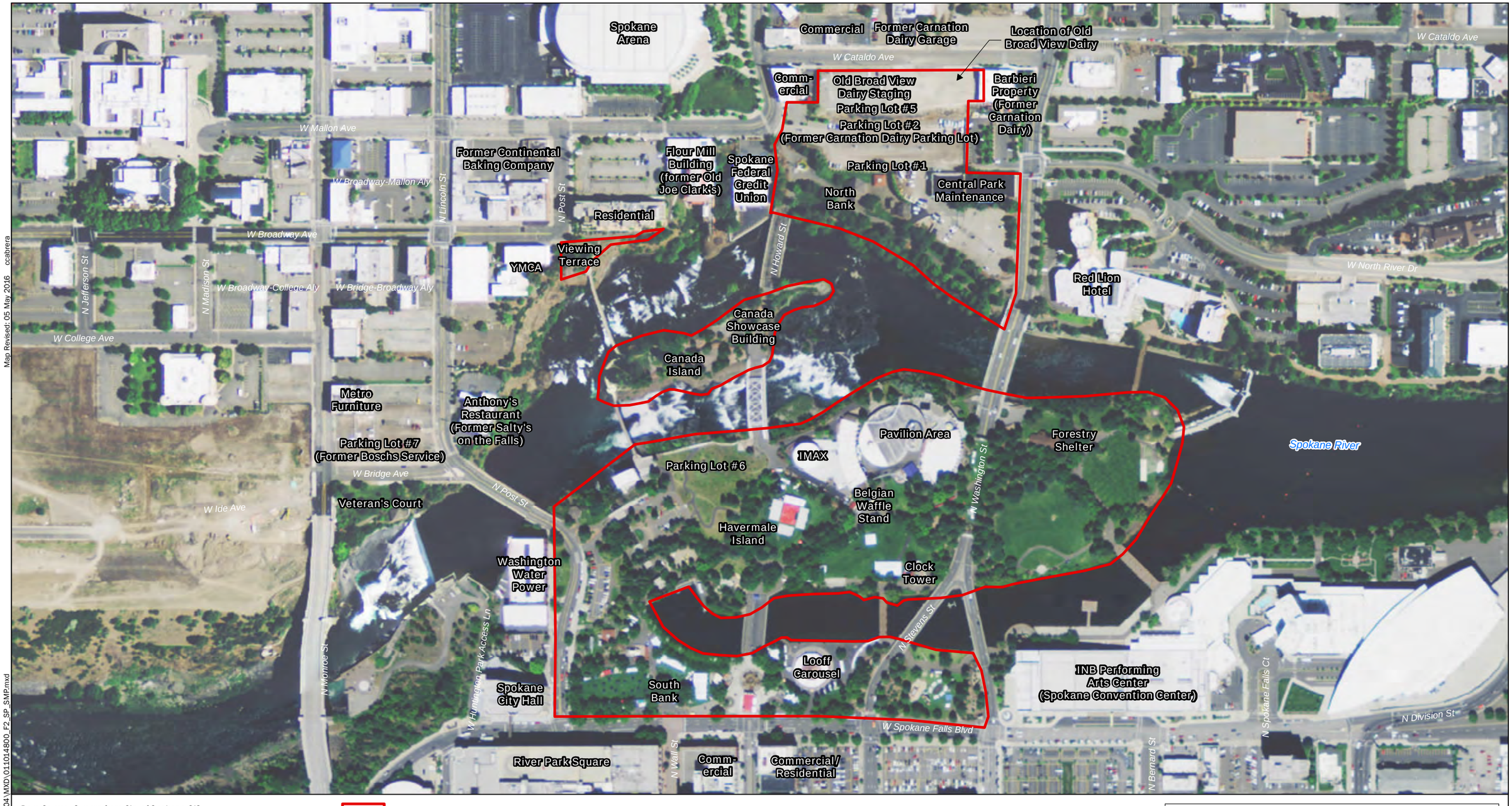
Vicinity Map

Riverfront Park Soil Management Plan
Spokane, Washington

GeoEngineers

Figure 1

P:\0\0110148\GIS\04\MXD\0110148O4_F1_VM.mxd Date Exported: 05/05/16 by ccabrera



Data Source: Streets from City of Spokane GIS.

Approximate Site Boundary

Notes:
1. The locations of all features shown are approximate.
2. This drawing is for information purposes. It is intended to assist in showing features discussed in an attached document. GeoEngineers, Inc. cannot guarantee the accuracy and content of electronic files. The master file is stored by GeoEngineers, Inc. and will serve as the official record of this communication.

Projection: NAD 1983 UTM Zone 11N

N W E S

300 0 300
Feet

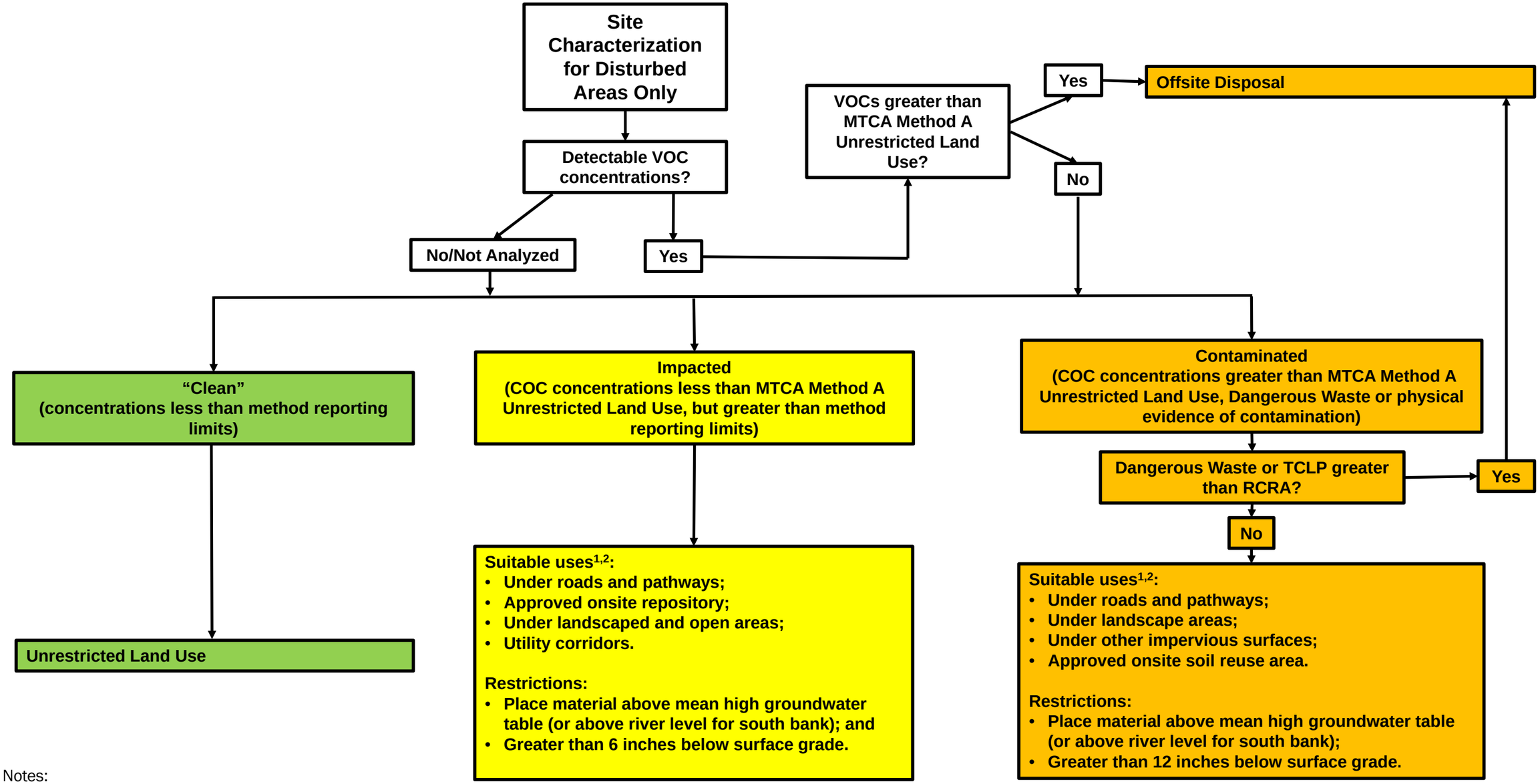
Site Plan

Riverfront Park Soil Management Plan
Spokane, Washington

GeoEngineers

Figure 2

Map Revised: 05 May 2016 ccabrera
Path: P:\0\0110148\GIS\04 MXD\0110148800_F2_SP_SMP.mxd
Office: PORT



Notes:

1. If VOCs are less than laboratory reporting limits the soil can be used under buildings or structures if soil properties meet geotechnical requirements.
2. If VOCs are greater than laboratory reporting limits, but less than MTCA Method A for Unrestricted Land Use, the soil can be used in open areas under roads and pathways, but not within 20 feet of buildings and structures where vapors could accumulate within enclosed areas if soil properties meet geotechnical requirements.

MTCA - Washington State Department of Ecology Model Toxics Control Act.
VOCs – Volatile Organic Compounds
PAHs – Polycyclic Aromatic Hydrocarbons
COCs – Contaminants of Concern
RCRA – Resource Conservation and Recovery Act
TCLP – Toxicity Characteristic and Leaching Procedure

Acceptable Soil Uses

Riverfront Park Soil Management Plan
Spokane, Washington

GeoEngineers

Figure 3

File No. 0110-148-04 5/6/16

APPENDICES

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APPENDIX A
Field Procedures

APPENDIX A
FIELD PROCEDURES

Field Screening of Soil Samples

Soil samples obtained from explorations shall be evaluated for evidence of possible contamination using field screening techniques. Field screening results can be used as a general guideline to delineate areas of possible petroleum- or VOC-related contamination in soil. In addition, screening results are often used as a basis for selecting soil samples for chemical analysis. The screening methods employed shall include: (1) visual examination, (2) water sheen testing, and (3) headspace vapor testing using a photoionization detector (PID).

Visual screening consists of observing the soil for stains indicative of petroleum-related contamination. Visual screening is generally more effective when contamination is related to heavy petroleum hydrocarbons such as motor oil, or when hydrocarbon concentrations are high. Sheen screening is a more sensitive screening method that can be effective in detecting petroleum-based products.

Water sheen testing involves placing soil in water and observing the water surface for signs of sheen. Sheens are classified as follows:

No Sheen (NS)	No visible sheen on water surface.
Slight Sheen (SS)	Light, colorless, dull sheen; spread is irregular, not rapid; sheen dissipates rapidly.
Moderate Sheen (MS)	Light to heavy sheen, may have some color/iridescence; spread is irregular to flowing; few remaining areas of no sheen on water surface.
Heavy Sheen (HS)	Heavy sheen with color/iridescence; spread is rapid; entire water surface may be covered with sheen.

Headspace vapor screening involves placing a soil sample in a plastic bag. Air is captured in the bag, and the bag is shaken to expose the soil to the air trapped in the bag. The probe of the PID is inserted into the bag. The PID measures the concentration of photoionizable gases and vapors in the sample bag headspace. The PID is designed to quantify photoionizable gases and vapors up to 2,000 ppm, and is calibrated with isobutylene. A lower threshold of significance of 1 ppm is used in application.

Field screening results are site- and exploration- specific. The results may vary with temperature, moisture content, soil lithology, organic content and type of contaminant.

APPENDIX B
Potentially Contaminant-Impacted Soil Notification Form

RIVERFRONT PARK REDEVELOPMENT
POTENTIALLY CONTAMINANT IMPACTED SOIL NOTIFICATION FORM

Prepared for:	**GENERAL INFORMATION**	
City of Spokane Department of Parks and Recreation 808 West Spokane Falls Boulevard, 5th Floor Spokane, Washington 99201	DATE OF DISCOVERY:	TIME OF DISCOVERY:
	PERSON DISCOVERING CONDITION:	PHONE NUMBER:
Prepared by: GeoEngineers 523 East Second Avenue Spokane, WA 99202 509.363.3125	PERSON FILLING OUT FORM:	PHONE NUMBER:
	APPROXIMATE LOCATION OF SOIL ON THE SITE:	

SOIL CHARACTERISTICS

PHYSICAL CHARACTERISTICS:

Odor:
- ☐ Yes (Describe_____)
- ☐ No

Staining:
- ☐ Yes (Describe_____)
- ☐ No

Other: _____

_____

SOIL DISTURBED:
- ☐ Soil in-place
- ☐ Soil stockpiled

FREE LIQUIDS:
- ☐ Yes (Content_____%)
- ☐ No

ACTIONS TAKEN: _____

_____

_____

_____

_____

ESTIMATED VOLUME OF CONTAMINATED SOIL:

NOTIFICATION CONTACT INFORMATION

City of Spokane	Environmental Professional	Contractor
Berry Ellison 509.625.6276 bellison@spokanecity.org		

ADDITIONAL INFORMATION

This record serves to document information, actions, and notifications regarding the discovery of and response to the presence of suspected and known contamination on the project.

APPENDIX C
Report Limitations and Guidelines for Use

APPENDIX C
REPORT LIMITATIONS AND GUIDELINES FOR USE[1]

This Appendix provides information to help you manage your risks with respect to the use of this report.

Read These Provisions Closely

Some clients, design professionals and contractors may not recognize that the geoscience practices (geotechnical engineering, geology and environmental science) are far less exact than other engineering and natural science disciplines. This lack of understanding can create unrealistic expectations that could lead to disappointments, claims and disputes. GeoEngineers includes these explanatory "limitations" provisions in our reports to help reduce such risks. Please confer with GeoEngineers if you are unclear how these "Report Limitations and Guidelines for Use" apply to your project or site.

Environmental Services Are Performed for Specific Purposes, Persons and Projects

This report has been prepared for the exclusive use of City of Spokane Parks and Recreation (Parks), their authorized agents and regulatory agencies. This report is not intended for use by others, and the information contained herein is not applicable to other sites.

GeoEngineers structures our services to meet the specific needs of our clients. For example, an environmental site assessment or remedial action study conducted for a property owner may not fulfill the needs of a prospective purchaser of the same property. Because each environmental study is unique, each environmental report is unique, prepared solely for the specific client and project site. No one except Parks should rely on this plan without first conferring with GeoEngineers. This report should not be applied for any purpose or project except the one originally contemplated.

This Environmental Report Is Based on a Unique Set of Project-Specific Factors

This report applies to the Riverfront Redevelopment Project in Spokane, Washington. GeoEngineers considered a number of unique, project-specific factors when establishing the scope of services for this project and report. Unless GeoEngineers specifically indicates otherwise, do not rely on this report if it was:

- not prepared for you,
- not prepared for your project,
- not prepared for the specific site explored, or
- completed before important project changes were made.

If important changes are made after the date of this remedial action plan, GeoEngineers should be given the opportunity to review our interpretations and recommendations and provide written modifications or confirmation, as appropriate.

[1] Developed based on material provided by ASFE, Professional Firms Practicing in the Geosciences; www.asfe.org.

Reliance Conditions for Third Parties

No third party may rely on the product of our services unless GeoEngineers agrees in advance, and in writing to such reliance. This is to provide our firm with reasonable protection against open-ended liability claims by third parties with whom there would otherwise be no contractual limits to their actions.

Environmental Regulations Are Always Evolving

Some substances may be present in the site vicinity in quantities or under conditions that may have led, or may lead, to contamination of the subject site, but are not included in current local, state or federal regulatory definitions of hazardous substances or do not otherwise present current potential liability. GeoEngineers cannot be responsible if the standards for appropriate inquiry, or regulatory definitions of hazardous substance, change or if more stringent environmental standards are developed in the future.

Uncertainty May Remain after Completion of Remedial Activities

Remediation activity completed in a portion of a site cannot wholly eliminate uncertainty regarding the potential for contamination in connection with a property. Our interpretation of subsurface conditions in this study is based on field observations and chemical analytical data from widely spaced sampling locations. It is always possible that contamination exists in areas that were not explored, sampled or analyzed.

Subsurface Conditions Can Change

This environmental report is based on conditions that existed at the time the study was performed. The findings and conclusions of this report may be affected by the passage of time, by manmade events such as construction on or adjacent to the site, by new releases of hazardous substances, or by natural events such as floods, earthquakes, slope instability or groundwater fluctuations. Always contact GeoEngineers before applying this report to determine if it is still applicable.

Soil and Groundwater End Use

The cleanup criteria referenced in this report are site- and situation-specific. The cleanup criteria may not be applicable for other sites or for other on-site uses of the affected media (soil and/or groundwater). Note that hazardous substances may be present in some of the site soil and/or groundwater at detectable concentrations that are less than the referenced cleanup criteria. GeoEngineers should be contacted prior to the export of soil or groundwater from the subject site or reuse of the affected media on site to evaluate the potential for associated environmental liabilities. We cannot be responsible for potential environmental liability arising out of the transfer of soil and/or groundwater from the subject site to another location or its reuse on site in instances that we were not aware of or could not control.

Most Environmental Findings Are Professional Opinions

Our interpretations of subsurface conditions are based on field observations and chemical analytical data from widely spaced sampling locations at the site. Site exploration identifies subsurface conditions only at those points where subsurface tests are conducted or samples are taken. GeoEngineers reviewed field and laboratory data and then applied our professional judgment to render an opinion about subsurface conditions throughout the site. Actual subsurface conditions may differ – sometimes significantly – from those indicated in this report. Our report, conclusions and interpretations should not be construed as a warranty of the subsurface conditions.

Geotechnical, Geologic and Geoenvironmental Reports Should Not Be Interchanged

The equipment, techniques and personnel used to perform an environmental study differ significantly from those used to perform a geotechnical or geologic study and vice versa. For that reason, a geotechnical engineering or geologic report does not usually relate any environmental findings, conclusions or recommendations; e.g., about the likelihood of encountering underground storage tanks or regulated contaminants. Similarly, environmental reports are not used to address geotechnical or geologic concerns regarding a specific project.

Biological Pollutants

GeoEngineers' Scope of Work specifically excludes the investigation, detection, prevention or assessment of the presence of Biological Pollutants. Accordingly, this report does not include any interpretations, recommendations, findings, or conclusions regarding the detecting, assessing, preventing or abating of Biological Pollutants and no conclusions or inferences should be drawn regarding Biological Pollutants, as they may relate to this project. The term "Biological Pollutants" includes, but is not limited to, molds, fungi, spores, bacteria, and viruses, and/or any of their byproducts.

If the client desires these specialized services, they should be obtained from a consultant who offers services in this specialized field.

Have we delivered World Class Client Service?

Please let us know by visiting **www.geoengineers.com/feedback**.

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APPENDIX B RESUMES

Chris Gdak BESc

Principal, Environmental Services

Western US Brownfield Grant Team Lead & Funding Specialist

Chris is a Civil/Environmental Engineer and Brownfield Grant Specialist with over 15 years of consulting experience. He has successfully assisted with grant applications, management, and/or technical aspects of over 30 EPA Brownfield Community-Wide Assessment (CWA) Grants. Chris has managed over 500 environmental site assessment (ESA) and/or cleanup projects throughout the US, and specializes in the assessment and cleanup of both petroleum and hazardous waste brownfield sites. Chris' diverse technical background and management expertise make him uniquely qualified to manage multi-discipline teams required for brownfield redevelopment projects.

As Stantec's Western US Brownfield Grant Team Lead and Funding Specialist, Chris oversees a team of 15 staff dedicated to supporting grant writing and implementation projects in EPA Regions 8, 9 and 10 for over 30 municipal clients. Chris' team is currently managing Brownfield Assessment Grant projects for communities of all shapes and sizes, from urban to rural environments.

Chris also specializes in site eligibility negotiations with EPA and identifying creative strategies to leverage grant funding by negotiating cost share agreements with property owners and preparing Targeted Brownfield Assessment (TBA) applications to secure supplemental funding. In addition, Chris is recognized as a brownfield grant expert throughout the western US and has been invited to co-present alongside EPA at regional brownfield workshops and conferences.

EDUCATION

Bachelor of Engineering Science – Civil/Environmental Engineering, University of Western Ontario, London, Ontario, 2001

PROJECT EXPERIENCE

Grant Management & Implementation, Various Communities throughout the US
(Project Manager & Funding Specialist)

Chris has managed and/or assisted with the technical aspects of over 30 EPA brownfield grants since 2004, including projects in Wisconsin, Indiana, Washington, Oregon, California, Colorado, Utah, Nevada and Alaska. Chris leads all aspects of EPA brownfield grants including grant management and reporting, community outreach/ public involvement, inventory/ prioritization, ESAs, and cleanup planning. He is managing or supporting EPA brownfield grant implementation for the cities of Kent (FY12), Everett (FY13), Vancouver (FY13), and Spokane (FY15), Washington; Salem (FY14), Coos Bay (FY15), Klamath Falls (FY15), and Metro Portland, Oregon (FY16); Lake County (FY14) and Trinidad (FY15), Colorado; Lodi (FY15), California; Uintah Basin Association of Governments (FY16) and Provo City, Utah (FY16); and Mat-Su Borough (FY16), Alaska. He recently assisted Everett and Kent with EPA Annual Performance Audits. These grantees received an excellent performance review and EPA complimented Stantec on the quality of reports.

Grant Funding and Acquisition, Various Communities throughout the US
(Project Manager & Funding Specialist)

Chris has helped prepare over 30 successful EPA brownfield grant applications since 2005. Since 2012, Chris has managed 31 successful EPA brownfield grants throughout the US. During the FY2015 U.S. EPA Brownfield Grant Competition alone, Chris helped prepare 11 successful grant applications, securing 100% of the Community-Wide Assessment (CWA) Grant funding awarded in EPA Region 10. During FY2016 competition, Chris assisted with 8 successful grant applications throughout the US.

Phillips 66 Sites, Site Investigation and Remediation, Various Locations throughout the US

Over a three-year period, Chris managed the environmental liabilities of over 100 Phillips66 Sites throughout the US. His work included underground storage tank (UST) removals, facility decommissioning, compliance monitoring, and investigation and remediation of releases of petroleum hydrocarbons and related constituents at retail gas stations, bulk storage facilities, terminals, and pipelines. This work resulted in obtaining multiple site closures from state environmental authorities.

Chris Gdak BESc

Principal, Environmental Services

Western US Brownfield Grant Team Lead & Funding Specialist

Environmental Due Diligence | 500+ Sites throughout the US (Project Manager & Project Engineer)

Chris has completed environmental due diligence projects at over 500 sites since 2001, specializing in historic fill/metals-impacted sites, petroleum-impacted sites, and dry cleaner/solvent contamination sites. Sites include a wide variety of residential, commercial, industrial, and institutional properties. Chris performed project management, research, planning, oversight, and performance of surface/subsurface investigations, including soil, sediment, sludge, groundwater, soil gas, and surface water sampling; design, operation, and maintenance of various remediation technologies; preparation of Phase I/II ESA Reports, Remedial Investigation (RI)/Feasibility Study (FS) Reports; and development of Remedial Objectives (RO), Analysis of Brownfield Cleanup Alternatives (ABCAs), and Cleanup Action Plans (CAPs).

Multi-Year Environmental Services Contract, Milwaukee, Wisconsin (Project Engineer)

As project engineer for a multi-year environmental services contract with the City of Milwaukee through 2005, Chris completed over 25 Phase I/II ESAs/cleanup projects at abandoned or underutilized brownfield parcels throughout the City. The sites ranged from vacant former residential lots to abandoned historic manufacturing facilities, rail yards, gas stations, and a two-block area of the City targeted for mixed-use redevelopment. A majority of the projects were performed in conjunction with redevelopment of City-owned parcels by private developers or sites targeted for acquisition by the City. A significant number of projects were performed in conjunction with U.S. EPA brownfield or other state and federal grants. The City of Milwaukee has received more U.S. EPA brownfield grants than any other local government in the U.S. Through his work with Milwaukee, Chris gained broad experience in best practices for use of EPA grants.

Multiple Dry Cleaner Sites, Illinois (Project Manager)

Chris managed compliance inspections and the assessment and remediation of chlorinated and petroleum solvent releases from multiple dry cleaner sites participating in the Illinois Dry Cleaner Environmental Response Trust Fund Program. Work included assessment of impacted soil, groundwater, surface water, and sediments; developing site-specific risk-based remedial objectives (ROs); and completing Remedial Action Plans (RAPs). This work resulted in site closures through the Illinois Environmental Protection Agency (IEPA) Site Remediation Program (SRP).

Josey Heights Subdivision Brownfields Investigation, Remediation and Redevelopment, Milwaukee, Wisconsin (Project Engineer)

Chris performed site investigation, remediation planning, and remediation oversight of a two-block area with over 100 years of commercial/industrial history. Remediation included excavation of over 1,000 truckloads of contaminated soil and historic fill from 88 different areas of concern with varying depths and types of contamination. It also involved the use of sub-centimeter GPS equipment and NITON XRF in-situ testing for metals. The resulting development included numerous single and multi-family residential units.

David B. Holmes PG

Senior Environmental Scientist/Brownfields Grant Specialist

Mr. Holmes has more than 30 years of professional consulting experience performing and managing environmental assessment, investigation, and cleanup projects and helping public and private sector clients to secure funding to implement these projects. David has worked on hundreds of brownfield sites on behalf of local government and developer clients throughout the US. He has exceptional experience securing state and federal grants to support brownfields redevelopment and habitat restoration projects (with more than 136 grants and $32.5 million in funding awarded to date).

EDUCATION

Master of Science Geology, University of Wisconsin, Milwaukee, Wisconsin, 1988

Bachelor of Science Geology, University of Wisconsin, Milwaukee, Wisconsin, 1984

Doctoral Program Coursework, Ongoing, University of Wisconsin, School of Freshwater Science, Milwaukee, Wisconsin, (2013-present)

REGISTRATIONS

Professional Geologist #887-13, State of Wisconsin

BROWNFIELDS PROJECT EXPERIENCE

Site Redevelopment Program Development and Implementation, Washington County, Wisconsin

David is assisting Washington County in the development of a County-led Site Redevelopment Program - a joint effort between the County Planning and Parks Department and the County's lead economic development agency. A goal for the program is to integrate the County's revitalization efforts focused on brownfields sites with the County's economic development and business retention /recruitment efforts, with a goal of increasing the degree to which brownfields redevelopment is effectively linked to private investment and jobs creation. David served initially on an "economic toolbox" advisory committee for the County's lead economic development agency, one outcome of which was the successful application for a $600,000 USEPA Brownfields Assessment Grant awarded in 2014 to a County-led coalition that included five of the County's incorporated cities and villages. David is managing implementation of grant-funded activities which include a county-wide inventory of brownfield sites, community outreach, and assessment and/or reuse planning for priority brownfields sites.

David was the lead writer for a successful application for an additional $600,000 USEPA brownfield assessment grant awarded in 2017 – a grant which David will also help implement. Over $42M in redevelopment projects are currently underway on sites assessed using the County's initial USEPA grant.

USEPA Assessment, Area-Wide Planning, and Cleanup Grant Applications Assistance, Various Clients (Grant Writer)

Since 2005, David has authored or coauthored more than 90 successful applications to the USEPA for brownfields assessment, cleanup, area-wide planning, and revolving loan fund grants totaling $20 million in funding. David has worked with local units of government (including cities, counties, and regional agencies) as well as non-profit organizations in 16 states (AK, CA, CO, FL, IL, IN, KS, MN, ND, NY, OR, SC, SD, UT, WA, and WI) in pursuing these grants. David has had significant success in working with first time grant applicants lacking previous experience in securing funding from USEPA Including grants resulting from resubmittal, David's overall success rate exceeds 90%.

USEPA Cleanup Grant Application Assistance, City of Rochester, New York (Grant Writer)

David, in collaboration with Stantec local staff, assisted the City of Rochester in preparing an application for USEPA FY2013 Cleanup Grant for a (FY2013) for a tax delinquent former auto repair and dry cleaning facility located at 937-941 Genesee Street. The application was successful, and Stantec was retained to implement the cleanup funded in part through the $200,000 grant. Although the City had significant past successes in preparing applications on their own, the increased "band width" provided by Stantec enabled City staff to focus on other priorities during the grant period.

USEPA Brownfield Grant Implementation

Since 2005, Dave has assisted with implementation of more than 30 USEPA brownfield grants in 14 states: AK, CA, CO, IL, IN, KS, MN, ND, NV, OR, SD, UT, WA, and WI. Responsibilities have included preparation of Quality Assurance Project Plans, preparation of eligibility determination requests, preparation of site-specific sampling and analysis plans, Phase I and II ESAs, environmental site investigation report, remedial action plans, and quarterly and annual reporting.

** denotes projects completed with other firms*

David B. Holmes PG

Senior Environmental Scientist/Brownfields Grant Specialist

City of Goshen Brownfields Program*, Goshen, Indiana (Project Manager)

David was responsible for implementation of two USEPA brownfields assessment grants, two USEPA cleanup grants, and five State of Indiana brownfields grants targeting an historic industrial area located adjacent to the Elkhart River. David was the primary author for brownfield grants totaling more than $1.25 million. Work included Phase I and II ESAs, site investigation, and development of remedial action plans. USEPA grant activities performed by David included preparation of initial site eligibility determination forms, a quality assurance project plan, site-specific sampling and analysis plans, and quarterly progress reports. Several firsts in the history of the USEPA brownfield grant program were reportedly achieved on this project related to effective use of the assessment grants for leveraging subsequent cleanup grants.

St. Ann Center for Intergenerational Care, Bucyrus Campus Development, Milwaukee, Wisconsin

David assisted St. Ann Center with environmental issues encountered on a 27-parcel brownfield site located in one of the poorest neighborhoods in Milwaukee. The property was being developed into a $25 million intergenerational care center that will employ more than 200 area residents. David assisted St. Ann Center in securing three state and USEPA brownfields cleanup grants totaling $550,000 to be used to complete cleanup at the site. The two USEPA cleanup grants were the first awarded to a not-for-profit entity in Wisconsin.

Brownfields Program*, Elkhart County, Indiana (Lead Grant Writer/Project Manager)

David was responsible for implementation of two USEPA brownfields assessment grants awarded to Elkhart County in 2006. David wrote the grant applications as well as applications for two additional assessment grants awarded by USEPA in 2009. As part of the brownfield inventory and prioritization task, a custom web-based geographic information system (GIS) computer application (the "e-Atlas") that uses ESRI ArcGIS Server technology designed specifically for brownfields identification, management, and analysis of environmental information. As part of the inventory, records for 5,600 potential brownfield sites stored in several non-spatial databases were mapped in the County's GIS and aligned with property parcels. In addition, more than 200,000 pages of paper inspection records collected for commercial and industrial properties throughout the County over 20 years as part of Groundwater Protection Program were indexed, scanned and linked into the County's document management system (Laserfiche). The web based GIS interface allows users to interact with the information via the map, and to view, query, buffer, and link to additional content. The e-Atlas subsequently served as the model for a similar system known as "INSIT" or Indianapolis Site Inventory tool, developed by the City of Indianapolis which is also a web based GIS application that utilizes ArcGIS Server technology.

White Stone Village Development, Fiduciary Real Estate Development and Cobalt Partners LLC, Menomonee Falls, Wisconsin

David is assisting two developer clients (Fiduciary Real Estate Development and Cobalt Partners LLC) with environmental assessment, funding, and cleanup of the former D&L Manufacturing property and adjoining parcels forming a 50-acre development site in suburban Milwaukee. Assistance to date has included conducting Phase I and II ESAs, environmental site investigations, remedial planning, and oversight of approximately $2 million in cleanup at the site (which includes four former manufacturing facilities, a bulk fuel storage facility, and a former gas station). The site is one of the largest redevelopment sites in suburban Milwaukee, both in terms of its land area and the value of the expected development (>$120 million) which to date includes a Costco store, mid-box retail stores, a hotel, and approximately 340 market rate apartments. Assistance also included securing $500,000 and $250,000 State of Wisconsin brownfield grants to help offset environmental cleanup costs.

City of Milwaukee Multi-Year Environmental Assessment Contracts*, Milwaukee, Wisconsin

David was the project manager for three multi-year environmental services contracts with the City of Milwaukee during 1994 through 2005. As part of these contracts, David managed more than 50 environmental assessment or environmental cleanup projects involving more than 500 vacant, abandoned, or underutilized brownfield parcels throughout the City.

The sites assessed ranged from vacant former residential lots to landfills, abandoned historic manufacturing facilities, rail yards, gas stations, to a 5-1/2 block area of the City being targeted for commercial redevelopment. Most of the projects were performed in conjunction with redevelopment of City-owned parcels by private developers, or sites targeted for acquisition by the City. A significant number of projects were performed in conjunction with USEPA or other state and federal grants. Milwaukee is noteworthy in having received more USEPA brownfields grants than any other local government in the U.S.

** denotes projects completed with other firms*

Kim Vik LG

Project Geologist

Kim has 25 years of experience as an environmental consultant in the Pacific Northwest. She has authored many documents ranging from simple site assessment and monitoring reports to large-scale investigations and management plans. She is responsible for evaluation and preparation of technical reports, including site investigation and Phase I and II Environmental Site Assessment (ESA) reports, as well as routine groundwater monitoring and compliance monitoring reports for stormwater and wastewater permit applications and compliance. She has worked with regulatory agencies in the states of Washington, Oregon, Idaho, and Alaska and is familiar with the associated state regulations. She is also familiar with federal and navy regulations, due to her extensive involvement providing environmental consulting services on U.S. Navy projects. Kim's responsibilities include managing large environmental databases, conducting data validation, and managing large data collection and routine sampling events. She also performs statistical analysis using the U.S. Environmental Protection Agency ProUCL.

EDUCATION

B.S., Geological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota, 1986

CERTIFICATIONS & TRAINING

Data Validation of a Superfund Site, Lorman Education Services, Webinar, 2013

Managing Environmental Data With Microsoft Access 2010, Northwest Environmental Training Center, Bellevue, Washington, 2012

Introduction to Managing Environmental Data with Microsoft Access 2010, Northwest Environmental Training Center, Bellevue, Washington, 2012

MTCA Spreadsheets Workshop, Northwest Environmental Training Center, Kirkwood, Washington, 2012

Model Toxics Control Act Series, EOS Alliance, Seattle, Washington, 2010

New Business Opportunities and Trends in the Property Due Diligence Market, Environmental Data Resources Inc., Seattle, Washington, 2010

REGISTRATIONS

Licensed Geologist #488, State of Washington

PROJECT EXPERIENCE

Data Management

EPA Brownfield CWA Grant Projects – Comprehensive QAPPs, Utah & Washington (Quality Manager)

As Stantec's Data Quality Manager, Kim is responsible for preparing Comprehensive Quality Assurance Project Plans (QAPPs) in support of EPA Brownfield Community-Wide Assessment (CWA) Grant implementation projects in EPA Regions 8 and 10. She recently prepared Comprehensive QAPPs and EPA Region 8 Crosswalks in support of Provo City and Uintah Association of Governments CWA Grant Implementation projects (both awarded by EPA in 2016).

EPA Brownfield CWA Grant Implementation –SAPs & Phase II ESAs, Washington (Project Geologist & Analytical Data Manager)

Kim develops site-specific Sampling and Analysis Plans (SAPs) and performs data validation on Phase II Environmental Site Assessment (ESA) projects completed as part of EPA Brownfield CWA Grant implementation projects. She also provides quality/independent review on technical deliverables to maintain consistency with EPA and client quality standards.

Former Dry Cleaning Operation – Site Investigation and Risk Analysis, Sandy, Utah (Analytical Data Manager)

Stantec is provided site investigation and remediation and risk analysis services for a former dry cleaning operation. The primary contaminate of concern is tetrachloroethene (PCE). Kim performed a statistical analysis of the cumulative data for this project using the EPA ProUCL software. The statistical analysis was conducted as a part of the risk analysis for this project.

Kim Vik LG

Project Geologist

Proposed Dairy Syncline Phosphate Mine – Hydrogeological Baseline Studies, Idaho (Analytical Data Manager and Project Geologist)

Kim is the database manager of an Access-based database, Epiphiny, for data collected in support of a large groundwater study and deep monitoring well installation project in support of construction of a new phosphate mine. Her database management responsibilities require Level III data validation under EPA protocols for routine surface water and groundwater sampling events; assigning of data qualifiers to the data; importing the data into the database; and generating tables for use in reporting or shapefiles for GIS graphics. Data management responsibilities also require tracking field versus laboratory analysis requests, reviewing draft laboratory reports, resolving of laboratory reporting limit and data quality issues, and reviewing of final EDDs.

Long Canyon Gold Mine – Environmental Impact Statement (EIS) Hydrogeological Baseline Studies, Elko County, Nevada (Analytical Data Manager and Project Geologist)

Kim assisted with review and preparation of an Environmental Impact Statement (EIS) for this proposed mining project. She was responsible for tabulation of data and interpretation and development of groundwater maps.

Mineral Exploration and Mine Permitting Project – Baseline Hydrogeologic Investigations*, Oregon (Analytical Data Manager and Project Geologist)

Stantec conducted subsurface investigations and quarterly and monthly groundwater and surface water sampling to assess baseline conditions at proposed mine site. The investigations were conducted to evaluate current groundwater aquifer characteristics and water quality and to collect the data necessary to obtain groundwater water rights for production water supply for use during mine processing activities. Kim performed data management and data validation services for the project. Her responsibilities included managing and importing data into the project database as well as providing technical support for the baseline hydrogeologic investigation report, including graphing the aquifer testing data.

Former Gasoline Retail Facility – Environmental Database Management, Mountlake Terrace, Washington (Project Geologist)

Kim is serving as the analytical data manager and project geologist for the management of a large Access-based database, Epiphiny, for thousands of soil and groundwater data results collected by Stantec and other consultants who previously worked at the project site. Her database management responsibilities require conducting Level III data validation under EPA protocols for multiple constituents; assigning data qualifiers to the data; importing data into the database; and generating tables for use in reporting or shapefiles for geographic information system (GIS) figures. In addition, her data management responsibilities require tracking field versus laboratory analysis requests; reviewing draft laboratory reports; resolving laboratory reporting limit and data quality issues; and reviewing final electronic deliverable documents (EDDs). Kim is also responsible for generating data tables from database output and field measurements. Her other project responsibilities include providing technical support for remedial activities at the site including oversight of groundwater monitoring activities; preparation of work plans; and coordination and oversight of discharge monitoring compliance reports.

Soil and Groundwater Investigation and Characterization Projects – Data Validation and Compliance Reports*, Various Locations (Analytical Data Manager)

Kim conducted Level II and III data validation using EPA protocols for various clients and projects for major types of contaminant types in soil and groundwater, including volatile organic compounds (VOCs), semi-VOCs, metals, petroleum constituents, and chlorinated phenols. Kim also conducted data validation for dioxin/furan analyses and low-level (selected ion monitoring) analyses for polycyclic aromatic hydrocarbons (PAHs) and Pentachlorophenol (PCP).

** denotes projects completed with other firms*

Cyrus Gorman LG

Project Manager, Environmental Services

Cyrus has more than 13 years of environmental consulting experience. He specializes site investigation and remediation projects. Cyrus has managed on and off-site projects, including field management off site investigations and remediation projects at railroad properties, former wood preservation facilities, dry cleaners, commercial redevelopment sites, and manufacturing facilities. Cyrus has conducted industrial hygiene projects, including AHERA building inspections, indoor air quality evaluations, exposure assessments, lead wipe sampling, clearance sampling, and site safety and health.

Cyrus performed numerous site investigations using ground-penetrating radar, direct- push, hollow stem auger, sonic drilling, and indoor air quality assessment. His field experience includes supervision of field implementation teams and subcontractors; design and installation of monitoring wells using hollow-stem auger, direct-push, continuous- core drilling; operation and maintenance of high-vacuum, soil vapor, and groundwater extraction systems. He also conducted tidal influence evaluations and slug tests to evaluate contaminant migration.

Cyrus served as the health and safety coordinator, responsible for conducting office inspection, developing office emergency action plans, coordinating health and safety training, and participating in monthly division calls with senior health and safety personnel. Cyrus is also a resource regarding the implementation internal subsurface clearance procedures.

EDUCATION

BS, Geology, The College of Sciences, Washington State University, Pullman, WA

MBA, Michael G. Foster School of Business, University of Washington, Seattle, WA

REGISTRATION

Licensed Geologist #2859, State of Washington

PROJECT EXPERIENCE

EPA Brownfields Assessment Grants | Alaska, Colorado, Utah, Washington

Cyrus is a project manager on implementation of EPA Community-Wide Assessment Grants, for the Matanuska-Susitna Borough in Alaska; Lake County, Colorado; the City of Provo and Uintah Basin Association of Governments in Utah; the Cities of Kent, Everett and Spokane, Washington. His responsibilities include preparing Phase II ESA Reports and Cleanup Action Plans; documenting threshold criteria; providing technical review of Phase I ESA Reports, site-specific SAPs and HASPs and supporting site inventory/prioritization efforts.

Site Assessment* | Tacoma, Washington

Cyrus planned, managed, and mobilized junior staff and subcontractors to support a Fortune 500 oil and gas client in the potential acquisition of a multi-parcel 200-acre site which included heavy industrial uses. He developed a list of data gaps and recommendations for additional investigation at the site. Because of historical operations at the site, Cyrus identified the potential presence of dioxin furans as a data gap in previous investigations, saving the client over $10 million dollars in remedial actions to make the site suitable for redevelopment.

Seattle-Tacoma International Airport* | Seattle, Washington

Cyrus was the senior geologist for multiple environmental projects conducted on behalf of United Airlines at Seattle-Tacoma International Airport. Projects included MTCA compliance evaluation for a release of hydraulic fluid, groundwater investigation, construction oversight, transaction services and personal exposure assessments.

Washington Air National Guard Site Assessments* | Various Locations

Cyrus performed collection of soil and groundwater samples to characterize historical areas of concern, including formers USTs, vehicle maintenance areas, suspected areas of dumping, and planter boxes filled with slag from the former ASARCO smelter in Tacoma, Washington.

** denotes projects completed with other firms*

Cyrus Gorman LG

Project Manager, Environmental Services

Air National Guard Station* | Various Locations, Washington

Cyrus served as the site manager for four Air National Guard sites located in Washington and Oregon. He developed work plans to meet objectives of the site investigation, managed field personnel, and completed the scope of work. He completed site investigations evaluating impacts from historical operations. Cyrus developed a program confirming arsenic was naturally-occurring and demonstrated that the impacted groundwater was not a threat to human health or environment addressing ecology concerns. Cyrus obtained No Further Action determination from Ecology based on results of the project.

Naval Air Station Whidbey Island Third Party Oversight* | Whidbey Island, Washington

Cyrus provided third-party oversight during demolition and renovation of two aircraft hangars. Services included clearance sampling following asbestos abatement, worker exposure assessments for lead and chromium, and AHERA surveys for suspect materials and buildings to be demolished. Additional services included technical oversight during the removal of soils contaminated with aviation fuel during the installation of a new fire suppression system in the hangar floor. Cyrus was responsible for report writing and data interpretation.

Resource Conservation and Recovery Act, Site investigation and Remediation* | Boise, Idaho

Cyrus worked with key stakeholders developing a work plan and field investigation program to comply with a Consent Decree issued by the Idaho Department of Environmental Quality. He managed multiple field investigations and the development of project submittals to meet project objectives.

Robert McAlister RG

Staff Scientist

Robert has seven years of experience in the environmental consulting field in California, Oregon and Washington States, specializing in technical field investigations and field management, including interaction with regulatory agencies. He has performed remedial excavation oversight and sampling; groundwater monitoring well installation and abandonment; direct-push soil assessments; remediation system operations and maintenance; in-situ remediation implementation and oversight; remediation system installation; and remedial injection implementation, oversight, and performance monitoring. Robert has also completed project budgets and proposals, hazardous materials surveys, data management and presentation, as well as phase I and phase II environmental site assessments.

EDUCATION

B.Sc., Earth Science, California Polytechnic State University, San Luis Obispo, California, 2007

REGISTRATIONS

Registered Geologist #G2359, State of Oregon

PROJECT EXPERIENCE

Site Management & Remediation

Former Plywood Mill, Shallow Dioxin Soil Contamination, Medford, Oregon

Over the course of four years, all field activities related to the environmental assessment and management of a former mill site have been organized and implemented by Robert. This has included preparation of health and safety plans, sampling and analysis plans (SAPs), and regulatory agency interaction. Prior to the soil assessment completed under Robert's direction, the site was relatively uncharacterized and the exact scope of required assessment was unknown and modifications to the SAP were required multiple times during the course of the project.

Oregon Department of Corrections, Chlorinated Solvent Plume, Salem, Oregon

Robert has managed the Department of Corrections site for three years and completed all associated fieldwork, reporting and regulatory interaction since that time. Tasks included a renewal of a NPDES permit with DEQ for an on-site treatment system as well as shallow soil assessments, worker protection plans for excavation and trenching at the site, and the preparation of a Focused Feasibility Study (FFS). As part of the FFS, the on-site treatment system was placed in idle and a monitored natural attenuation groundwater sampling plan was designed and implemented to evaluate plume stability and geochemical indicators of natural chemical breakdown in the subsurface.

Oregon Department of Corrections, Chlorinated Solvent Plume, Salem, Oregon

Robert has managed the Department of Corrections site for three years and completed all associated fieldwork, reporting and regulatory interaction since that time. Tasks included a renewal of a NPDES permit with DEQ for an on-site treatment system as well as shallow soil assessments, worker protection plans for excavation and trenching at the site, and the preparation of a Focused Feasibility Study (FFS). As part of the FFS, the on-site treatment system was placed in idle and a monitored natural attenuation groundwater sampling plan was designed and implemented to evaluate plume stability and geochemical indicators of natural chemical breakdown in the subsurface.

Hazardous Materials Management

Former Oregon State Hospital North Campus, Salem, Oregon

In late 2013, Stantec completed a hazardous materials survey of the recently-vacated North Campus of the Oregon State Hospital. Robert was the primary assessor and hazardous materials sampler for the assessment, consisting of over 500,000 square-feet of buildings, interconnected underground tunnels, and outdoor areas of the 48-acre campus.

Environmental Site Assessments

Various Phase I Environmental Assessments, Multiple Locations

To date, Robert has completed over a dozen Phase I Environmental Site Assessments. Locations of the previous assessments include former city libraries, former chemical warehouses, vacant land, residential buildings and commercial properties.

** denotes projects completed with other firms*

Robert McAlister RG

Staff Scientist

Landfill Services

King City Landfill, King City, California (Field Staff)

Robert completed groundwater monitoring events at the site, an inactive landfill formally serving King City. Included in the scope of work was sampling deep groundwater monitoring wells using standard purge, low-flow sampling techniques, and passive diffusion (PDBS-bag type) sampling.

King City Landfill, King City, California (Field Staff)

Robert completed groundwater monitoring events at the site, an inactive landfill formally serving King City. Included in the scope of work was sampling deep groundwater monitoring wells using standard purge, low-flow sampling techniques, and passive diffusion (PDBS-bag type) sampling.

Oil and Gas Pipelines

Numerous Oil Pipeline Assessments Throughout San Luis Obispo County, California, Shandon, Creston, San Luis Obispo, and Santa Margarita, California (Project Staff/Field Supervisor)

Robert conducted numerous oil pipeline assessments in locations ranging from agricultural fields, downtown city streets, and within ConocoPhillips pump stations. Providing historic records review and project scoping, Robert was integral in developing the specific scope of work and sampling plans required to complete assessments of pipelines with little or no environmental case history. While in the field, Robert was able to collect sufficient data concerning soil conditions, aquifer characteristics and contamination to effectively meeting the client's needs as well as the needs of the county Water Board without the need for numerous re-mobilizations to the site.

Oil and Gas Downstream

Retail Petroleum Sites, Multiple Locations

Over his 7-year career, Robert has implemented a wide array of environmental services at former and active retail petroleum sites. Scopes of work have included: Groundwater monitoring, drilling, remedial injections, underground storage tank removal and associated remedial excavations, and other related tasks.

Oil and Gas Upstream

Former Bulk Petroleum & Wood Treatment Facility, Portland, Oregon

Robert has completed direct field support at a former petroleum storage and wood treatment facility on the Willamette River in North Portland (part of the Willbridge Terminal Group Superfund site). The Project scope implemented by Robert includes health and safety management, routine operations and maintenance of an on-site remediation system and system compliance sampling, including coordination with the local regulatory agency.

Casmalia Oilfield Abandonment, Casmalia, California (Field Supervisor – Production Related Features Soil and Groundwater Assessment)

Robert provided direct field oversight of numerous soil borings and installation of groundwater monitoring wells associated with production features of the former Chevron Casmalia Oilfield. Included in this scope of work was the delineation of soil contamination within areas of pipeline corridors, former oil production wells, holding tanks, and various product conveyance pump locations. Additionally, Robert completed site-wide groundwater sampling of the former oilfield for aquifer biochemical conditions and various constituents of concern including dissolved minerals and metals, solvents, and petroleum hydrocarbons.

Remedial Investigations, Options, Pilot Testing

Scotts Valley Dry Cleaners, Scotts Valley, California (Project Staff / Field Supervisor)

Robert directly supported the Stantec project manager during the planning, implementation, and performance monitoring phases of remedial sodium permanganate injection for the Scotts Valley Dry Cleaners in Santa Cruz County, California. Additionally, Robert worked closely with the regional water quality control board and City of Scotts Valley in obtaining all necessary permits and ensuring that the scope of work was in accordance with all interested parties. Robert provided direct field oversight of all aspects of the injection; including determining the optimum locations of injection wells, health and safety oversight during injection activities, and subsequent post-injection groundwater monitoring events.

** denotes projects completed with other firms*

Carol B. Shestag PG

Senior Geologist

Carol has worked in the environmental industry for more than 31 years, specializing in geologic, geotechnical, groundwater, soil, and soil vapor investigations and remediation at numerous oil/petroleum, aerospace, manufacturing, and hazardous and non-hazardous waste disposal facilities. Her experience includes geologic and hydrogeologic characterizations as part of contaminant migration investigations; preparation of Environmental Impact Reports (EIRs) and California Environmental Quality Act [CEQA] compliance documents; soil and groundwater remediation design and implementation; public agency interaction; environmental compliance; and geotechnical investigations. While primarily employed in California, Carol has also worked in Alaska, Arizona, Colorado, Nevada, and Texas. Prior to performing environmental services, she worked in the mining industry.

EDUCATION

BS, Geology, Scripps College/Pomona College, Claremont, California, 1982

Groundwater and Aquifer Mechanics, National Water Well Association, San Diego, California, 1986

40-Hour HAZWOPPER Training, OSHA, Irvine, California, 1988

8-Hour HAZWOPPER Supervisor Training, OSHA, Irvine, California, 1988

8-Hour HAZWOPPER Annual Update, OSHA, Thousand Oaks, California, 2015

REGISTRATIONS

Professional Geologist #8439, State of California

PROJECT EXPERIENCE

Aboveground and Underground Storage Tank Investigation

Clarifier, Aboveground, and Underground Storage Tank (UST) Investigations

Carol gas managed and conducted numerous assessments, remediation, and groundwater monitoring programs. Contaminants have included chlorinated solvents, heavy metals, fuels (gasoline, diesel, aviation gas, jet fuels), waste oils, cutting oils, hydraulic oil, pesticides, herbicides, fertilizers, and pharmaceutical chemicals. Clients include aerospace firms, major and California-only oil companies, Ventura County airports, national trucking and distribution centers, agricultural facilities, car dealerships, state and county maintenance yards, and Los Angeles and Ventura County fire stations.

Environmental Site Remediation

Remediation System Design and Build; Treatment System Operation and Maintenance (O&M)

Carol has conducted the remediation of solvent, fuel- and metal impacted soil and/or groundwater at numerous aerospace, bulk fueling, manufacturing, and dry cleaning facilities. Following assessment, work has included feasibility studies, preparing RAPs, designing and building remediation systems, and conducting O&M programs. Remediation of fuel impacted materials utilize conventional activated carbon, custom activated carbon, thermal oxidation, and in-situ chemical oxidation (ISCO). Remediation of solvent-impacted materials utilize custom carbon units, air stripping, bioremediation, and ISCO. Remediation of metals impacted soil utilize excavation with offsite treatment/fixation.

Hydrogeologic Assessments

Hydrogeologic Characterization at a Former Aerospace Facility, Chlorinated Solvent Migration, and Remediation Design, Newbury Park, California

Carol installed multi-depth groundwater monitoring and remediation wells for a detailed hydrogeologic characterization, chlorinated solvent migration, aquifer testing, and remediation design at a former aerospace manufacturing facility. Air rotary and casing hammer drill rigs were used to drill through the soil (colluvium) and into the underlying Conejo Volcanics to install wells to depths of 250 feet bgs. Carol conducted conventional aquifer testing and Spinner Logging to obtain estimates of groundwater flow in the four identified water-bearing zones, to evaluate which of the four zones was the primary zone contributing to the migration of chlorinated solvents in groundwater, and to design an expanded remediation system based on the results of the aquifer testing.

Carol B. Shestag PG

Senior Geologist

Geotechnical Investigations

General Geologic and Geotechnical Investigations Related to Faults and Landslides, southern California

Carol performed surface geologic mapping and trench logging for siting studies of proposed industrial and residential developments and for landslide evaluations. Work was conducted in Imperial (class I hazardous waste landfill siting studies), Riverside, and Los Angeles Counties for slope stability investigations.

Permitting and Regulatory Compliance

Environmental Planning/Permitting/Compliance

Carol has managed and implemented Waste Discharge Requirement (WDR) compliance monitoring programs in accordance with RWQCB regulations. This has included partial preparation and implementation of Spill Prevention Control and Countermeasure Plans (SPCC), Storm Water Pollution Prevention Plans (SWPPP), and Environmental Impact Reports (EIR). She has managed stormwater compliance sampling programs following heavy rains for surface water disposal/discharge purposes. She has also conducted audits at industrial facilities for environmental compliance for the management, storage, use, generation, and/or treatment of petroleum products and hazardous materials.

Landfill Services

Landfill Leachate Investigations and Siting Studies – Existing, Closed, and Proposed Class I, II, and III Landfills, Burn Dumps, and Septic Ponds

Carol has performed investigations and aquifer testing to evaluate leachate migration from existing and closed landfills, to obtain remedial design data, and to evaluate site suitability for new landfills in a wide variety of geologic and hydrogeologic regimes across California. She has performed trenching to evaluate Holocene fault activity and for design of leachate collection systems. Investigations have included approximately 40 water quality Solid Waste Assessment Tests (SWATs), Hydrogeologic Assessment Reports (HARs), Reports of Waste Discharges (RWDs), RCRA Part B Applications, and Five-Year Engineering Reviews. Work was conducted for environmental compliance with other legislative requirements such as the Katz (Toxic Pits) and Eastin (AB 2448) Bills, and was performed for multiple Regional Water Quality Control Boards for a variety of clients (municipal and county governments; a large, private hazardous waste transportation and disposal company; and military installations).

Oil and Gas Downstream

Terminal Investigation, Vapor Intrusion, and Remediation Expansion, Los Angeles, California

With sensitive public and regulatory agency concerns and with legal issues, on and offsite assessment and remediation system expansion activities are being performed. Fuel related contaminants (both dissolved-phase and free product hydrocarbons [FHP]) from the terminal have migrated downgradient and offsite beneath adjacent properties. Compounding the issue is the use of chlorinated solvents at the same adjacent offsite properties by those offsite property owners/tenants. Assessment methodologies include conventional drilling and soil sampling with single-and nested vapor and groundwater well installation, CPT-UVOST borings, continuous core soil borings, multi-depth soil gas and Hydropunch sampling, geotechnical analyses, and vapor intrusion sampling (indoor and outdoor ambient air, sub-slab vapor, and 5-foot-below-slab vapor sampling and analysis). The temporary remediation systems were upgraded and expanded with new on and offsite remediation wells, above-ground conveyance piping replaced with below-ground piping, existing manifolds re-built, three additional manifolds installed, a second SVE unit installed, and the pre-existing 240-gallon FPH holding tank replaced by a 2,000-gallon-capacity FPH tank.

** denotes projects completed with other firms*

Dana Hutchins GIT

Project Specialist, Geology

Mr. Hutchins has over six years of experience supporting a variety of environmental projects throughout the Pacific Northwest. Types of projects he has supported include due diligence/Phase I and II Environmental Site Assessments (ESAs); surface and subsurface soil and groundwater investigations; and remedial investigations (RIs). He has been responsible for field crew management, including oversight of exploratory drilling and sampling programs; field program coordination and implementation; field data acquisition; data analyses and interpretation; and report preparation. Mr. Hutchins also has extensive experience supporting exploratory drilling and sampling programs for resource exploration projects. Specifically, he has worked on mineral exploration projects for chromium, nickel, gold, copper, zinc and cobalt mineralization.

In addition, Mr. Hutchins has worked on multiple projects involving sub-meter global positioning system (GPS) data collection and geographic information system (GIS) applications ranging from large-scale mining operations to small-scale environmental project work. He has provided GIS support for the creation of various site maps included in project reports as well as large-scale display wall maps.

EDUCATION

B.S., Geology, Southern Oregon University, Ashland, Oregon, 2007

CERTIFICATIONS & TRAINING

Erosion Prevention and Sediment Control Inspector, Medford, Oregon, 2016

CPR, AED and First Aid, Medford, Oregon, 2016

Green Defensive Driving Course, Medford, Oregon, 2016

MSHA Annual Refresher, Medford, Oregon, 2016

Responder Level Training, Medford, Oregon, 2016

REGISTRATIONS

Geologist-In-Training, State of Oregon

PROJECT EXPERIENCE

Former Riverfront Graving Dock Facility – Phase I & II ESA*, Douglas County, Oregon (Staff Geologist and GIS Technician)

Mr. Hutchins served as the field geologist for a Phase II ESA performed at an inactive riverfront graving dock facility owned by Douglas County and leased to Knife River Materials. Services were provided for the purpose of negotiating expedited cleanup efforts to obtain a NFA determination. Mr. Hutchins's responsibilities included historical research; sampling and characterization of soil and estuary sediment potentially impacted by metals associated with anti-fouling paints, petroleum hydrocarbons, and polychlorinated biphenyls (PCBs); and preparation of tables and figures for the final report. Estuary sampling in the Umpqua River consisted of collecting three depth-discrete samples at 10 locations for a total of 30 estuary samples. Mr. Hutchins also created all of the GIS figures for the Phase I & II ESA as well as collected all of the GPS data that were incorporated into the figures.

Former Processing Plant – Phase I & II ESA and Soil Removal Oversight*, Eagle Point, Oregon (Field Geologist)

Mr. Hutchins assisted with Phase I and II ESA activities at this former mixed-use industrial and residential property. His Phase I ESA responsibilities included photo documentation and documentation of current site conditions. His Phase II responsibilities included soil sampling and analyses for a septic field uncovered during soil excavation efforts. Soil containing high levels of lead was excavated and disposed of at a local landfill.

** denotes projects completed with other firms*

Dana Hutchins GIT

Project Specialist, Geology

Private Property Owner: Heating Oil Tank Release – Indoor Soil Vapor Sampling*, Ashland, Oregon (Field Geologist)

Following completion of surface and subsurface site investigation services in support of heating oil tank decommissioning and soil cleanup activities, the property owner hired the firm to perform indoor air quality sampling services. Services were provided for the purpose of obtaining site closure approval from Oregon Department of Environmental Quality (DEQ). Mr. Hutchins performed sub-slab soil vapor sampling below the residence and assisted with preparing the final Heating Oil Tank Decommissioning & Stream Investigation Report that was submitted to Oregon DEQ. The No Further Action (NFA) determination request was approved in 2012.

"B" Street Maintenance & Storage Yard Facility Clean-Up – Phase II ESA*, Ashland, Oregon (Field Geologist)

Mr. Hutchins conducted groundwater monitoring and assisted with preparation of the final site assessment report for this historical maintenance and storage yard owned by the City of Ashland. His responsibilities included assisting with evaluation of the nature and extent of soil and groundwater contamination associated with former underground storage tanks (USTs). Activities included installation of four groundwater monitoring wells; soil borings and soil sample collection; quarterly groundwater monitoring and reporting; and identification and comparison of contaminants of concern to applicable Oregon DEQ risk-based concentration (RBC) levels.

Ashland Gun Club – Site Characterization Work Plan Development and Implementation*, Ashland, Oregon (Field Geologist and GIS Technician)

Mr. Hutchins conducted surface and subsurface soil investigations at this 32-acre property used as a shooting range since 1968. Over 160 total soil samples were collected and analyzed for lead to vertically and horizontally delineate potential contamination. Additionally, six groundwater monitoring wells were installed using hollow-stem auger drilling to obtain groundwater quality information both on-site and downgradient from the site. Mr. Hutchins supported soil sampling and analyses activities and provided field oversight of subcontractors. He also created GIS figures for the work plan prepared by the firm and performed a GPS survey to locate all well and sampling locations in the field.

Former Gasoline Retail Facility – Groundwater Investigation and Remediation*, Vancouver, Washington (Field Geologist)

The firm conducted an environmental investigation to determine the magnitude and extent of contamination at a former gasoline retail facility. Mr. Hutchins performed quarterly groundwater sampling and provided field oversight during installation of the monitoring wells.

Confidential Investment Group: Residential Development – Site Investigation and Characterization*, Southern, Oregon (Field Geologist)

The firm conducted follow-up site characterization activities at this property to determine if groundwater concentrations had attenuated since previous site characterization activities had been performed four years earlier. The original site data indicated the need for deed restrictions prior to obtaining a NFA letter. The client did not want deed restrictions and retained the firm to perform additional site characterization activities. Mr. Hutchins conducted soil and groundwater sampling and reporting efforts to collect data showing that the site contaminants had attenuated.

Confidential Financial Institution: On-Call Contract – Phase I ESA*, Oregon and Washington (Staff Geologist and GIS Technician)

The firm is providing Phase I ESA services under an ongoing on-call contract with a large regional lending institution. Due diligence services have been requested by the client prior to property repossessions or for the purpose of assessing new loan evaluations. Mr. Hutchins has supported five Phase I ESA projects under this contract. His responsibilities have included environmental records research and review as well as preparation of GIS figures, site maps, and final reports. The subject properties have included a lumber mill, auto repair facility, food processing facility, and two industrial facilities.

Confidential Utility Provider: Multiple Property Transactions – Phase I ESAs*, Washington and California (Staff Geologist)

Mr. Hutchins provided Phase I ESA services to a confidential utility provider in support of two proposed property transactions in Washington and California. His responsibilities included performing background research, environmental records review, and co-authoring the final reports.

** denotes projects completed with other firms*

Jackie M. Brenner

Project Scientist

Jacqueline is an Environmental Scientist in the Portland – Barnes Road office of Stantec. At Stantec she has gained experience conducting Phase I and Phase II Environmental Site Assessments, environmental remediation monitoring, creating GIS property and land use inventories, and conducting Regulated Building Material surveys in assisting with brownfield redevelopment efforts. She is AHERA Asbestos Inspector certified.

Previous to Stantec, she researched the watersheds of hundreds of Oregon lakes and their natural and anthropogenic sources of nitrates and phosphates, discovering strong regional correlations. She has also helped EPA map agricultural use and changes to groundwater nitrates over time throughout Oregon's Willamette Valley. She also has two years of experience as a junior level industrial hygienist.

EDUCATION

Graduate Certificate in GIS, Oregon State University, Corvallis, Oregon, 2015

BS Ecology and Evolutionary Biology, University of California, Santa Cruz, Santa Cruz, California, 2011

MS Environmental Sciences - Water Resource Science focus, Oregon State University, Corvallis, Oregon, 2015

CERTIFICATIONS & TRAINING

40-hour Hazardous Waste Operations and Emergency Response, Hygiene Technologies, 40-hour Hazardous Waste Operations and Emergency Response, Hygiene Technologies Inc., Torrance, California, 2011

AHERA Asbestos Building Inspector, AHERA Accreditation for Asbestos Inspectors, PBS Environmental, Portland, Oregon, 2016

Marc Sauze P.E.

Principal, Environmental Services

Marc creates better communities by using his extensive remediation expertise to address sites with contaminated soils and groundwater. He has over 20 years of experience helping industries solve environmental compliance issues through technical and management expertise in areas of site assessment, remediation, risk assessment, and regulatory compliance. Marc's assessment and remediation experience includes projects from transportation, mining, forestry, and petroleum industries. His extensive practice includes assessing and remediating large-scale sites such as industrial factories, refineries, rail-yards, and mine sites. Marc's work is coordinated with various stakeholders including regulators, site owners, operators, and the public.

EDUCATION

Forest Technology Diploma, Northern Alberta Institute of Technology, Edmonton, Alberta, 1986

BS, University of British Columbia / Engineering Program, Vancouver, British Columbia, 1994

REGISTRATIONS

Professional Engineer, State of Oregon

Professional Engineer #37828, State of Washington

Professional Engineer #24803, Engineers and Geoscientists British Columbia

MEMBERSHIPS

Point of Contact, Society of American Military Engineers, Seattle Post

PROJECT EXPERIENCE

Environmental Consulting

US EPA Brownfields Assessment Grants, Washington

Marc is the quality assurance / quality control manager on implementation of six US EPA Community Wide Assessment Grants, two for each of the cities of Everett, Kent and Vancouver. Marc oversaw and reviewed preparation of Quality Assurance Project Plans (QAPPs), Site Specific Sampling and Analysis Plans (SSSAPs) and site-specific HASPs. The EPA Brownfields Program is designed to empower states, communities, and other stakeholders to work together in a timely manner to prevent, assess, safely clean up, and sustainably reuse brownfields. EPA provides technical and financial assistance for brownfields activities through an approach based on four main goals: protecting human health and the environment, sustaining reuse, promoting partnerships, and strengthening the marketplace. Brownfields grants serve as the foundation of the Brownfields Program and support revitalization efforts by funding environmental assessment, cleanup, and job training activities. Thousands of properties have been assessed and cleaned up through the Brownfields Program.

Environmental Site Remediation

Port of Grays Harbor, site Assessment and Clean-up Funding, Westport, Washington

Marc assisted the Port of Grays Harbor to secure funding for assessment and remediation of a contaminated site in Westport, WA. Gasoline contamination resulting from leaking underground storage tanks (USTs) was confirmed at the site. Shortly after discovery of the contamination site assessment was completed and the results were summarized in a remedial investigation/feasibility study (RI/FS). The RI/FS was submitted to Ecology and remedial actions were undertaken. Marc reviewed the project history and determined a suitable source for funding and reimbursement was the Washington Department of Ecology Toxics Clean-up Program Remedial Action Grant. Marc prepared the application for the grant and secured the funding in 2013. Marc continues to assist the Port of Grays Harbor with assessment and remediation on a variety of properties.

7-Eleven Corporation, Washington

Remediation engineer for a portfolio of sites owned by 7-Eleven Corporation. The portfolio includes up to 50 sites in the Northwest. Environmental services for these sites include wide-area inventory delineation and remediation of subsurface soil and groundwater contamination originating from convenience stores with underground storage and aboveground fuel distribution facilities. Mr. Sauze completed design and construction review of a high profile remediation system for a site clean-up in downtown Seattle.

** denotes projects completed with other firms*

Marc Sauze P.E.

Principal, Environmental Services

Former Boat Manufacturer, Marysville, Washington

Marc is managing assessment and planning remediation of contaminated soils and groundwater associated with a former ship maintenance facility situated at the confluence of the Snohomish River and Port Gardner Bay in Everett. The site's industrial history dates back to the early 1900s with part of the site consisting of fill material placed in Port Gardner Bay. The various past uses and historical operations resulted in heavy metals contamination (arsenic, lead and zinc) as well as polycyclic aromatic hydrocarbons in the soil and groundwater. The groundwater contamination is a particular concern because of the proximity to Port Gardner Bay and the potential impact to aquatic life. Marc prepared a comprehensive Remedial Investigation/Feasibility Study (RI/FS) Work Plan consistent with the Washington State Department of Ecology's Model Toxics Control Act (MTCA) to characterize the site and develop a Clean-up Action Plan. The RI/FS was accepted by Ecology as part of an Agreed Order and implementation began in 2011. Marc is working with the various stakeholders (former facility operator, property owner, neighbors and Ecology) to insure assessment and clean-up activities are completed in a cost-effective manner while maintaining consistency regulatory expectations and the requirements.

Oregon State Penitentiary, Salem, Oregon

Marc currently manages the remediation of a chlorinated solvent plume originating from inside the Oregon State Penitentiary (OSP). Remediation is accomplished by pumping groundwater from the subsurface at rates of up to 400 gallons per minute and treating the contaminated groundwater prior to discharge at a nearby stream. The system was originally installed in the 1990s, and Marc has completed design modifications and upgrades over the past three years to optimize inefficiency and adjust to the fluctuating contaminant concentrations. He continues to provide engineering advice to OSP regarding system operation and alternative remedial approaches. Project investigations included installation monitoring wells to depths ranging from 25 to 150 feet below ground surface. Replaced a 500 gpm pump and redesigned the pumping infrastructure to handle increased capacity. Continue to provide engineering advise to OSP on system operation and alternative remedial approaches.

ConocoPhillips Portfolio Management, Washington and Oregon (Portfolio Manager and Lead Engineer)

Managed a large portfolio of retail service stations for ConocoPhillips. Mr. Sauze devised numerous approaches to site clean-up that resulted in significant savings to the client. For example, a restaurant was planned for construction on a site which contained residual soil contamination. Mr. Sauze designed engineering controls consisting of a subsurface vapor barrier and passive venting system to mitigate potential vapor intrusion into the restaurant. These actions satisfied the regulatory requirements and resulted in construction of the restaurant without a costly remedial excavation.

Former Dry Cleaning Facility, Eugene, Oregon

Prescribed and implemented in-situ chemical oxidation using permanganate for a former dry-cleaning facility in Eugene, Oregon. The facility is located in an active shopping center. The remedial approach involved installing fixed injection points and several extraction points. Chemicals were injected and then 'pulled' towards the extraction points to allow blanket coverage of the impacted area and accelerated remediation.

Hazardous Waste

US Navy Base, Washington (Project Manager and Design Engineer)

Provided consulting services for the clean-up of residual soil contamination at a Naval base in Western Washington. The Navy was considering excavating the impacted soils and disposing of the soils off-site. The contaminants consisted of 'heavier end' hydrocarbons. Mr. Sauze used recently adopted new guidelines for clean-up standards for 'heavier-end hydrocarbons' which allowed fractionalization of the carbon chains. Based on the new guidelines, the soils could be left in place.

** denotes projects completed with other firms*

Patrick H. Vaughan CEM, MS

Principal, Facility Assessment and Indoor Environment

Patrick has more than 30 years of experience managing complex site characterization and exposure assessment projects with both Federal and state oversight. Throughout his tenure as a consultant, he has established excellent client communication, including having a clear understanding of their needs, management resources, and completing projects on schedule and within budget.

Patrick's experience brings a unique multi-media approach to vapor intrusion evaluation. He has consulted with various states, including Washington, Oregon, California, and Arizona regarding developing vapor intrusion guidance documents and screening levels.

Currently, Patrick serves as a technical advisor for vapor intrusion and inhalation risk to a majority of Stantec nationwide offices and is a member of the Stantec National Risk Assessment and Toxicology Practice.

EDUCATION

BS, Biology, Chemistry, and Public Health, Portland State University, Portland, Oregon, 1973

MS, Microbiology and Biochemistry, University of Oregon Medical School, Portland, Oregon, 1976

REGISTRATIONS

Certified Environmental Manager #1984, Nevada Department of Conservation & Natural Resources

PROJECT EXPERIENCE

Soil Vapor Intrusion Assessment
EPA Superfund (COE Area), Palo Alto, California (Technical Lead, Vapor Intrusion Assessment)
Patrick has overall responsibility for the vapor intrusion assessment of all residential and commercial properties within the COE Superfund Study Area. He is designing sampling protocols; interpreting results; helping ensure that the Quality Assurance/Quality Control (QA/QC) procedures as specified in the QA Project Plan (QAPP) and other pertinent analytical procedures are met; providing performance oversight of tasks under this contract; and evaluating potential inhalation risk from vapor intrusion. Project challenges to date include several changes to sampling protocol made by EPA Region 9 after initial work plan approval and Region 9 implementation of TCE short term action levels.

Vapor Mitigation System Design and Installation, Jantzen Beach Retail Center, Portland, Oregon (Senior Scientist)
Patrick designed and supervised constructing a passive sub-slab depressurization system to control possible transport of petroleum impacted soil vapor into a retail center.

Vapor Intrusion Assessment, Oregon State Penitentiary, Salem, Oregon (Senior Scientist)
Patrick modeled statistically valid groundwater concentrations to derive COPC indoor air concentrations. The modeled air concentrations were then used to prepare a site-specific human health inhalation risk assessment of current inmate/guard and warden receptors and hypothetical future residential receptors.

Edgewood Shopping Center, Eugene, Oregon (Senior Project Manager/Investigator)
The shopping center formerly included a dry cleaner tenant for approximately 20 years. Tenant operating and disposal practices resulted in releases of chlorinated solvents to soil and groundwater. Patrick managed the initial soil and groundwater investigations as well as a preliminary assessment of potential vapor intrusion in response to tenant complaints. His proposed imminent tasks included delineating off-site groundwater contamination, further source identification, soil gas sampling and analysis, and indoor air monitoring. The site is currently awaiting acceptance into the Oregon DEQ VCP.

Patrick H. Vaughan CEM, MS

Principal, Facility Assessment and Indoor Environment

Decatur Condominiums, Seattle, Washington (Senior Scientist)
Patrick conducted a vapor intrusion screening assessment in accordance with ASTM E2600-08 "Standard Practice for Assessment of Vapor intrusion into Structures on Property Involved in Real Estate Transactions."

Brown Property, Vancouver, Washington (Senior Scientist)
Patrick conducted biological testing (enumeration and speciation) in an office building in response to occupant complaints. He designed and implemented a remedial action plan to remove pathogens (Aspergillis niger) from the interior spaces and corrective measures to prevent re-colonization.

Vancouver Iron and Steel Facility, Portland, Oregon (Forensic Scientist)
Patrick is working as forensic expert conducting fingerprinting of PCBs detected on facility property. He is helping prepare an escrow agreement for property transfer that addressed environmental conditions. Patrick is also conducting monitoring activities and analyzing analytical results to assess noise and odor factors in defense of various complaints by neighboring property owners.

Former Stages Building, Portland, Oregon (Project Manager)
Patrick conducted an endangerment assessment to evaluate human health and ecological impacts resulting from the release of numerous carcinogenic polycyclic aromatic hydrocarbons, metals, and chlorinated solvents.

Abandoned Lumber Mill, Crescent City, California (Risk Assessor)
Patrick designed and conducted both human health and ecological risk assessments for contamination originating at a former wood treatment/sawmill facility. The site is contaminated with heavy metals, chlorophenols, dioxins, and furans and is in close proximity to estuarine and marine environments.

Environmental Site Remediation
Various Project for the U.S. EPA, Various Sites, Various States (Work Assignment Manager)
Patrick was a work assignment manager for several projects assigned by the Stationary Source Compliance Division (SSCD) in support of the Clean Air Act Amendments. He designed permanent total enclosures for the capture of volatile organic chemicals; developed inspection procedures for the benzene NESHAP; and developed procedures for the use of continuous emission monitors to monitor Title V compliance.

Liliblad/SolPro Joint Venture Site, Tacoma, Washington (Senior Project Manager)
Patrick performed a remedial investigation of a solvent recycling facility, conducted under MTCA with US EPA oversight. He collected and analyzed more than 200 soil samples and placed monitoring wells across three water bearing units.

Environmental Risk Assessments
Risk Assessment for Pacific Stainless Products, Tualatin, Oregon (Risk Assessor)
Patrick performed human health and ecological risk assessments for an unauthorized disposal facility where site related contaminants (i.e. PCBs) were released into soil, air, and groundwater.

Exposure Assessment
Public Health Laboratory, Portland, Oregon (Senior Microbiologist)
Patrick identified viral and bacteriological pathogens throughout Oregon. He acted as state liaison for implementing national testing programs for Legionnaire's Disease and Swine Influenza. Patrick also coordinated with the Center for Disease Control and established testing and analytical protocol for local evaluation of biological hazards. He assisted the Oregon State Department of Public Health with epidemiological investigations, modeling, and analysis and guest-lectured in epidemiology at Portland State University.

Apartment Complex, Portland, Oregon (Sr Scientist)
Patrick performed a human health hazard assessment of a 600-unit apartment complex that included microbiological, VOCs, and asbestos air sampling. He developed and implemented remedial action plans so that the maximum numbers of units were returned to service in the shortest amount of time.

** denotes projects completed with other firms*

Patrick H. Vaughan CEM, MS

Principal, Facility Assessment and Indoor Environment

Exposure Assessments (Occupational Assessments)
Building Company, Tualatin, Oregon (Sr Scientist)
Patrick designed a bilingual employee questionnaire for retrospective epidemiological evaluation of employee symptomology. He conducted volatile organic compound (VOC) and microbiological sampling and analysis. Ultimately, a correlation was detected between the nature and extent of worker health complaints and the presence of significant numbers of fungi within the ventilation system. Based on this, Patrick developed a remedial plan to correct deficiencies in the air handling system.

** denotes projects completed with other firms*

APPENDIX C LABORATORY CERTIFICATES

The State of Washington Department of Ecology

TestAmerica Seattle-Tacoma
Tacoma, WA

has complied with provisions set forth in Chapter 173-50 WAC and is hereby recognized by the Department of Ecology as an ACCREDITED LABORATORY for the analytical parameters listed on the accompanying Scope of Accreditation. This certificate is effective February 18, 2018 and shall expire February 17, 2019.

Witnessed under my hand on February 16, 2018

Rebecca Wood
Acting Lab Accreditation Unit Supervisor

Laboratory ID
C553

WASHINGTON STATE DEPARTMENT OF ECOLOGY

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM

SCOPE OF ACCREDITATION

TestAmerica Seattle-Tacoma

Tacoma, WA

is accredited for the analytes listed below using the methods indicated. Full accreditation is granted unless stated otherwise in a note. EPA is the U.S. Environmental Protection Agency. SM is "Standard Methods for the Examination of Water and Wastewater." SM refers to EPA approved method versions. ASTM is the American Society for Testing and Materials. USGS is the U.S. Geological Survey. AOAC is the Association of Official Analytical Chemists. Other references are described in notes.

Matrix/Analyte	Method	Notes
Drinking Water		
1,2-Dibromo-3-chloropropane (DBCP)	EPA 504.1_1.1_1995	7
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 504.1_1.1_1995	7
Non-Potable Water		
Specific Conductance	EPA 120.1_1982	7
n-Hexane Extractable Material (O&G)	EPA 1664A_1_1999	7
Turbidity	EPA 180.1_2_1993	7
Bromide	EPA 300.0_2.1_1993	7
Chloride	EPA 300.0_2.1_1993	7
Fluoride	EPA 300.0_2.1_1993	7
Nitrate	EPA 300.0_2.1_1993	7
Nitrate + Nitrite	EPA 300.0_2.1_1993	7
Nitrite	EPA 300.0_2.1_1993	7,10
Sulfate	EPA 300.0_2.1_1993	7
Cyanide, Total	EPA 335.4_1_1993	7
Ammonia	EPA 350.1_2_1993	7
Nitrate	EPA 353.2_2_1993	7
Nitrate + Nitrite	EPA 353.2_2_1993	7
Nitrite	EPA 353.2_2_1993	7
Orthophosphate	EPA 365.1_2_1993	7
Phosphorus, Total	EPA 365.1_2_1993	7
Turbidity	SM 2130 B-2011	7,88

Matrix/Analyte	Method	Notes
Non-Potable Water		
Alkalinity	SM 2320 B-2011	7,88
Carbonate/Bicarbonate	SM 2320 B-2011	
Hardness (calc.)	SM 2340 B-2011	7,88
Hardness, Total (as CaCO3)	SM 2340 C-2011	7,88
Specific Conductance	SM 2510 B-2011	7,88
Salinity	SM 2520 B-2011	7,88
Solids, Total	SM 2540 B-2011	7,88
Solids, Total Dissolved	SM 2540 C-2011	7,88
Solids, Total Suspended	SM 2540 D-2011	7,88
Solids, Settleable	SM 2540 F-2011	7,88
Chromium, Hexavalent	SM 3500-Cr B-2011	7,88
Cyanide, Weak Acid Dissociable	SM 4500 CN-I-2011	7,88
Cyanide, Total	SM 4500-CN^- E-2011	7,88
pH	SM 4500-H+ B-2011	7,10,88
Ammonia	SM 4500-NH3 G-2011	7,88
Biochemical Oxygen Demand (BOD)	SM 5210 B-2011	7,88
Chemical Oxygen Demand (COD)	SM 5220 C-2011	7,88
Chemical Oxygen Demand (COD)	SM 5220 D-2011	7,88
Total Organic Carbon	SM 5310 B-2011	7,88
Aluminum	EPA 200.7_4.4_1994	7
Antimony	EPA 200.7_4.4_1994	7
Arsenic	EPA 200.7_4.4_1994	7
Barium	EPA 200.7_4.4_1994	7
Beryllium	EPA 200.7_4.4_1994	7
Boron	EPA 200.7_4.4_1994	7
Cadmium	EPA 200.7_4.4_1994	7
Calcium	EPA 200.7_4.4_1994	7
Chromium	EPA 200.7_4.4_1994	7
Cobalt	EPA 200.7_4.4_1994	7
Copper	EPA 200.7_4.4_1994	7
Hardness, Total (as CaCO3)	EPA 200.7_4.4_1994	7
Iron	EPA 200.7_4.4_1994	7

Matrix/Analyte	Method	Notes
Non-Potable Water		
Lead	EPA 200.7_4.4_1994	7
Magnesium	EPA 200.7_4.4_1994	7
Manganese	EPA 200.7_4.4_1994	7
Molybdenum	EPA 200.7_4.4_1994	7
Nickel	EPA 200.7_4.4_1994	7
Potassium	EPA 200.7_4.4_1994	7
Selenium	EPA 200.7_4.4_1994	7
Silica as SiO2	EPA 200.7_4.4_1994	7
Silicon	EPA 200.7_4.4_1994	7
Silver	EPA 200.7_4.4_1994	7
Sodium	EPA 200.7_4.4_1994	7
Strontium	EPA 200.7_4.4_1994	7
Thallium	EPA 200.7_4.4_1994	7
Tin	EPA 200.7_4.4_1994	7
Titanium	EPA 200.7_4.4_1994	7
Vanadium	EPA 200.7_4.4_1994	7
Zinc	EPA 200.7_4.4_1994	7
Antimony	EPA 200.8_5.4_1994	7
Arsenic	EPA 200.8_5.4_1994	7
Barium	EPA 200.8_5.4_1994	7
Beryllium	EPA 200.8_5.4_1994	7
Cadmium	EPA 200.8_5.4_1994	7
Chromium	EPA 200.8_5.4_1994	7
Cobalt	EPA 200.8_5.4_1994	7
Copper	EPA 200.8_5.4_1994	7
Lead	EPA 200.8_5.4_1994	7
Manganese	EPA 200.8_5.4_1994	7
Molybdenum	EPA 200.8_5.4_1994	7
Nickel	EPA 200.8_5.4_1994	7
Selenium	EPA 200.8_5.4_1994	7
Silver	EPA 200.8_5.4_1994	7

Matrix/Analyte	Method	Notes
Non-Potable Water		
Strontium	EPA 200.8_5.4_1994	7
Thallium	EPA 200.8_5.4_1994	7
Titanium	EPA 200.8_5.4_1994	7
Total Uranium	EPA 200.8_5.4_1994	7
Vanadium	EPA 200.8_5.4_1994	7
Zinc	EPA 200.8_5.4_1994	7
Mercury	EPA 245.1_3_1994	7
4,4'-DDD	EPA 608	7
4,4'-DDE	EPA 608	7
4,4'-DDT	EPA 608	7
Aldrin	EPA 608	7
alpha-BHC (alpha-Hexachlorocyclohexane)	EPA 608	7
alpha-Chlordane	EPA 608	7
Aroclor-1016 (PCB-1016)	EPA 608	7
Aroclor-1221 (PCB-1221)	EPA 608	7
Aroclor-1232 (PCB-1232)	EPA 608	7
Aroclor-1242 (PCB-1242)	EPA 608	7
Aroclor-1248 (PCB-1248)	EPA 608	7
Aroclor-1254 (PCB-1254)	EPA 608	7
Aroclor-1260 (PCB-1260)	EPA 608	7
Aroclor-1262 (PCB-1262)	EPA 608	7
Aroclor-1268 (PCB-1268)	EPA 608	7
beta-BHC (beta-Hexachlorocyclohexane)	EPA 608	7
Chlordane (tech.)	EPA 608	7
delta-BHC	EPA 608	7
Dieldrin	EPA 608	7
Endosulfan I	EPA 608	7
Endosulfan II	EPA 608	7
Endosulfan sulfate	EPA 608	7
Endrin	EPA 608	7
Endrin aldehyde	EPA 608	7
Endrin ketone	EPA 608	7

Matrix/Analyte	Method	Notes
Non-Potable Water		
gamma-BHC (Lindane, gamma-Hexachlorocyclohexane)	EPA 608	7
gamma-Chlordane	EPA 608	7
Heptachlor	EPA 608	7
Heptachlor epoxide	EPA 608	7
Methoxychlor	EPA 608	7
Toxaphene (Chlorinated camphene)	EPA 608	7
1,1,1,2-Tetrachloroethane	EPA 624	7
1,1,1-Trichloroethane	EPA 624	7
1,1,2,2-Tetrachloroethane	EPA 624	7
1,1,2-Trichloroethane	EPA 624	7
1,1-Dichloroethane	EPA 624	7
1,1-Dichloroethylene	EPA 624	7
1,1-Dichloropropene	EPA 624	7
1,2,3-Trichlorobenzene	EPA 624	7
1,2,3-Trichloropropane	EPA 624	7
1,2,4-Trichlorobenzene	EPA 624	7
1,2,4-Trimethylbenzene	EPA 624	7
1,2-Dibromo-3-chloropropane (DBCP)	EPA 624	7
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 624	7
1,2-Dichlorobenzene	EPA 624	7
1,2-Dichloroethane (Ethylene dichloride)	EPA 624	7
1,2-Dichloropropane	EPA 624	7
1,3,5-Trimethylbenzene	EPA 624	7
1,3-Dichlorobenzene	EPA 624	7
1,3-Dichloropropane	EPA 624	7
1,4-Dichlorobenzene	EPA 624	7
2,2-Dichloropropane	EPA 624	7
2-Butanone (Methyl ethyl ketone, MEK)	EPA 624	7
2-Chloroethyl vinyl ether	EPA 624	7
2-Chlorotoluene	EPA 624	7
2-Hexanone	EPA 624	7

Matrix/Analyte	Method	Notes
Non-Potable Water		
4-Chlorotoluene	EPA 624	7
4-Isopropyltoluene (p-Cymene)	EPA 624	7
4-Methyl-2-pentanone (MIBK)	EPA 624	7
Acetone	EPA 624	7
Acetonitrile	EPA 624	7
Acrolein (Propenal)	EPA 624	7
Acrylonitrile	EPA 624	7
Benzene	EPA 624	7
Bromobenzene	EPA 624	7
Bromochloromethane	EPA 624	7
Bromodichloromethane	EPA 624	7
Bromoform	EPA 624	7
Carbon disulfide	EPA 624	7
Carbon tetrachloride	EPA 624	7
Chlorobenzene	EPA 624	7
Chlorodibromomethane	EPA 624	7
Chloroethane (Ethyl chloride)	EPA 624	7
Chloroform	EPA 624	7
cis-1,2-Dichloroethylene	EPA 624	7
cis-1,3-Dichloropropene	EPA 624	7
Dibromomethane	EPA 624	7
Dichlorodifluoromethane (Freon-12)	EPA 624	7
Di-isopropylether (DIPE)	EPA 624	7
Ethylbenzene	EPA 624	7
Hexachlorobutadiene	EPA 624	7
Iodomethane (Methyl iodide)	EPA 624	7
Isobutyl alcohol (2-Methyl-1-propanol)	EPA 624	7
Isopropylbenzene	EPA 624	7
m+p-xylene	EPA 624	7
Methyl bromide (Bromomethane)	EPA 624	7
Methyl chloride (Chloromethane)	EPA 624	7
Methyl tert-butyl ether (MTBE)	EPA 624	7

Matrix/Analyte	Method	Notes
Non-Potable Water		
Methylene chloride (Dichloromethane)	EPA 624	7
Naphthalene	EPA 624	7
n-Butyl alcohol (1-Butanol, n-Butanol)	EPA 624	7
n-Butylbenzene	EPA 624	7
n-Propylbenzene	EPA 624	7
o-Xylene	EPA 624	7
sec-Butylbenzene	EPA 624	7
Styrene	EPA 624	7
tert-Butylbenzene	EPA 624	7
Tetrachloroethylene (Perchloroethylene)	EPA 624	7
Tetrahydrofuran (THF)	EPA 624	7
Toluene	EPA 624	7
trans-1,2-Dichloroethylene	EPA 624	7
trans-1,3-Dichloropropylene	EPA 624	7
trans-1,4-Dichloro-2-butene	EPA 624	7
Trichloroethene (Trichloroethylene)	EPA 624	7
Trichlorofluoromethane (Freon 11)	EPA 624	7
Vinyl acetate	EPA 624	7
Vinyl chloride	EPA 624	7
Xylene (total)	EPA 624	7
1,2,4-Trichlorobenzene	EPA 625	7
1,2-Dichlorobenzene	EPA 625	7
1,3-Dichlorobenzene	EPA 625	7
1,4-Dichlorobenzene	EPA 625	7
1-Methylnaphthalene	EPA 625	7
2,2'-Oxybis(1-chloropropane)	EPA 625	7
2,3,4,6-Tetrachlorophenol	EPA 625	7
2,3,5,6-Tetrachlorophenol	EPA 625	7
2,3,5-Trichlorophenol	EPA 625	7
2,3,6-Trichlorophenol (4C)	EPA 625	7
2,4,5-Trichlorophenol	EPA 625	7

Matrix/Analyte	Method	Notes
Non-Potable Water		
2,4,6-Trichlorophenol	EPA 625	7
2,4-Dichlorophenol	EPA 625	7
2,4-Dimethylphenol	EPA 625	7
2,4-Dinitrophenol	EPA 625	7
2,4-Dinitrotoluene (2,4-DNT)	EPA 625	7
2,6-Dinitrotoluene (2,6-DNT)	EPA 625	7
2-Chloronaphthalene	EPA 625	7
2-Chlorophenol	EPA 625	7
2-Methylnaphthalene	EPA 625	7
2-Methylphenol (o-Cresol)	EPA 625	7
2-Nitroaniline	EPA 625	7
2-Nitrophenol	EPA 625	7
3,3'-Dichlorobenzidine	EPA 625	7
3-Nitroaniline	EPA 625	7
4,6-Dinitro-2-methylphenol	EPA 625	7
4-Bromophenyl phenyl ether (BDE-3)	EPA 625	7
4-Chloro-3-methylphenol	EPA 625	7
4-Chloroaniline	EPA 625	7
4-Chlorophenyl phenylether	EPA 625	7
4-Nitrophenol	EPA 625	7
Acenaphthene	EPA 625	7
Acenaphthylene	EPA 625	7
Aniline	EPA 625	7
Anthracene	EPA 625	7
Benzo(a)anthracene	EPA 625	7
Benzo(a)pyrene	EPA 625	7
Benzo(g,h,i)perylene	EPA 625	7
Benzo(k)fluoranthene	EPA 625	7
Benzo[b]fluoranthene	EPA 625	7
Benzoic acid	EPA 625	7
Benzyl alcohol	EPA 625	7
bis(2-Chloroethoxy)methane	EPA 625	7

Matrix/Analyte	Method	Notes
Non-Potable Water		
bis(2-Chloroethyl) ether	EPA 625	7
bis(2-Ethylhexyl) phthalate (DEHP)	EPA 625	7
Butyl benzyl phthalate	EPA 625	7
Carbazole	EPA 625	7
Chrysene	EPA 625	7
Dibenz(a,h) anthracene	EPA 625	7
Dibenzofuran	EPA 625	7
Diethyl phthalate	EPA 625	7
Dimethyl phthalate	EPA 625	7
Di-n-butyl phthalate	EPA 625	7
Di-n-octyl phthalate	EPA 625	7
Fluoranthene	EPA 625	7
Fluorene	EPA 625	7
Hexachlorobenzene	EPA 625	7
Hexachlorobutadiene	EPA 625	7
Hexachlorocyclopentadiene	EPA 625	7
Hexachloroethane	EPA 625	7
Indeno(1,2,3-cd) pyrene	EPA 625	7
Isophorone	EPA 625	7
Naphthalene	EPA 625	7
n-Decane	EPA 625	7
Nitrobenzene	EPA 625	7
n-Nitrosodimethylamine	EPA 625	7
N-Nitroso-di-n-propylamine	EPA 625	7
n-Nitrosodiphenylamine	EPA 625	7
n-Octadecane	EPA 625	7
Pentachlorophenol	EPA 625	7
Phenanthrene	EPA 625	7
Phenol	EPA 625	7
Pyrene	EPA 625	7
Dibutyltin	Krone 1988	3

Matrix/Analyte	Method	Notes
Non-Potable Water		
Monobutyltin	Krone 1988	3
Tetrabutyltin	Krone 1988	3
Tributyltin	Krone 1988	3
Solid and Chemical Materials		
Bromide	EPA 300.0_2.1_1993	7
Chloride	EPA 300.0_2.1_1993	7
Fluoride	EPA 300.0_2.1_1993	7
Nitrate	EPA 300.0_2.1_1993	7
Nitrate + Nitrite	EPA 300.0_2.1_1993	7
Nitrite	EPA 300.0_2.1_1993	7,10
Sulfate	EPA 300.0_2.1_1993	7
Cyanide, Total	EPA 9012 B-04	7
Cyanides, Amenable to Chlorination	EPA 9012 B-04	7
pH	EPA 9045C_3_1995	7
Bromide	EPA 9056A_(02/07)	7
Chloride	EPA 9056A_(02/07)	7
Fluoride	EPA 9056A_(02/07)	7
Nitrate	EPA 9056A_(02/07)	7
Nitrite	EPA 9056A_(02/07)	7,10
Sulfate	EPA 9056A_(02/07)	7
Total Organic Carbon	EPA 9060A_1_2004	7
Aluminum	EPA 6010D_(7/14)	7
Antimony	EPA 6010D_(7/14)	7
Arsenic	EPA 6010D_(7/14)	7
Barium	EPA 6010D_(7/14)	7
Beryllium	EPA 6010D_(7/14)	7
Boron	EPA 6010D_(7/14)	7
Cadmium	EPA 6010D_(7/14)	7
Calcium	EPA 6010D_(7/14)	7
Chromium	EPA 6010D_(7/14)	7
Cobalt	EPA 6010D_(7/14)	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
Copper	EPA 6010D_(7/14)	7
Iron	EPA 6010D_(7/14)	7
Lead	EPA 6010D_(7/14)	7
Magnesium	EPA 6010D_(7/14)	7
Manganese	EPA 6010D_(7/14)	7
Molybdenum	EPA 6010D_(7/14)	7
Nickel	EPA 6010D_(7/14)	7
Potassium	EPA 6010D_(7/14)	7
Selenium	EPA 6010D_(7/14)	7
Silica	EPA 6010D_(7/14)	7
Silicon	EPA 6010D_(7/14)	7
Silver	EPA 6010D_(7/14)	7
Sodium	EPA 6010D_(7/14)	7
Strontium	EPA 6010D_(7/14)	7
Thallium	EPA 6010D_(7/14)	7
Tin	EPA 6010D_(7/14)	7
Titanium	EPA 6010D_(7/14)	7
Vanadium	EPA 6010D_(7/14)	7
Zinc	EPA 6010D_(7/14)	7
Antimony	EPA 6020B_(7/14)	7
Arsenic	EPA 6020B_(7/14)	7
Barium	EPA 6020B_(7/14)	7
Beryllium	EPA 6020B_(7/14)	7
Cadmium	EPA 6020B_(7/14)	7
Chromium	EPA 6020B_(7/14)	7
Cobalt	EPA 6020B_(7/14)	7
Copper	EPA 6020B_(7/14)	7
Lead	EPA 6020B_(7/14)	7
Manganese	EPA 6020B_(7/14)	7
Mercury	EPA 6020B_(7/14)	7
Molybdenum	EPA 6020B_(7/14)	7
Nickel	EPA 6020B_(7/14)	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
Selenium	EPA 6020B_(7/14)	7
Silver	EPA 6020B_(7/14)	7
Strontium	EPA 6020B_(7/14)	7
Thallium	EPA 6020B_(7/14)	7
Titanium	EPA 6020B_(7/14)	7
Uranium	EPA 6020B_(7/14)	7
Vanadium	EPA 6020B_(7/14)	7
Zinc	EPA 6020B_(7/14)	7
Mercury, Liquid Waste	EPA 7470A_1_1994	7
Mercury, Solid Waste	EPA 7471A_1_1994	7
1,2-Dibromo-3-chloropropane (DBCP)	EPA 8011-94	1,7
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 8011-94	1,7
Diesel range organics (DRO)	EPA 8015B_2_1996	7
Gasoline range organics (GRO)	EPA 8015B_2_1996	7
Motor Oil	EPA 8015B_2_1996	7
4,4'-DDD	EPA 8081B_(2/07)	7
4,4'-DDE	EPA 8081B_(2/07)	7
4,4'-DDT	EPA 8081B_(2/07)	7
Aldrin	EPA 8081B_(2/07)	7
alpha-BHC (alpha-Hexachlorocyclohexane)	EPA 8081B_(2/07)	7
alpha-Chlordane	EPA 8081B_(2/07)	7
beta-BHC (beta-Hexachlorocyclohexane)	EPA 8081B_(2/07)	7
Chlordane (tech.)	EPA 8081B_(2/07)	7
delta-BHC	EPA 8081B_(2/07)	7
Dieldrin	EPA 8081B_(2/07)	7
Endosulfan I	EPA 8081B_(2/07)	7
Endosulfan II	EPA 8081B_(2/07)	7
Endosulfan sulfate	EPA 8081B_(2/07)	7
Endrin	EPA 8081B_(2/07)	7
Endrin aldehyde	EPA 8081B_(2/07)	7
Endrin ketone	EPA 8081B_(2/07)	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
gamma-BHC (Lindane, gamma-Hexachlorocyclohexane)	EPA 8081B_(2/07)	7
gamma-Chlordane	EPA 8081B_(2/07)	7
Heptachlor	EPA 8081B_(2/07)	7
Heptachlor epoxide	EPA 8081B_(2/07)	7
Hexachlorobenzene	EPA 8081B_(2/07)	7
Hexachlorobutadiene	EPA 8081B_(2/07)	7
Methoxychlor	EPA 8081B_(2/07)	7
Toxaphene (Chlorinated camphene)	EPA 8081B_(2/07)	7
Aroclor-1016 (PCB-1016)	EPA 8082A_(2/07)	4,6,7
Aroclor-1221 (PCB-1221)	EPA 8082A_(2/07)	4,6,7
Aroclor-1232 (PCB-1232)	EPA 8082A_(2/07)	4,6,7
Aroclor-1242 (PCB-1242)	EPA 8082A_(2/07)	4,6,7
Aroclor-1248 (PCB-1248)	EPA 8082A_(2/07)	4,6,7
Aroclor-1254 (PCB-1254)	EPA 8082A_(2/07)	4,6,7
Aroclor-1260 (PCB-1260)	EPA 8082A_(2/07)	4,6,7
Aroclor-1262 (PCB-1262)	EPA 8082A_(2/07)	4,6,7
Aroclor-1268 (PCB-1268)	EPA 8082A_(2/07)	4,6,7
2,4,5-T	EPA 8151A_(1/98)	7
2,4-D	EPA 8151A_(1/98)	7
2,4-DB	EPA 8151A_(1/98)	7
4-Nitrophenol	EPA 8151A_(1/98)	7
Dalapon	EPA 8151A_(1/98)	7
Dicamba	EPA 8151A_(1/98)	7
Dichloroprop (Dichlorprop)	EPA 8151A_(1/98)	7
Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)	EPA 8151A_(1/98)	7
MCPA	EPA 8151A_(1/98)	7
MCPP	EPA 8151A_(1/98)	7
Pentachlorophenol	EPA 8151A_(1/98)	7
Silvex (2,4,5-TP)	EPA 8151A_(1/98)	7
C8-C10 Aliphatic EPH	WDOE EPH_(1997)	2,7
C8-C10 Aromatic EPH	WDOE EPH_(1997)	2,7
>C10-C12 Aliphatic EPH	WDOE EPH_(1997)	2,7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
>C10-C12 Aromatic EPH	WDOE EPH_(1997)	2,7
>C12-C16 Aliphatic EPH	WDOE EPH_(1997)	2,7
>C12-C16 Aromatic EPH	WDOE EPH_(1997)	2,7
>C16-C21 Aliphatic EPH	WDOE EPH_(1997)	2,7
>C16-C21 Aromatic EPH	WDOE EPH_(1997)	2,7
>C21-C34 Alpihatic EPH	WDOE EPH_(1997)	2,7
>C21-C34 Aromatic EPH	WDOE EPH_(1997)	2,7
Diesel range organics (DRO)	WDOE NWTPH-Dx_(1997)	2,7
Gasoline range organics (GRO)	WDOE NWTPH-Gx_(1997)	2,7,9
C8-C10 Aromatic VPH	WDOE VPH_(1997)	2,7
C5-C6 Aliphatic VPH	WDOE VPH_(1997)	2,7
>C10-C12 Aliphatic VPH	WDOE VPH_(1997)	2,7
>C10-C12 Aromatic VPH	WDOE VPH_(1997)	2,7
>C12-C13 Aromatic VPH	WDOE VPH_(1997)	2,7
>C6-C8 Aliphatic VPH	WDOE VPH_(1997)	2,7
Benzene	WDOE VPH_(1997)	2,7
C8-C10 Aliphatic VPH	WDOE VPH_(1997)	2,7
Ethylbenzene	WDOE VPH_(1997)	2,7
m+p-xylene	WDOE VPH_(1997)	2,7
Methyl tert-butyl ether (MTBE)	WDOE VPH_(1997)	2,7
n-Hexane	WDOE VPH_(1997)	2,7
o-Xylene	WDOE VPH_(1997)	2,7
Toluene	WDOE VPH_(1997)	2,7
Xylene (total)	WDOE VPH_(1997)	2,7
1,1,1,2-Tetrachloroethane	EPA 8260C SIM	7
1,1,2,2-Tetrachloroethane	EPA 8260C SIM	7
1,1,2-Trichloroethane	EPA 8260C SIM	7
1,1-Dichloroethylene	EPA 8260C SIM	7
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 8260C SIM	7
1,2-Dichloroethane (Ethylene dichloride)	EPA 8260C SIM	7
1,3-Butadiene	EPA 8260C SIM	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
1,4-Dichlorobenzene	EPA 8260C SIM	7
2-Hexanone	EPA 8260C SIM	7
Benzene	EPA 8260C SIM	7
Bromodichloromethane	EPA 8260C SIM	7
Bromoform	EPA 8260C SIM	7
Chlorodibromomethane	EPA 8260C SIM	7
Chloroform	EPA 8260C SIM	7
cis-1,3-Dichloropropene	EPA 8260C SIM	7
Dibromomethane (Methylene bromide)	EPA 8260C SIM	7
Hexachlorobutadiene	EPA 8260C SIM	7
Isopropyl alcohol (2-Propanol, Isopropanol)	EPA 8260C SIM	7
Methyl bromide (Bromomethane)	EPA 8260C SIM	7
Naphthalene	EPA 8260C SIM	7
Tetrachloroethylene (Perchloroethylene)	EPA 8260C SIM	7
trans-1,3-Dichloropropylene	EPA 8260C SIM	7
Trichloroethene (Trichloroethylene)	EPA 8260C SIM	7
Vinyl chloride	EPA 8260C SIM	7
1,1,1,2-Tetrachloroethane	EPA 8260C_(8/06)	7
1,1,1-Trichloroethane	EPA 8260C_(8/06)	7
1,1,2,2-Tetrachloroethane	EPA 8260C_(8/06)	7
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	EPA 8260C_(8/06)	7
1,1,2-Trichloroethane	EPA 8260C_(8/06)	7
1,1-Dichloroethane	EPA 8260C_(8/06)	7
1,1-Dichloroethylene	EPA 8260C_(8/06)	7
1,1-Dichloropropene	EPA 8260C_(8/06)	7
1,2,3-Trichlorobenzene	EPA 8260C_(8/06)	7
1,2,3-Trichloropropane	EPA 8260C_(8/06)	7
1,2,4-Trichlorobenzene	EPA 8260C_(8/06)	7
1,2,4-Trimethylbenzene	EPA 8260C_(8/06)	7
1,2-Dibromo-3-chloropropane (DBCP)	EPA 8260C_(8/06)	7
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 8260C_(8/06)	7
1,2-Dichlorobenzene	EPA 8260C_(8/06)	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
1,2-Dichloroethane (Ethylene dichloride)	EPA 8260C_(8/06)	7
1,2-Dichloropropane	EPA 8260C_(8/06)	7
1,3,5-Trimethylbenzene	EPA 8260C_(8/06)	7
1,3-Dichlorobenzene	EPA 8260C_(8/06)	7
1,3-Dichloropropane	EPA 8260C_(8/06)	7
1,4-Dichlorobenzene	EPA 8260C_(8/06)	7
2,2-Dichloropropane	EPA 8260C_(8/06)	7
2-Butanone (Methyl ethyl ketone, MEK)	EPA 8260C_(8/06)	7
2-Chloroethyl vinyl ether	EPA 8260C_(8/06)	7
2-Chlorotoluene	EPA 8260C_(8/06)	7
2-Hexanone	EPA 8260C_(8/06)	7
4-Chlorotoluene	EPA 8260C_(8/06)	7
4-Isopropyltoluene (p-Cymene)	EPA 8260C_(8/06)	7
4-Methyl-2-pentanone (MIBK)	EPA 8260C_(8/06)	7
Acetone	EPA 8260C_(8/06)	7
Acetonitrile	EPA 8260C_(8/06)	7
Acrolein (Propenal)	EPA 8260C_(8/06)	7
Acrylonitrile	EPA 8260C_(8/06)	7
Benzene	EPA 8260C_(8/06)	7
Bromobenzene	EPA 8260C_(8/06)	7
Bromochloromethane	EPA 8260C_(8/06)	7
Bromodichloromethane	EPA 8260C_(8/06)	7
Bromoform	EPA 8260C_(8/06)	7
Carbon disulfide	EPA 8260C_(8/06)	7
Carbon tetrachloride	EPA 8260C_(8/06)	7
Chlorobenzene	EPA 8260C_(8/06)	7
Chlorodibromomethane	EPA 8260C_(8/06)	7
Chloroethane (Ethyl chloride)	EPA 8260C_(8/06)	7
Chloroform	EPA 8260C_(8/06)	7
cis-1,2-Dichloroethylene	EPA 8260C_(8/06)	7
cis-1,3-Dichloropropene	EPA 8260C_(8/06)	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
cis-1,4-Dichloro-2-butene	EPA 8260C_(8/06)	7
Dibromomethane	EPA 8260C_(8/06)	7
Dichlorodifluoromethane (Freon-12)	EPA 8260C_(8/06)	7
Di-isopropylether (DIPE)	EPA 8260C_(8/06)	7
Ethylbenzene	EPA 8260C_(8/06)	7
Ethyl-t-butylether (ETBE)	EPA 8260C_(8/06)	7
Hexachlorobutadiene	EPA 8260C_(8/06)	7
Iodomethane (Methyl iodide)	EPA 8260C_(8/06)	7
Isobutyl alcohol (2-Methyl-1-propanol)	EPA 8260C_(8/06)	7
Isopropylbenzene	EPA 8260C_(8/06)	7
m+p-xylene	EPA 8260C_(8/06)	7
Methacrylonitrile	EPA 8260C_(8/06)	7
Methyl acetate	EPA 8260C_(8/06)	7
Methyl bromide (Bromomethane)	EPA 8260C_(8/06)	7
Methyl chloride (Chloromethane)	EPA 8260C_(8/06)	7
Methyl tert-butyl ether (MTBE)	EPA 8260C_(8/06)	7
Methylcyclohexane	EPA 8260C_(8/06)	7
Methylene chloride (Dichloromethane)	EPA 8260C_(8/06)	7
Naphthalene	EPA 8260C_(8/06)	7
n-Butyl alcohol (1-Butanol, n-Butanol)	EPA 8260C_(8/06)	7
n-Butylbenzene	EPA 8260C_(8/06)	7
n-Propylbenzene	EPA 8260C_(8/06)	7
o-Xylene	EPA 8260C_(8/06)	7
sec-Butylbenzene	EPA 8260C_(8/06)	7
Styrene	EPA 8260C_(8/06)	7
tert-amylmethylether (TAME)	EPA 8260C_(8/06)	7
tert-Butylbenzene	EPA 8260C_(8/06)	7
Tetrachloroethylene (Perchloroethylene)	EPA 8260C_(8/06)	7
Tetrahydrofuran (THF)	EPA 8260C_(8/06)	7
Toluene	EPA 8260C_(8/06)	7
trans-1,2-Dichloroethylene	EPA 8260C_(8/06)	7
trans-1,3-Dichloropropylene	EPA 8260C_(8/06)	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
trans-1,4-Dichloro-2-butene	EPA 8260C_(8/06)	7
Trichloroethene (Trichloroethylene)	EPA 8260C_(8/06)	7
Trichlorofluoromethane (Freon 11)	EPA 8260C_(8/06)	7
Vinyl acetate	EPA 8260C_(8/06)	7
Vinyl chloride	EPA 8260C_(8/06)	7
2,3-Dichloroaniline	EPA 8270C_3_1996	5,7
1,2-Dichlorobenzene	EPA 8270D_(2/07)	5,7
1,2-Diphenylhydrazine	EPA 8270D_(2/07)	5,7
1,3-Dichlorobenzene	EPA 8270D_(2/07)	5,7
1,4-Dichlorobenzene	EPA 8270D_(2/07)	5,7
1-Methylnaphthalene	EPA 8270D_(2/07)	5,7
2,3,4,6-Tetrachlorophenol	EPA 8270D_(2/07)	5,7
2,3,5,6-Tetrachlorophenol	EPA 8270D_(2/07)	5,7
2,4,5-Trichlorophenol	EPA 8270D_(2/07)	5,7
2,4,6-Trichlorophenol	EPA 8270D_(2/07)	5,7
2,4-Dichlorophenol	EPA 8270D_(2/07)	5,7
2,4-Dimethylphenol	EPA 8270D_(2/07)	5,7
2,4-Dinitrophenol	EPA 8270D_(2/07)	5,7
2,4-Dinitrotoluene (2,4-DNT)	EPA 8270D_(2/07)	5,7
2,6-Dinitrotoluene (2,6-DNT)	EPA 8270D_(2/07)	5,7
2-Chloronaphthalene	EPA 8270D_(2/07)	5,7
2-Chlorophenol	EPA 8270D_(2/07)	5,7
2-Methylnaphthalene	EPA 8270D_(2/07)	5,7
2-Methylphenol (o-Cresol)	EPA 8270D_(2/07)	5,7
2-Nitroaniline	EPA 8270D_(2/07)	5,7
2-Nitrophenol	EPA 8270D_(2/07)	5,7
3,3'-Dichlorobenzidine	EPA 8270D_(2/07)	5,7
3-Nitroaniline	EPA 8270D_(2/07)	5,7
4,6-Dinitro-2-methylphenol	EPA 8270D_(2/07)	5,7
4-Bromophenyl phenyl ether (BDE-3)	EPA 8270D_(2/07)	5,7
4-Chloro-3-methylphenol	EPA 8270D_(2/07)	5,7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
4-Chloroaniline	EPA 8270D_(2/07)	5,7
4-Chlorophenyl phenylether	EPA 8270D_(2/07)	5,7
4-Nitroaniline	EPA 8270D_(2/07)	5,7
4-Nitrophenol	EPA 8270D_(2/07)	5,7
Acenaphthene	EPA 8270D_(2/07)	5,7
Acenaphthylene	EPA 8270D_(2/07)	5,7
Acetophenone	EPA 8270D_(2/07)	5,7
Aniline	EPA 8270D_(2/07)	5,7
Anthracene	EPA 8270D_(2/07)	5,7
Benzo(a)anthracene	EPA 8270D_(2/07)	5,7
Benzo(a)pyrene	EPA 8270D_(2/07)	5,7
Benzo(g,h,i)perylene	EPA 8270D_(2/07)	5,7
Benzo(k)fluoranthene	EPA 8270D_(2/07)	5,7
Benzo[b]fluoranthene	EPA 8270D_(2/07)	5,7
Benzoic acid	EPA 8270D_(2/07)	5,7
Benzyl alcohol	EPA 8270D_(2/07)	5,7
bis(2-Chloroethoxy)methane	EPA 8270D_(2/07)	5,7
bis(2-Chloroethyl) ether	EPA 8270D_(2/07)	5,7
Butyl benzyl phthalate	EPA 8270D_(2/07)	5,7
Carbazole	EPA 8270D_(2/07)	5,7
Chrysene	EPA 8270D_(2/07)	5,7
Di(2-ethylhexyl)phthalate	EPA 8270D_(2/07)	5,7
Dibenz(a,h) anthracene	EPA 8270D_(2/07)	5,7
Dibenzofuran	EPA 8270D_(2/07)	5,7
Diethyl phthalate	EPA 8270D_(2/07)	5,7
Dimethyl phthalate	EPA 8270D_(2/07)	5,7
Di-n-butyl phthalate	EPA 8270D_(2/07)	5,7
Di-n-octyl phthalate	EPA 8270D_(2/07)	5,7
Fluoranthene	EPA 8270D_(2/07)	5,7
Fluorene	EPA 8270D_(2/07)	5,7
Hexachlorobenzene	EPA 8270D_(2/07)	5,7
Hexachlorobutadiene	EPA 8270D_(2/07)	5,7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
Hexachlorocyclopentadiene	EPA 8270D_(2/07)	5,7
Hexachloroethane	EPA 8270D_(2/07)	5,7
Indeno(1,2,3-cd) pyrene	EPA 8270D_(2/07)	5,7
Isophorone	EPA 8270D_(2/07)	5,7
m+p Cresol	EPA 8270D_(2/07)	5,7
Naphthalene	EPA 8270D_(2/07)	5,7
Nitrobenzene	EPA 8270D_(2/07)	5,7
n-Nitrosodimethylamine	EPA 8270D_(2/07)	5,7
N-Nitroso-di-n-propylamine	EPA 8270D_(2/07)	5,7
n-Nitrosodiphenylamine	EPA 8270D_(2/07)	5,7
Pentachlorophenol	EPA 8270D_(2/07)	5,7
Phenanthrene	EPA 8270D_(2/07)	5,7
Phenol	EPA 8270D_(2/07)	5,7
Pyrene	EPA 8270D_(2/07)	5,7
Pyridine	EPA 8270D_(2/07)	5,7
1-Methylnaphthalene	EPA 8270D_(2/07) SIM	7
2,4,6-Trichlorophenol	EPA 8270D_(2/07) SIM	7
2,4-Dinitrophenol	EPA 8270D_(2/07) SIM	7
2,4-Dinitrotoluene (2,4-DNT)	EPA 8270D_(2/07) SIM	7
2,6-Dinitrotoluene (2,6-DNT)	EPA 8270D_(2/07) SIM	7
2-Methylnaphthalene	EPA 8270D_(2/07) SIM	7
Acenaphthene	EPA 8270D_(2/07) SIM	7
Acenaphthylene	EPA 8270D_(2/07) SIM	7
Anthracene	EPA 8270D_(2/07) SIM	7
Benzo(a)anthracene	EPA 8270D_(2/07) SIM	7
Benzo(a)pyrene	EPA 8270D_(2/07) SIM	7
Benzo(g,h,i)perylene	EPA 8270D_(2/07) SIM	7
Benzo(k)fluoranthene	EPA 8270D_(2/07) SIM	7
Benzo[b]fluoranthene	EPA 8270D_(2/07) SIM	7
bis(2-Chloroethyl) ether	EPA 8270D_(2/07) SIM	7
Chrysene	EPA 8270D_(2/07) SIM	7

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
Dibenz(a,h) anthracene	EPA 8270D_(2/07) SIM	7
Fluoranthene	EPA 8270D_(2/07) SIM	7
Fluorene	EPA 8270D_(2/07) SIM	7
Hexachlorobenzene	EPA 8270D_(2/07) SIM	7
Hexachlorobutadiene	EPA 8270D_(2/07) SIM	7
Hexachlorocyclopentadiene	EPA 8270D_(2/07) SIM	7
Hexachloroethane	EPA 8270D_(2/07) SIM	7
Indeno(1,2,3-cd) pyrene	EPA 8270D_(2/07) SIM	7
Naphthalene	EPA 8270D_(2/07) SIM	7
Nitrobenzene	EPA 8270D_(2/07) SIM	7
N-Nitrosodimethylamine	EPA 8270D_(2/07) SIM	7
N-Nitroso-di-n-propylamine	EPA 8270D_(2/07) SIM	7
Pentachlorophenol	EPA 8270D_(2/07) SIM	7
Phenanthrene	EPA 8270D_(2/07) SIM	7
Pyrene	EPA 8270D_(2/07) SIM	7
Dibutyltin	Krone 1988	3
Monobutyltin	Krone 1988	3
Tetrabutyltin	Krone 1988	3
Tributyltin	Krone 1988	3
Particle Size Distribution	ASTM D 422	7,8
Ignitability	EPA 1020A_1_1992	7
Corrosivity	EPA 9045C_3_1995	7
Particle Size Distribution	PLUMB 1981	7
Particle Size Distribution	PSEP 1986 Wet Sieve	

Matrix/Analyte	Method	Notes

Accredited Parameter Note Detail

(1) Limited to water only. (2) Washington Department of Ecology Analytical Methods for Petroleum Hydrocarbons, Publication Number ECY 97-602, June 1997. (3) Procedure is an Ion Trap method for determination of tetra-, tri-, di-, and monobutyltin in sediments and pore water. (4) Includes oil matrix. (5) For sediments, modifications are: Extraction of 20 grams of sample with an initial solvent volume of 35-50 mL instead of extraction of 30 grams of sample with an initial solvent volume of 60 mL. (6) When acid cleanup is not necessary, lab runs according to EPA 8082A protocol. (7) Accreditation based in part on recognition of Oregon NELAP accreditation. (8) Includes hydrometer and modified methods. (9) Includes determination by GCMS.(10) Provisional accreditation pending submittal of acceptable Proficiency Testing (PT) results (WAC 173-50-110).(88) Interim Washington accreditation pending receipt of an updated Scope from ORELAP. This accreditation is based in part on recognition of your currently held accreditations for previous method versions.

Authentication Signature
Rebecca Wood, Acting Lab Accreditation Unit Supervisor

02/16/2018
Date

APPENDIX D LABORATORY QA MANUAL AND SOPS

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **1664 9070 / NV03-112.11a** Effective Date: **12/30/2016**

Last Mod. Date: 11/9/15

SOP Title: **n-Hexane Extractable Material and Silica Gel Treated n-Hexane Extractable Material by Extraction and Gravimetry, Method 1664/9070A**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 03P

Revision Number with Mod ID: **11b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

Section 6.2, Supplies

- SPE Disks: Pacific Premium, 100 mm, O&G disks, 1664-100-PHT, or equivalent. ~~90 mm (Pacific O & G Disks, JT Baker Speedisk™ 50 mm, CPI Nu-Phase™ SPE Disks, Whatman® SPE Oil % Grease, or 3m Empore™ Oil and Grease Extraction Disks.)~~
- Syringe, Hamilton, certified.

Section 9.1, Sample QC, Precision and Recovery (PAR) / Laboratory Control Sample (LCS)

1	Fill a clean sample bottle with approximately 800 mL of reagent water. ~~Note the volume.~~
2	Acidify the water to pH 2.0 with concentrated HCl or H_2SO_4. DO NOT over-acidify the water as this could cause the disk packing to break down. Bring the volume to 1 L with reagent water. Cap the bottle and shake well. Record the volume.
3	Using a certified Hamilton ~~calibrated 10.0 mL~~ syringe, transfer 4.0 ~~10~~ mL of the HEM standard. Verify that there are no air bubbles in the syringe.
4	Touching the tip of the syringe to the inside of the neck of the bottle, allow the standard to slowly and gently flow down the side of the bottle and to settle on the water layer. A cloudy precipitate will form on the water. *Avoid shooting the standard into the water or introducing it too quickly. Use of automatic pipettes will pose a problem because they shoot the standard into the water and the rate of introduction cannot be controlled. If the standard is not properly floated, it can cause flow problems during the sample-processing step.*
5	DO NOT SHAKE THE BOTTLE. Attach a closed water inlet valve to the bottle with the correct bottle adapter.

12/22/16	
Department Supervisor Date	
12/22/16	12/22/16
Department Manager Approval Date	Technical Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **1664 9070 / NV03-112.11** Effective Date: **11/9/2015**

Last Mod. Date: 5/31/15

SOP Title: **n-Hexane Extractable Material and Silica Gel Treated n-Hexane Extractable Material by Extraction and Gravimetry, Method 1664/9070A**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 03P

Revision Number with Mod ID: **11a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

Section 9.1, Sample QC, Precision and Recovery (PAR) / Laboratory Control Sample (LCS)

1	Fill a clean sample bottle with approximately 800 mL of reagent water. Note the volume.
2	Acidify the water to pH 2.0 with concentrated HCl or H_2SO_4. DO NOT over-acidify the water as this could cause the disk packing to break down. Bring the volume to 1 L with reagent water. Cap the bottle and shake well.
3	Using a calibrated 5.0- ~~10.0~~-mL syringe, transfer 4.0 ~~10~~ mL of the HEM standard. Verify that there are no air bubbles in the syringe.
4	Touching the tip of the syringe to the inside of the neck of the bottle, allow the standard to slowly and gently flow down the side of the bottle and to settle on the water layer. A cloudy precipitate will form on the water. *Avoid shooting the standard into the water or introducing it too quickly. Use of automatic pipettes will pose a problem because they shoot the standard into the water and the rate of introduction cannot be controlled. If the standard is not properly floated, it can cause flow problems during the sample-processing step.*
5	DO NOT SHAKE THE BOTTLE. Attach a closed water inlet valve to the bottle with the correct bottle adapter.

11/9/15	
Department Manager Date	
11/9/15	11/9/15
Quality Manager Approval Date	Technical Approval Date

SOP Number/Revision No.: 1664 9070 / NV03-112.11a Effective Date: 11/9/2015

Title: n-HEXANE EXTRACTABLE MATERIAL (HEM; OIL AND GREASE) AND SILICA GEL TREATED n-HEXANE EXTRACTABLE MATERIAL (SGT-HEM; NON-POLAR MATERIAL) BY EXTRACTION AND GRAVIMETRY
METHODS EPA 1664A/B AND SW-846 9070A

Approvals (Signature/Date)

Steve Miller Quality Assurance Manager	5/15/15 Date	Ryan Fitzwater Organics Operations Manager Health & Safety Coordinator/Manager	5/7/15 Date
		Michael H. Dunn Technical Director	5/5/15 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used for determination of n-Hexane extractable material (HEM; oil and grease) and n-Hexane extractable material that is not adsorbed by silica gel (SGT-HEM; non-polar material) in surface and saline waters and in industrial domestic and industrial aqueous wastes. It is based on prior EPA methods for determination of "oil and grease" and "total petroleum hydrocarbons".

1.2 Reporting Limits: The required method detection limit is 1.4 mg/L and the minimum level of quantitation (ML) is 4.0 mg/L.

1.3 This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation, and Liability Act; and other EPA regulatory programs.

1.4 This method is not applicable to measurement of materials that volatilize at temperatures below approximately 85 ℃. Petroleum fuels from gasoline through #2 fuel oil may be partially lost in the solvent removal operation.

1.5 Some crude oils and heavy fuel oils contain a significant percentage of materials that are not soluble in n-Hexane. Accordingly, recoveries of these materials may be low.

1.6 The laboratory is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met.

1.7 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 A one liter sample (or less if the concentration is > 1000 mg/L) is acidified to pH <2 with HCl or H_2SO_4 and extracted by automated solid phase extraction. Sub-sampling is generally not allowed. The solvent is evaporated and the residue weighed and reported as HEM.

2.2 If the HEM is to be used for determination of SGT-HEM, the HEM is re-dissolved in n-Hexane. An amount of silica gel proportionate to the amount of HEM is added to the solution containing the re-dissolved HEM to remove polar materials. The solution is filtered to remove the silica gel, the solvent is evaporated, and the SGT-HEM is weighed.

3.0 Definitions

3.1 HEM and SGT-HEM are method-defined analytes; i.e., the definitions of both HEM and SGT-HEM are dependent on the procedure used. The nature of the oils and/or greases, and the presence of extractable non-oily matter in the sample will influence the material measured and interpretation of results.

3.2 Silica Gel Treated N-Hexane Extractable Material (SGT-HEM): components of n-Hexane extractable material (HEM) that are not absorbed by silica gel; i. e., non-polar material (NPM).

3.3 Oil and grease is a conventional pollutant under the Clean Water Act and codified at 40 CFR 401.16. The term "n-Hexane extractable material" reflects that this method can be used to determine materials other than oils and greases. Similarly, the term "silica gel treated n-Hexane extractable material" reflects that this method can be used to determine material that is not adsorbed by silica gel (non-polar material).

3.4 See TestAmerica Nashville's Quality Assurance Manual for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory blanks.

4.2 Sodium sulfate and silica gel fines have the potential to inflate results for HEM and SGT-HEM by passing through the filter paper. Use Whatman 41 filter paper or finer to ensure that no fines pass through to the weighing receptacle.

4.3 Interferences extracted from samples will vary considerably from source to source, depending upon the diversity of the site being sampled. For those instances in which samples are thought to consist of complex matrices containing substances (such as particulates or detergents) that may interfere with the extraction procedure, a smaller sample may need to be collected for analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- n-Hexane has been shown to have increased neuro-toxic effects over other Hexanes and some other solvents. Inhalation of n-Hexane should be minimized by performing all operations with n-Hexane in an explosion-proof hood or well-ventilated area.
- n-Hexane has a flash point of -23℃ (-9℉), has exp losive limits in air in the range of 1 – 7 percent, and poses a serious fire risk when heated or exposed to flame. n-Hexane can react vigorously with oxidizing materials.
- Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

5.2 Primary Materials Used: There are no materials used in this method that have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-Ceiling	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydro-chloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; Symptoms may parallel inhalation exposure. Irritant to the eyes.
Sulfuric acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Horizon SPE-DEX ® 1000XL or 3000 XL Automated Extractor System.
- Horizon Speed Vap™Solvent evaporation System.

6.2 Supplies

- SPE Disks: 90 mm (Pacific O & G Disks, JT Baker Speedisk™ 50 mm, CPI Nu-Phase ™ SPE Disks, Whatman® SPE Oil % Grease, or 3m Empore™ Oil and Grease Extraction Disks.)
- Fast-flow pre-filters, 90 mm, Pacific Par# FFP-90HT, or equivalent.
- 1-L Boston Round bottles 33 X 400-mm, 89 X 400, 53 X 400, 48 X 400, 58 X 400, 63 X 400, 83 X 400 mm, and I-Chem 33 X 430 mm bottles.
- Bottle cap adapters for wide-mouth sample containers. The Water Inlet Valves for the SPE-DEX® 3000 XL and 1000 XL are designed to fit a 33 X 400-mm Boston Round bottle.
- 40-mL collection vessels (VOA vials) for 47 mm disks or 125-mL Erlenmeyer flasks for 90 mm disks.
- 19/22 adapter for 40-mL VOA vessel (cat # 160-0001).
- 5-Gal safety-coated water waste recovery bottle (P/N 180-0005-01).
- 2.5-L safety-coated solvent bottles (P/N 27-0042), 2 for 1000XL unit, 4 for 3000XL.
- Aluminum weighing pans: 70-mm if using 47-mm disks (P/N 40-002-HT), 105-mm if using 900-mm disks (P/N 50-005-02-HT).
- pH indicator strips, non-bleeding pH 0.0-14.0 range.
- Boiling chips: Silicon carbide.
- Volumetric flasks, Class A, various sizes.
- Oven, drying.
- Balance, analytical.
- Pipettes, Class A, glass.
- Ruler.
- Graduated cylinder, 500 ± 5 mL.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Gas (dry N_2) source or any inert gas source. Air suppressors are not recommended.

7.3 **Methanol**, ACS Reagent grade.
7.4 **Hydrochloric Acid (HCl) and Sulfuric Acid (H_2SO_4)**, concentrated, reagent, ACS-grade.
7.5 **Hexane**, 85% minimum purity, 99% minimum saturated C6 isomers, residue < 1 mg/L.
7.6 **Acetone**, ACS-grade, residue less than 1 mg/L
7.7 **Sodium Sulfate**, ACS-grade, granular anhydrous. Dry at 400℃ for 4 hours minimum or buy a commercially certified-clean product. Store in a sealed glass container. It is acceptable to use solvent-phase separation paper.
7.8 **Silica Gel,** anhydrous, 75 - 150 micrometers, Davisil Grade 923 (Supelco 21447-7A, or equivalent). Dry at 150℃ for 24 hours minimum and store in a desiccator or tightly sealed container. Silica gel can also be kept in the oven until use. Determine the n-Hexane soluble material content of the silica gel by extracting 30 g of silica gel with n-Hexane and distilling the n-Hexane to dryness. The silica gel must contain less than 5 mg of n-Hexane soluble material per 30 g (< 0.17 mg/g). (The method blank checks for this criterion.)
7.9 **HEM Standard:**

7.9.1 **Hexadecane**, 98% minimum purity, commercial source.
7.9.2 **Stearic Acid**, 98% minimum purity, commercial source.
7.9.3 **Hexadecane/ Stearic Acid (1:1) spiking solution:** Prepare in Acetone at a concentration of 4,000 µg/mL each. Commercial, certified standards are acceptable. If using a certified standard, a second-source standard is required. It must be analyzed monthly.

- Place 2000 ± 5 mg (2 g) Stearic acid and 2000 ± 5 mg (2 g) hexadecane in a 1000-mL volumetric flask and fill to the mark with Acetone. The solution may require warming for complete dissolution of Stearic acid. (5000 ± 5 (5 g) portions are also acceptable.
- After the Hexadecane and Stearic acid have dissolved, transfer the solution to a 1L glass container with fluoropolymer-lined cap. **Mark the solution level on the vial and store in the dark at room temperature**.
- Each HEM standard vial contains 2000 µg/mL of Hexadecane and 2000 µg/mL of Stearic acid, yielding a combined weight of 4000 µg/mL. A concentration of 40 mg/L can be achieved by spiking 10.0 mL of the solution into a 1-L sample.

7.9.4 Immediately prior to use, verify the level on the vial and bring to volume with Acetone, if required. Warm to re-dissolve all visible precipitate. If in doubt of the concentration, verify the concentration by removing 10.0 ± 0.1 mL in a volumetric pipet and place in a tared weighing pan, and evaporate to dryness in a fume hood. The weight must be 40 ± 1 mg. If not, prepare a fresh solution. The spiking solutions should be checked frequently for signs of degradation or evaporation. Replace after six months or sooner if degradation has occurred.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Glass, Teflon™-lined cap	1 L	Cool 0-6℃, HCl or H_2SO_4 to pH < 2.	28 days	40 CFR Part 136, Table II

- Collect approximately one liter of representative sample in a glass bottle following conventional sampling practices, except that the bottle must not be pre-rinsed with sample before collection. To allow for potential QC failures, it is recommended that additional sample aliquots be collected.

- Adjust the sample pH to less than 2 with HCl or H_2SO_4 solution at the time of collection, and refrigerate at 0–6℃ (40 CFR 136, Table II). To establish the volume of HCl or H_2SO_4 required, collect a **separate aliquot**, adjust the pH of this aliquot to less than 2 with acid, and add the volume of acid determined to each sample bottle prior to collection.
- If a sample is known or suspected to contain greater than 1000 mg/L of extractable material, **collect** a proportionately smaller volume of sample (the volume required will depend upon the estimated amount of extractable material) in a glass bottle. Add a proportionately smaller amount of HCl or H_2SO_4 solution to the smaller sample if preservation is necessary.
- Collect an additional two aliquots of a sample for each set of 20 samples or less for the matrix spike. For those circumstances requiring the collection of multiple aliquots of one sample, each aliquot is to be collected in either of the following ways: 1) collect simultaneously in parallel, if possible, or 2) collect as grab samples in rapid succession.
- The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of oil and grease. Therefore, samples must be collected as grab samples. If a composite measurement is required, individual grab samples collected at prescribed time intervals must be analyzed separately and the concentrations averaged.
- If visual observation indicates solids, then determine whether the sample contains >20% solids. Using a ruler, measure total sample height. Next, measure solids layer. Calculate using the following equation: height soil (100) / height sample = % solids. If the sample contains greater than about 20% solids, notify the client to obtain instruction on how to proceed (i. e., approval to use Method 9071B).

9.0 Quality Control

Refer to TestAmerica-Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC: The following quality control samples are prepared with **each batch of no more than 20 samples.**

Quality Controls	Control Limit	Corrective Action
Method Blank (MB)	< RL	Re-prep batch, rerun
Laboratory Control Sample[1] (LCS), ongoing PAR	HEM 78-114% recovery SGT-HEM 64-132% recovery	Rerun batch
Matrix Spike (MS Duplicate for MN)	HEM 78-114% recovery SGT-HEM 64-132% recovery; See LIMS for MN MS RPD.	Qualify. Obtain less sample volume and re-prep.

1 All AZ, MA, and TX samples require a LCS duplicate in each batch.

- QC samples are prepared in the same manner as the samples.
- **Laboratory blanks:** Extract and concentrate a laboratory reagent water blank with each analytical batch or each day.
- **Calibration verification:** Verify calibration of the balance per Section 10.4 before and after each analytical batch. If calibration is not verified after measurement of the analytical batch, recalibrate the balance and reweigh the batch. Record the two balance checks.
- **Precision and Recovery (PAR) / Laboratory Control Sample (LCS):** To demonstrate that the analysis system is in control, and acceptable accuracy is being maintained with each analytical batch, the laboratory extracts and concentrates a LCS with each analytical batch. Compare the recovery with the limits for ongoing recovery in the above table.
  - If the recovery is in the range specified, the extraction, evaporation, and weighing processes are in control and analysis of blanks and samples may proceed.

- If, however, the recovery is not in the specified range, the analytical process is not in control. In this event, correct the problem, re-extract the analytical batch, and repeat the LCS.
- The laboratory monitors performance using PAR/LCS % recovery and prepares control charts to calculate average and standard deviation periodically. Calculated control limits are compared against the method-defined on-going precision and accuracy.

1	Fill a clean sample bottle with approximately 800 mL of reagent water. Note the volume.
2	Acidify the water to pH 2.0 with concentrated HCl or H_2SO_4. DO NOT over-acidify the water as this could cause the disk packing to break down. Bring the volume to 1 L with reagent water. Cap the bottle and shake well.
3	Using a calibrated 10.0-mL syringe, transfer 10 mL of the HEM standard. Verify that there are no air bubbles in the syringe.
4	Touching the tip of the syringe to the inside of the neck of the bottle, allow the standard to slowly and gently flow down the side of the bottle and to settle on the water layer. A cloudy precipitate will form on the water. *Avoid shooting the standard into the water or introducing it too quickly. Use of automatic pipettes will pose a problem because they shoot the standard into the water and the rate of introduction cannot be controlled. If the standard is not properly floated, it can cause flow problems during the sample-processing step.*
5	DO NOT SHAKE THE BOTTLE. Attach a closed water inlet valve to the bottle with the correct bottle adapter.

- **Quality Control Sample (QCS):** Obtain a QCS from a certified proficiency provider (a **source different** from the source for the hexadecane and Stearic acid used routinely in this method), and that the QCS be used for verification of the concentrations of HEM and SGT-HEM. The QCS should be analyzed approximately quarterly by the laboratory. Use of previous PT concentrates is acceptable so long as the spiked concentration is known.
- **Matrix spikes:** The laboratory must spike a minimum of 1 in 20 samples from a **given sampling site** or, if for compliance monitoring, from a given discharge/waste stream (matrix spike) with an aliquot of the Hexadecane/Stearic acid spiking solution (same as the LCS). Calculate the percent recovery of HEM or SGT-HEM in each aliquot and compare with the limits in the table in Section 9.1.
  - If the results of the spike fail the acceptance criteria, and the recovery of the LCS for the analytical batch is within the acceptance criteria, an interference is present and the failed recovery will be flagged on the report. In this case, the result may not be reported or used for regulatory compliance purposes and the laboratory must assess the potential cause for the interference. The laboratory will notify the client of the potential interference, and proceed as requested by the client. If the interference is attributable to sampling, the site or discharge/waste stream should be re-sampled. If the interference is attributable to a matrix problem and if sufficient sample is provided, the laboratory must modify the method, i.e., reduce the sample volume and repeat the analysis of the sample and the MS. Most matrix interference problems are attributable to the formation of emulsions in the extraction. The extraction section provides suggestions for overcoming emulsion problems.
  - If the results of both the spike and the LCS fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample batch reanalyzed. **All samples must be associated with a valid MS and LCS.**
  - As part of the QC program for the laboratory, the method accuracy for samples is assessed and records maintained. After the analysis of five or more spiked samples in

which the recovery passes the QC criteria, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if P_a = 90% and s_p = 10% for five or more analyses of HEM or SGT-HEM, the accuracy interval is expressed as 70–110%. Although this exercise is performed, the method initial control limits are those used for client samples.

- **If a sample from Minnesota is in the batch, a matrix spike duplicate must be performed.**

9.2 Instrument QC: Not applicable.

10.0 Procedure

10.1 Balance Calibration: The analytical balance is calibrated at 2 mg and 1000 mg using class "S" weights. Calibration must be within ± 10% (i.e., ± 0.2 mg) at 2 mg and ± 0.5% (i. e., ±5 mg) at 1000 mg. If values are not within these limits, the balance is adjusted / repaired, or use another balance. This calibration is performed before and after residue weighing or before and after each day; record these balance checks on the benchsheet. See SOP Balance Calibration / NV03-213.

10.2 Sample Preparation

Matrix	Sample Size
Water	Nominally 1 L of sample

- Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229. Sub-sampling is not allowed.

1	Bring the analytical batch of samples (containing less than 20% solids as determined in Section 8.0), including the sample aliquot for the MS, to room temperature
2	Verify that the pH of the sample is less than 2: • Adjust the pH if needed. Record the ID of the acid. If the acid volume is greater than 1% of the sample volume, correct for dilution. DO NOT over acidify the samples, as this will cause the disk material to break down and result in low recoveries. Cap and invert the sample bottle several times to mix. • Insert and withdraw the glass rod, or equivalent, and allow a drop of the sample to fall on or touch the pH paper. Record the pH. Do NOT dip the pH paper into the bottle or touch it to the sample on the lid. • Rinse the glass rod with a small portion of n-Hexane that will be used for extraction (to ensure that no extractable material is lost on the glass rod). Collect the rinsate back into the client container to be used for sample extraction.
3	Measure the volume by comparing the meniscus to a calibrated bottle of the same size and shape. (See Section 17 of SOP 3510 608 608.2 610 625 / NV03-24 for how to calibrate bottles.)
4	Add the appropriate amount of HCl or H_2SO_4 solution to the blank, LCS, and MS to adjust the pH of these solutions to <2. Add the spike to the LCS and the sample for MS. Mix.
5	Attach a closed Water Sample Inlet Valve to the bottle. Use an adapter if necessary.
6	The standard, samples, and blank are now ready for processing.

10.3 System Performance Checks, Startup Procedure

1	Verify that all connections are properly in place.
2	Empty all waste recovery bottles (water and solvent) if necessary.

3	Fill the solvent bottles with appropriate solvents as follows: Pre-wet 1: Hexane connected to Pre-wet Fitting #1 on Extractor Pre-wet 2: Methanol connected to Pre-wet Fitting #2 on Extractor Rinse: Hexane connected to Rinse Fitting #2 on Extractor Secure the caps on the solvent bottles. Loss of pressure in the bottles occurs if the caps are loose.
4	Turn on the main power switch on the back of the Controller and allow the Liquid Level Sensor(s) to stabilize for 3 to 5 minutes.
5	Turn on the gas source and slowly increase the main gas source pressure while checking for liquid and gas leak. Adjust the main gas source pressure in increments, checking for leaks as the pressure is increased to minimum of 60 psi and a maximum of 80 psi.
6	Turn on the vacuum pump and check for vacuum leaks. The main vacuum source gauge should read between -25” Hg and -30” Hg.
7	Verify that there are no crimped lines that may impede the flow of liquids, gas, and vacuum.
8	Free the Elute Check valve(s) using the Check Valve Release Tool (P/N 02-0725). In the center of the platform, below the drain hole, is the Sample Collect Check Valve. Gently insert the needle straight down into the opening and tap the head several times to free the check valve. This will move the Check Valve Ball off of the seat assembly. An internal spring will gently push the ball back into the sealing position.
9	Lift and move the Liquid Sensor / Pre-wet Arm into the Disk Holder Base.
10	If using a VOA vial as a collection vessel, attach a glass adapter to the vessel by screwing it on using the turquoise cap. Do not screw on the adapter by using the glass part; this may not produce a good seal. Place the collection vessel in position on the Taper of the unit by lifting and twisting to ensure a vacuum tight seal. An adapter is not required for an Erlenmeyer flask with 19/22 taper.
11	Lower the Water Sample Bottle Arm.
12	Attach an empty sample bottle to the Water Sample Inlet Valve and place the valve into position on the Water Sample Bottle Arm.
13	A Purge sequence is run to remove any air from the solvent lines and to wash the parts of the extractor. This is also a good way to verify that the system is installed correctly and operating properly. The Purge sequence performs much like an actual extraction method by introducing the selected pre-wet and rinse solvents. Press the STATUS key to display the status for all three stations.
14	Select Station #1 by pressing the A-key. Press the DRAIN function key (E-key). Then press the PURGE key (D-key). Press the A-key for YES to begin the purge on Station #1. Follow the same procedure for Stations #2 & 3 if using the 3000XL extractor system. Run the purge sequence three times to ensure all air has been removed from the lines when first installed or when refilling the solvent bottles.
15	Use the following conditions: Methanol Pre-wet: 5 sec Dispense 1 sec Saturate 10 Sec Saturate 0 sec Drain Air Dry 10 sec 3 sec Dispense

10.4 Extraction Procedure

1	Attach the Water Sample Inlet Valve(s) to the sample bottle(s). Use an adapter if required.

2	Place the screen in the Disk Holder Base. Place the SPE disk on the screen. Use a 90-mm pre-filter and disk if processing dirty samples. SPE filters must be of the same manufacturer, diameter, and lot number for all samples in the batch.
3	Insert the Riser into the Disk Holder Base over the disk. The Riser holds the disk in place. Screw on the aluminum Locking Ring, load the Disk Holder assembly onto the Extractor platform and place the Liquid Sensor / Pre-wet Arm in the Disk Holder Assembly. Load the Disk Holder Assembly on each station being used.
4	Place a collection vessel with adapter in position by lifting and twisting to ensure a vacuum tight seal. Use 40-mL VOA vials if using 47-mm disks and 125-mL flasks if using 90-mm disks for dirty samples.
5	Lower the Sample Holder Arm on the extractor unit for each station used.
6	Load the sample bottles onto the unit. Minimize the agitation of the standard (refer to Section 10.1 Sample Preparation). With the Water Sample Inlet Valve aluminum shaft facing you, place your finger over the solvent rod on the right-hand side. This will prevent the sample from leaking out. Gently invert the bottle and place it onto the Holder Arm of the unit. Help guide the Water Sample Inlet Valve shaft onto the actuator key. Firmly press the valve in place.
7	Select the appropriate method for the extraction process according to the disk size and type. EPA Method 1664A Method 2 - Programmed into the SPE-DEX® 3000XL Controller (90mm Pacific Premium SPE disk)

Method 2	Time		Time
Pre-wet Hexane		Pre-wet Methanol	
Dispense	6 seconds	Dispense	6 seconds
Saturate	1 second	Saturate	1 second
Soak	30 seconds	Soak	30 seconds
Drain	1 minute	Drain	3 seconds
	Air dry	3.00 minutes	
Rinse	Dispense	Soak	Elute
1. Hexane	4 seconds	45 seconds	0 seconds
2. Hexane	4 seconds	45 seconds	45 seconds
3. Hexane	4 seconds	45 seconds	0 seconds
4. Hexane	4 seconds	45 seconds	45 seconds

	From STATUS mode, select the station with the sample loaded for processing by pressing the appropriate key. Press A-key to increase the method number or the B-key to decrease the method number to the one desired.
8	Return to the STATUS mode and proceed as in step 7 of this section to load the method to each station being used.
9	Return to the STATUS screen and confirm that the stations are set to the desired method.
10	Press the E-key to run all stations. If running only one station, select the station by pressing the appropriate key and then press the A-key to start the extraction. Confirm the start of the extraction by pressing the A-key again.

10.5 Gravimetric Determination

1	Turn on the Speed-Vap™ using the switch located on the back of the unit. Set the temperature to 40℃. Record in the logbook or in L IMS.

2	Pre-weigh disposable, clean, dessicated, aluminum pans using a calibrated analytical balance and record the initial weighs.
3	After the extraction has been completed, remove the collection vessel(s) from the unit. Remove the adapted, if applicable.
4	Transfer the Hexane extract by opening the separatory funnel's Teflon™ stopcock. Once the Hexane has been transferred, RINSE THE SIDES OF THE COLLECTION VESSEL THREE TIMES using small volumes of clean Hexane. Transfer each rinse to the pre-weighed pan. Repeat for each sample extracted. Then carefully pour the Hexane extract into the weighed aluminum pan. Use tweezers or gloves when handling the aluminum pan to avoid adding moisture or oil from the fingers.
5	Place the pans containing the Hexane extracts in the Speed-Vap™ until all visible liquid is evaporated. Place in the desiccator for at least 30 minutes.
6	Weight the pan with the residue once evaporation is complete. Record this as "Weight Check" on the benchsheet.
7	Place the pan back in the desiccator for about 30 minutes.
8	Weigh the pan with residue again. Record this as "Final Weight" on the benchsheet. If there is a difference greater than 4% (0.0005 g) between the "Weight Check" and the "Final Weight," place the pan back in desiccator for about another 30 minutes. Continue until a constant weight has been achieved. Record each weighing.
9	Proceed to calculations.

10.6 SGT-HEM Determination: Use the HEM residue for the SGT-HEM determination.

1	To ensure that the capacity of the silica gel is not exceeded, the amount of HEM must be less than 100 mg or, if above 100 mg, must be known. It is presumed that 3 g will normally adsorb 100 mg of all absorbable materials. Use a proportionate amount of silica for HEM above 100 mg up to a maximum of 30 g for 1000 mg HEM.
2	Add a small aliquot of n-Hexane to the pan to re-dissolve the HEM. Warm the solution if necessary.
3	Transfer the extract to a clean collection vessel (VOA vial or 125-mL flask, depending on volume of Hexane used) containing 3.0 ± 0.3 g of anhydrous silica gel for every 100 mg of HEM. Record.
4	Repeat steps 10.6.2 and 10.6.3 several times to ensure that all residue has been re-dissolved. Add each Hexane rinse to the collection vessel containing the silica gel.
5	Gently shake the collection vessel for about 5 minutes. Let the collection vessel sit for a few minutes and allow the silica gel to settle.
6	Transfer the Hexane by preparing a filter cone with Whatman 41 filter paper, or equivalent, and 3 to 10 g sodium sulfate. Pour the silica gel-treated Hexane into the filter cone to drain into a clean, weighed, aluminum pan. If silica gel gets into the pan, results will be overstated.
7	Rinse the collection vessel at least three times with aliquots of Hexane, transferring with each rinse to the evaporation pans.
8	Evaporate the Hexane and determine the weight of SGT-HEM by subtracting the tare weight from the total weight. Refer to Section 10.5 for how to accomplish the constant weight check. Refer to Section11.3 for calculation of the result.
9	Place the pans containing the Hexane extracts in the Speed-Vap™ until all visible liquid is evaporated. Place in the desiccator for at least 30 minutes.
10	Weigh the pan with the residue once evaporation is complete. Record this as "Weight Check" on the benchsheet.
11	Place the pan back in the desiccator for about 30 minutes.
12	Weigh the pan with residue again. Record this as "Final Weight" on the benchsheet. If there

	is a difference greater than 4% (0.0005 g) between the "Weight Check" and the "Final Weight," place the pan back in desiccator for about another 30 minutes. Continue until a constant weight has been achieved. Record each weighing.
13	Proceed to calculations.

10.7 Shut-down Procedure for Extractors

1	Remove the Disk Holder Assembly(s) from the extractor unit and discard the used disks.
2	Pour water in the platform cavity of the station(s). Select the station from the STATUS mode. Press the DRAIN (E-key) function and then the ELUTE (C-key). Repeat for each station. This procedure will remove any residual solvent from the check valve.
3	Turn off the vacuum pump and vent by removing the line attached to the waste bottle.
4	Turn off the gas supply.
5	Turn off the controller power.
6	Flush the Water Sample Inlet Valves by manually turning them open and closed while flushing under warm running water. Non-surfactant soap may be used to clean the valves. Make sure to thoroughly rinse them out. Do not scrub using a cleaning brush.
7	Leave the Water Sample Inlet Valves in a half-open position to allow the water to drain.

10.8 Example Analysis Queue / Sequence*

1	Method Blank
2	PAR/LCS
3	Samples 1
4	Matrix Spike
5	Matrix Spike Duplicate (optional)**
	Samples 2-20

*May be up to 20 samples for a 12-hour shift.
**MN requires a Matrix Spike Duplicate.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value} - \text{dup. sample value)} \times 100}{[(\text{Orig. sample value} + \text{dup. sample value})/2]}$$

11.3 Concentration Calculations

1	Weigh the pan with the standard residue once evaporation is complete and calculate the recovery as follows: $[(W_2 - W_1) / 40\ mg] \times 100\% = \%\ Rec.$ *W_1 = Weight of empty aluminum pan (mg)* *W_2 = Weight of aluminum pan with sample (mg)*
2	Calculate the concentration of HEM content from the samples as follows: $(W_2 - W_1) / V_s = mg/L$

	V_s = Volume of original sample (L)
3	Calculate the concentration of SGT-HEM (non-polar material) content as follows: $(W_2 - W_1) / V_s = mg/L$ *V_s = Volume of original sample (L)*
4	Calculate the concentration of the polar material as follows: $C_P = C_T - C_{NP}$ *C_P = Concentration of the polar material* *C_T = Total oil and grease (HEM-oil and grease)* *C_{NP} = Concentration of non-polar material (SGT-HEM)*

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

- **A MDL less than or equal to the required MDL of 1.4 mg/L or less than 1/3 the regulatory compliance limit must be achieved prior to the use of this method.**

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

- **Initial precision and recovery (IPR):** To accomplish the ability to generate acceptable precision and accuracy, the laboratory must determine the concentration of HEM and/or SGT-HEM in four samples of the PAR/LCS standard and compute the average percent recovery (X) and the standard deviation of the percent recovery (s) for HEM and for SGT-HEM (if determined). When determining SGT-HEM, the true concentration (T) must be divided by 2 to reflect the concentration of hexadecane that remains after removal of Stearic acid. Calculate the standard deviation of the percent recovery and compare with the corresponding limits. If the acceptance criteria are met, system performance is acceptable and analysis of samples may begin. If not, correct the problem and repeat the test.

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n-1}}$$

N= Number of Samples

X=% Recovery in each sample

- The same criteria are used on an ongoing basis as for this initial evaluation.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an acceptable manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Unused samples are neutralized and discharged to the sanitary sewer.
- Solid residues are disposed to a trash receptacle.
- Solvent waste is placed in mixed flammable waste drums for disposal off-site.

15.0 References / Cross-References

15.1 Method 1664A, U.S. EPA Office of Water, EPA-821-R-98-002, February 1999, and **1664B**, February 2010, promulgated May 18, 2012.
15.2 SW-846 Method 9070A, Update IIIB, November 2004
15.3 Horizon Technology User's Guide, SPE-DEX® 1000XL Series Extractor
15.4 Horizon Technology User's Guide, SPE-DEX® 3000XL Series Extractor
15.5 Horizon Technology User's Guide, SPEED-VAP™ II 9000
15.6 Horizon Technology User's Guide, Solvent Trap™.
15.7 Horizon Technology Standard Operating Procedure for the Gravimetric Determination of Oil and Grease in Water Using Automated Solid Phase Extraction, SPE-DEX® 1000/3000XL Extractors, 12/9/02.
15.8 TestAmerica Nashville's Quality Assurance Manual.
15.9 Corporate Environmental Health and Safety Manual (CW-E-M-001)
15.10 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Method Start-up / NV08-203, Sample Homogenization, Sub-sampling, and Compositing / NV08-229, 3510 608 608.2 610 625 / NV03-24.
15.11 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	For Minnesota samples, add a Matrix Spike Duplicate to each batch.

17.0 Attachment

None.

18.0 Revision History

- Revision 6, dated 20 June 2008
  - Integration for TestAmerica and STL operations.
  - Make Horizon automated solid phase extraction system the primary extraction process.
- Revision 7, dated 25 September 2009
  - Replace 37% HCl with concentrated HCl.
  - Add option of using 90 mm fast flow pre-filters.
  - Add Minnesota requirement for MSD.
- Revision 8, dated 30 October 2010
  - Added Sulfuric Acid to section 5.2 and section 7; Added additional supplies to section 6.2
  - Added "Note" to section 10.1 regarding what to do when solids are present.
  - Clarified language on SPE disk and pre-filter use in section 10.3.
  - Addition of QAF-45 and Section 14.2.
- Revision 9, dated 28 September 2012
  - Organizational changes.
  - Addition of Amendments 8a (2/18/11) and 8b (10/31/11)
  - Addition of EPA 1664B.
  - Requirement for a second-source standard if using a certified standard.
  - OK and WY now allow 20-sample batches.
  - pH lower limit for preservation depending on which acid is used.
  - Use a glass rod instead of a pipette to verify sample pH with pH paper (Sample Preparation section).
  - Clarify the use of desiccators in the procedure.
  - Modify Example Analysis Queue/Sequence.
  - Clarification that unused samples are neutralized before discharge to the sanitary sewer.
- Revision 10, dated 30 April 2013
  - Add amendment 9a.
  - Correct volume of spike added to 4.0 mL.
  - Add solvent waste disposal.
  - Added AZ and TX to the states that require LCSD.
- Revision 11, dated 31 May 2015
  - Organizational changes.
  - Addition of change form 10a (modification of gravimetric procedure and the SGT-HEM determination for clarity.)
  - Add reference to SOP 3510 608 608.2 610 625 / NV03-24 for how to calibrate bottles for volume measurement.

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Title: Organophosphorus Pesticides by Gas Chromatography [Methods 8141A, 8141B and 614]

Approvals (Signature/Date):

Tegan Moore — 12/7/17 — Date
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Doug Gomer — 12/7/17 — Date
Health & Safety Manager / Coordinator

Roxanne Sullivan — 12/7/17 — Date
Quality Assurance Manager

William S. Cicero — 12/7/17 — Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This method is applicable to the determination of the concentration of certain organophosphorus pesticides in extracts of waters, waste waters, oils, soils, and sludges. It is based on SW-846 Method 8141A, 8141B and EPA Method 614.

1.2 Table 1 shows reporting limits for compounds routinely analyzed by this method. The compounds that can be analyzed by this SOP include, but are not limited to, those shown in Table 1.

2.0 Summary of Method

2.1 Instructions for the extraction of aqueous samples using a separatory funnel by SW-846 Method 3510C are provided in SOP DV-OP-0006. Instructions for preparing solid samples using SW-846 Method 3540C Soxhlet extraction are provided in SOP DV-OP-0010. Instructions for concentrating organic extracts are provided in SOP DV-OP-0007.

2.1.1 A one-liter portion of an aqueous sample is extracted using methylene chloride and solvent exchanged to hexane with a final volume of 2 mL.

2.1.2 A 30-gram portion of a soil sample is extracted using a 1:1 mixture of methylene chloride and acetone. The extract is solvent exchanged to hexane with a final volume of 2 mL.

2.2 The sample extract is introduced into a dual column gas chromatograph (GC) equipped with nitrogen-phosphorous detectors (NPD). The concentrations of target analytes are determined on the primary column by comparing chromatographic peaks at predetermined retention times to the same chromatographic peaks for calibration standards. The internal standard method of calibration is used, and target analyte confirmation is made using a second dissimilar capillary column.

3.0 Definitions

Refer to the Denver Quality Assurance Manual and SOP DV-QA-003P for definitions of QA/QC terms used in this document.

4.0 Interferences

4.1 Contamination from carryover can occur when a low concentration sample is analyzed after a high concentration. Typically significant carryover is not observed until sample concentrations greatly exceed the upper calibration range. A method blank is prepared with each batch in order to monitor the interferences that may be present in the solvents, glassware, and reagents. Interferences are also minimized by second column confirmation.

4.2 Interferences in the GC analysis arise from many compounds that are amenable to gas chromatography that give a measurable response on the NPD detector. The NPD detector is also selective enough that much interference in the background of the sample extract

will go undetected but will result in interferences with the chromatography. Interferences from individual sample matrices vary considerably from source to source. The presence of interferences may result in an elevated reporting limit for individual samples. Cleanup procedures are not routinely employed for this method and sample dilution may be used to reduce interferences where needed. Florisil clean-up procedures are not recommended due to poor recoveries.

4.3 Many organophosphorous pesticides will degrade on active sites in the chromatographic system. Therefore, injection port maintenance is critical. Regular replacement of the glass liner, glass wool, septum, gold seal, and clipping of the guard column should be performed.

4.4 Retention times of some analytes may increase with increasing concentrations in the injector. Retention time shifts must be monitored and evaluated, especially for highly contaminated samples.

4.5 Triazine herbicides, such as atrazine and simazine, and other nitrogen-containing compounds may interfere when using a nitrogen-phosphorus detector.

4.6 Tetraethyl pyrophosphate (TEPP) is an unstable diphosphate that is readily hydrolyzed in water and decomposes at 170°C. Methyl parathion is also readily hydrolyzed.

4.7 The water solubility of dichlorvos (DDVP) is 10 g/L at 20°C, and recovery is poor from aqueous samples.

4.8 Naled can be converted to dichlorvos (DDVP) by debromination; and this reaction may occur during sample work-up or on-column.

4.9 Demeton is a mixture of two isomers, demeton-S and demeton-O. Two peaks are observed in all chromatograms corresponding to these two compounds. Depending on project requirements, results may be reported in terms of individual components and/or total demeton.

4.10 Merphos is a single component pesticide that is readily oxidized to merphos oxone. Chromatographic analysis of merphos almost always results in two peaks. As the relative amounts of oxidation of the sample and the calibration standard are probably different, quantitation of this compound is performed by summation of the area of peaks.

4.11 Mevinphos is a mixture of cis and trans isomers. Both isomers are combined for quantitation of mevinphos. Depending on instrument conditions these may or not may split into two distinct peaks.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual, and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the

responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.3.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material [(1)]	Hazards	Exposure Limit [(2)]	Signs and Symptoms of Exposure
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.

Material [1]	Hazards	Exposure Limit [2]	Signs and Symptoms of Exposure
Organo-phosphorus Pesticide Standards	Toxic		In almost all cases, the pesticide standards are purchased as stock standards made up in one of the solvents listed in this table and the hazards associated with the standard solutions are primarily those of the solvent. Exposure to organophosphorus pesticides produces effects on the nervous system. Acute exposure compromises neuromuscular functions, decreases motor activity and body temperature, alters cardiovascular function, and can also have a delayed neuromuscular effect that is irreversible and leads to paralysis.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 An analytical system consisting of a dual column gas chromatograph and nitrogen-phosphorus detectors (NPD). The instruments used for this analysis are HP 6890 instrument D and Agilent 6890N instrument D2 (or equivalent). A data system capable of measuring peak area and/or height.

6.1.1 Suggested columns: Rtx®-1MS (30 m X 0.32 mm X 0.25 μm), or Rtx®-OPP2 (30 m X 0.32 mm X 0.5 μm).

6.1.2 Autosampler Vials: Crimp cap with PTFE-faced septa, 1.8 mL, Varian No. 96-000099-00 or equivalent.

6.1.3 Micro Syringes: Various sizes, for standards preparation, sample injection, and extract dilution.

6.1.4 Standard Solution Storage Containers: 15 mL bottles with PTFE-lined screw caps.

6.1.5 GC Supplies: Y-splitter (universal presstight), septa, guard columns (10 m IP deactivated .32mm diameter), ferrules, Restek 4mm Gooseneck splitless 20799, Siltek glass wool.

6.1.6 Various class A volumetric flasks for standard preparation.

6.1.7 Black ceramic NPD Bead (Agilent part number 5183-2007) and NPD Ceramic insulator/metal seal kit (Agilent part number 5182-9722)

6.2 Computer Software and Hardware

Please refer to the master list of documents, software, and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data

processing.

7.0 Reagents and Standards

7.1 Stock Standards

7.1.1 Standards are purchased commercially and are received as certified solutions in flame-sealed ampoules.

NOTE: The availability of the specific commercial standard solutions upon which the following sections are based may change at any time. As a result, it may be necessary to alter the dilution scheme presented herein to accommodate changes in stock standard concentrations. All such changes are documented in the standards preparation records.

7.1.2 Standards are verified before use as described in SOP DV-QA-0015.

7.1.3 Stock standards are stored refrigerated at $\leq$ 6 ^{o}C, or as recommended by the manufacturer. All stock standards must be protected from light.

7.1.4 Stock standard solutions should be brought to room temperature before using.

7.1.5 Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced annually from the date of receipt or earlier if the vendor indicates an earlier date.

7.1.6 Primary standards

7.1.6.1 Restek (32277), 8140/8141 OP Pesticides Calibration Mix A at 200 μg/mL **(8141CalA)**

7.1.6.2 Supelco Custom (21751372) contains azinphos ethyl, benthiocarb, carbophenothion, phosmet, and anilazine at 200 μg/mL **(8141SupelCST)**

7.1.6.3 Restek (567818) 8141 Standard #2 at 1000ug/mL **(8141ResCal2)**

7.1.6.4 Restek (568752) 8141 Standard #3 at 1000ug/mL **(8141ResCal3)**

7.1.6.5 ChemService (MET-11408A), Carbophenothion methyl (primary source) – 100 μg/mL **(8141MCarb)**

7.1.6.6 AccuStandard (P-192S-10x), Triphenyl Phosphate (surrogate) – 1000 μg/mL **(8141Su_TPP)**

7.1.6.7 AccuStandard (P-329S), Chlormephos (surrogate) – 1000 μg/mL **(8141Su_CHL)**

7.1.7 Second source standards (8141_SS_Acc)

7.1.7.1 AccuStandard (M-8140M-5x), 8140 Organo Phosphorous Pesticides Calibration Mix A (second source, LCS/MS)– 200 μg/mL **(M-8140M-5x)**

7.1.7.2 AccuStandard (S-18291-R2), 8141 Custom Spike Standard – 200 μg/mL **(8141CSTMix)**

7.1.7.3 AccuStandard (P-652S), Methyl Trithion – 100 μg/mL **(M-trithionStk)**

7.1.7.4 AccuStandard P-180S Benthiocarb at 100ug/mL **(8141Thiob_Acc)**

7.1.7.5 AccuStandard (P-329S), Chlormephos (surrogate) – 1000 μg/mL

7.1.7.6 AccuStandard (P-192S-10x), Triphenyl Phosphate (surrogate) – 1000 μg/mL

7.1.8 Second source standards (8141_SS_RES)

7.1.8.1 Restek (32277.sec) 8140/8141 OP Pesticide Calibration Mix A second source at 200 μg/mL.**(8141ResSSCalA)**

7.1.8.2 Restek (567818.sec) 8141 Standard #2 at 1000 μg/mL. **(8141ResSSCal2)**

7.1.8.3 Ultra Scientific (CUS-15236) custom standard contains azinphos ethyl, benthiocarb, carbophenothion, dimethoate, EPN, ethyl parathion, malathion, phosmet, anilazine, and sulfotepp at 200 μg/mL. **(8141 Ult CST)**

7.1.8.4 Restek (568205.sec), 8141 Standard #1 second source at 1000 μg/mL **(8141ResSSCal1)**

7.1.8.5 Restek (32281.sec) Triphenylphosphate Standard at 1000 μg/mL **(8141ResTPP)**

7.1.8.6 AccuStandard (P-652S), Methyl Trithion – 100 μg/mL **(M-trithionStk)**

7.1.9 Internal standards

7.1.9.1 Restek (32280), Tributyl phosphate (internal standard) – 1000 μg/mL **(8141IS_TBP)**

7.1.9.2 ChemService (S-13631J4-1ML), Tri-o-cresyl phosphate (internal standard) – 1000 μg/mL **(8141IS_TOCP)**

7.2 Calibration Standards and CCV

The Level 7 calibration standard is prepared as both an ICAL point and as a secondary standard for further dilution to prepare the other ICAL levels. The dilution scheme is outlined in the table below.

Calibration Level	Conc.	Final Volume	Recipe
ICAL Level 7	5 g/mL	10 mL	0.25 mL Restek 8140/8141 OP Pesticides Cal Mix A
			0.25 mL Restek 8141 Custom Spike Standard
			0.05 Restek 8141 Standard #2
			0.05 Restek 8141 Standard #3
			0.5 mL ChemService Carbophenothion Methyl
			0.05 mL Accustandard Chlormefos (surr.)
			0.05 mL Accustandard Triphenyl Phosphate (surr.)
ICAL Level 6	4 g/mL	0.250 mL	0.200 mL of ICAL Level 7
ICAL Level 5	3 g/mL	0.250 mL	0.150 mL of ICAL Level 7
ICAL Level 4	2 g/mL	0.250 mL	0.100 mL of ICAL Level 7
ICAL Level 3	1 g/mL	0.250 mL	0.050 mL of ICAL Level 7
ICAL Level 2	0.5 g/mL	0.250 mL	0.025 mL of ICAL Level 7
ICAL Level 1	0.2 g/mL	0.250 mL	0.010 mL of ICAL Level 7
Continuing Calibration (CCV)	2.5 g/mL	10 mL	5.0 mL of ICAL Level 7

7.2.1 Dilutions from stock standards are made in pesticide-grade hexane and acetone (90:10) solvent mixture because some certified stock standards are prepared in methanol.

7.2.2 All standards must be refrigerated at $\leq$ 6 ^{o}C and protected from light.

7.2.3 The secondary standards should be monitored for degradation and prepared fresh every two months. Particular attention should be made to check methyl parathion and merphos. The secondary standards cannot have a later expiration date than the date assigned to the parent stock standards from which they are prepared.

7.3 Second Source Standards, 2 μg/mL

7.3.1 Two separate second source standards are prepared due to the inconsistency of concentrations often found with the stock standard materials. The table below outlines the preparation process for each.

Calibration Level	Conc.	Final Volume	Recipe
8141_SS_Acc	2 g/mL	5 mL	0.050 mL Accustandard 8140 OPP Cal Mix A
			0.050 mL Accustandard 8141 Custom Spike Std.

Calibration Level	Conc.	Final Volume	Recipe
			0.100 mL Accustandard Methyl Trithion
			0.100 mL Accustandard Benthiocarb
			0.010 mL Accustandard Chlormefos (surr.)
			0.010 mL Accustandard Triphenyl Phosphate (surr.)
8141_SS_Res	5 g/mL	5 mL	0.125 mL Restek 8141 OP Pest Cal Mix A (sec. src.)
			0.025 mL Restek 8141 Standard #2
			0.125 mL Ultra Scientific custom standard
			0.250 mL Accustandard Methyl Trithion
			0.025 mL 8141 Standard #1 (second source)
			0.025 mL Triphenylphosphate (second source)

7.3.2 All standards are prepared in Hexane:Acetone (90:10).

7.3.3 All standards must be refrigerated at $\leq$ 6 ^{o}C and protected from light.

7.3.4 The secondary standards should be monitored for degradation and prepared fresh every two months. Particular attention should be made to check methyl parathion and merphos. The secondary standards cannot have a later expiration date than the date assigned to the parent stock standards.

7.4 Non-Routine Standards

Other, non-routine compounds not listed in this section may be requested by a client and may be added to this procedure as long as the appropriate development requirements are met.

7.4.1 In these cases, all stock solutions will be obtained from commercial sources and will be verified with a second-source standard as described in Section 7.1 above.

7.4.2 Non-routine standards will be stored and treated as described in Section 7.1 above.

7.4.3 Subsequent dilutions of specially requested compounds will be determined in a manner consistent with the client's recommendations for number of calibration points, inclusion of reporting limit, and concentration range adequate to represent the linearity of the instrument.

7.4.4 These specially requested, non-routine compounds either may be added to the dilution scheme used for routine compounds or may be prepared as a separate calibration. All standards preparation for non-routine compounds shall be documented using the same method that is used for routine compounds

7.5 RL Standard

The Level 1 calibration standard (see Table 3) is typically used as the RL Standard.

7.6 Laboratory Control Standard (LCS, same as QCS) and Matrix Spike Standards.

The standard spiking solution is prepared from the second source material listed in Section 7.1.7 diluted with acetone. See Table 4 for the concentrations and list of target constituents. The solution is prepared by diluting 1 mL of S-18291-R2, 1 mL of M8140M-5x, 2ml of P-180S, and 2 mL of P652S to a final volume of 50 mL. (See Section 7.1.7 for standard solution identifications.)

7.7 Surrogate Standards

Chlormefos and triphenyl phosphate are the surrogate standards. Refer to Table 4 for details of surrogate standards. The surrogate solution is prepared at 2ug/mL by diluting 0.5 mL of P-329S-10x and 0.1 mL of M-507-1S-10x to a final volume of 250 mL.

7.8 Internal Standard (IS) Solution, 100 μg/mL (8141WkgIS)

An internal standard solution is prepared containing tributyl phosphate and tri-o-cresylphosphate at a final concentration of 100 μg/mL in hexane. The IS solution is prepared by combining 1 mL of each of these solutions listed in 7.1.6 and diluting to 10 mL in Hexane:Acetone (90:10). The IS is added to each calibration standard, calibration verification standard, field sample extract, and QC sample extract that is analyzed. The internal standard is added to the extract just prior to analysis.

7.9 Reagents

7.9.1 Hexane, pesticide grade

7.9.2 Acetone, pesticide grade

7.9.3 Helium gas, ≥ 99.99999% pure

7.9.4 Hydrogen gas, ≥ 99.99999% pure

8.0 <u>Sample Collection, Preservation, Shipment and Storage</u>

8.1 Samples must be collected in pre-cleaned amber glass bottles fitted with a Teflon-lined cap. To achieve routine reporting limits, a full one-liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 The pH of aqueous samples is to be checked upon arrival at the lab and adjusted to a pH of 5 to 8 using sodium hydroxide or sulfuric acid as soon as possible.

8.3 Samples are stored at $\leq$ 6 ^{o}C.

8.4 Extracts must be refrigerated at $\leq$ 6 ^{o}C.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	1 Liter	Cool $\leq$ 6 ^{o}C	7 Days	40 Days from extraction	SW-846 40 CFR Part 136
Soils	Glass	30 grams	Cool $\leq$ 6 ^{o}C	14 Days (8141A) 7 Days (8141B)	40 Days from extraction	SW-846

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviations or exceptions from QSM 5.0 requirements must have prior approval in the project requirements. See Table 6 for summary of these requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst. On-going proficiency must be demonstrated by each analyst on an annual basis.

See Section 13 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. A batch is a set of up to 20 field samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. To the extent possible, samples that require a preparation step should be analyzed together with their associated QC samples. If the samples in a given QC batch require separate analytical runs, the minimum batch QC in each run is an acceptable MB or instrument/calibration blank. To the extent possible, the QC samples should not be analyzed independently of the field samples on a different instrument. See policy DV-QA-003P for further details.

9.4 Method Blank

Each batch of samples must include a method blank. For aqueous sample batches, the method blank consists of reagent water with the addition of surrogate spike compounds. For soil sample batches, the method blank consists of Ottawa sand spiked with the surrogate compounds. The method blank is subject to the entire extraction and analysis process.

Acceptance Criteria: The method blank must not contain any analyte of interest at or above 1/2 the reporting limit or above one-tenth of the concentration found in the associated samples or above one-tenth of the regulatory limit for that analyte.

For DoD QSM 4.2 or QSM 5.0 the acceptance criteria is no analytes detected >1/2 RL (i.e., LOQ) or >1/10 the regulatory limit whichever is greater.

Corrective Action: If the method blank exceeds allowable levels, all associated samples that have detections for targeted compounds must be re-extracted and reanalyzed.

9.5 Quality Control Check Sample (QCS) / Laboratory Control Sample (LCS)

The LCS contains representative analytes of interest, as well as the surrogate compounds, added to reagent water or Ottawa sand, depending on the sample matrix. The LCS is subject to the entire extraction and analysis process.

Acceptance Criteria: The percent recovery of each analyte of interest must fall within the established control limits. Control limits are set at ± 3 standard deviations around the historical mean, unless otherwise dictated by project requirements.

When there are more than 11 target analytes in the LCS, then NELAC allows a specified number of results to fall beyond the LCS control limit (3 standard deviations), but within the marginal

exceedance (ME) limits, which are set at ± 4 standard deviations around the mean of historical data. The number of marginal exceedances is based on the number of analytes in the LCS, as shown in the following table:

Allowed Marginal Exceedances

# of Analytes in LCS	# of Allowed MEs
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

If more analytes exceed the LCS control limits than is allowed, or if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be random. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem. The source of the error must be identified and corrective action taken.

Note: Some programs (e.g., South Carolina) do not allow MEs. Please see the QAS's in the public folders for the current requirements. DoD QSM work does not allow MEs for compounds identified as "risk drivers" without prior approval.

Corrective Action: If recoveries are not within the acceptance limits as defined above, the system is out of control and corrective action must occur. All associated samples must be re-extracted and reanalyzed. If recoveries are high-biased and the associated samples are ND, then the data may be reported with narration in an NCM.

9.6 Matrix Spike and Matrix Spiked Duplicate (MS/MSD)

9.6.1 At a minimum, the laboratory must prepare one MS/MSD pair in every batch of 20 samples. If there is insufficient volume to prepare a MS/MSD pair, a LCS/LCSD must be prepared to provide precision data for the batch. For DoD QSM 4.2 or QSM 5.0, the MS/MSD must be from the project site and if insufficient sample to analyze the MS/MSD pair is available, this is documented in an NCM but no LCSD is performed. This is addressed in the case narrative.

9.6.2 For method 614, the laboratory must spike one sample in every batch and spike 10% of all samples. If the batch has more than 10 samples, then two matrix spikes must be performed. The two matrix spikes are to be performed on two different samples.

9.6.3 An MS is prepared by adding representative analytes of interest and surrogate compounds to an aliquot of a designated field sample. The MSD is prepared by adding the same analytes and surrogates to a second aliquot of the designated sample.

Acceptance Criteria: The percent recovery and Relative Percent Difference (RPD) of each analyte of interest must fall within the established control limits stored in the LIMS.

Corrective Actions: The information obtained from MS data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If the MS and/or MSD recovery falls outside of the established control limits, the bracketing CCV and batch LCS recoveries must be within control limits in order to accept results for the associated samples. The following corrective actions are required for MS/MSD recovery failures to rule out lab error:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly (e.g., very low or very high recoveries);
- Consider objective evidence of matrix interference (e.g., heterogeneous sample, interfering peaks seen on chromatograms, or interference demonstrated by prior analyses);
- Flag the data for any results outside of acceptance limits.
- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample inhomogeneity; and flag the data.
- If both the parent sample and associated matrix spike results are over range the parent and the spikes shall be diluted by the same amount and the results from the reanalysis reported for both. If the analyte concentration in the parent sample is greater than four times the concentration of spike added, then spike recovery results are not compared to control limits, and the recovery is either reported as “NC” (not calculated) or with a qualifier flag to indicate that the spike was less than four times the analyte concentration in the sample. If the dilution will cause the spike to be less than two times the reporting limit, the MS/MSD do not need to be diluted and the recovery reported as “NC” (not calculated).

- For MS/MSD that serve as batch QC, if the parent sample result is within the calibration range and the MS/MSD results are above the calibration range, the results are reported with the MS/MSD result being flagged as an over-range measurement (e.g., the E-flag qualifier).
- If the MS/MSD are client requested, the parent sample result is within calibration range and the MS/MSD results are above the calibration range, the sample and spike should be diluted, keeping in mind that we need to assess whether or not the dilution will best serve the client's needs. Consult with the PM as needed. Both the parent sample and MS/MSD samples must have the same dilution factor. Some EDDs do not accept data that are at different dilution factors.
- If the native analyte concentration in the MS/MSD sample exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated) and the appropriate qualifier flags are added.

NOTE: See Denver Policy Memorandum P16-001 and Corporate Policy Memorandum CA-Q-QM-013 for more detail.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

9.7 Surrogates

The surrogate compounds chlormefos and triphenyl phosphate are added to all field and QC samples. Refer to Section 7.7 for preparation of the surrogate spike solution. Surrogate recoveries must be assessed to ensure that analytical recoveries are within established limits.

Acceptance Criteria: The percent recovery of each analyte of interest must fall within the established control limits. Control limits are set at ± 3 standard deviations around the historical mean, unless otherwise dictated by project requirements.

Corrective Action: Check all calculations for error.

Ensure that instrument performance is acceptable.

Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem.

Re-extract and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. Re-extraction may not be necessary if there is obvious and well documented chromatographic interference.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to re-extract / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.8 Internal Standard

Internal standard compounds are added to all field and QC sample extracts. Internal standard compound recoveries must be assessed to ensure that analytical recoveries are within established limits.

Acceptance Criteria: The measured area of the internal standard must be no more than 200% and no less than 50% different than the midpoint of the calibration for an ICAL batch or the opening CCV for analytical batches that do not contain an initial calibraiton.

Corrective Action: Check all calculations for error.

Ensure that instrument performance is acceptable.

Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem. Where interferences are indicated reanalysis at a dilution may be required to resolve this issue.

10.0 Calibration and Standardization

10.1 TestAmerica Denver gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

10.1.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-P-003, *Calibration Curves and the Selection of Calibration Points* and under the public folder, Arizona Calibration Training.

10.1.2 Use the ChemStation chromatography data system to set up GC conditions for calibration. See Table 2 for typical operating conditions.

10.1.3 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.1.4 Unprocessed calibration data are transferred to the Chrom database for processing. After processing the calibration data, print the calibration report and

review it using the calibration review checklist (GC and HPLC Data Review Checklist - ICAL). Submit the calibration report to a qualified peer or the group leader for final review.

10.2 The laboratory routinely calibrates using seven concentration levels. A minimum of five calibration levels are required (six if a second order regression fit is used). The lowest point on the calibration curve is below the RL, and is close to the MDL concentrations. These concentrations define the working range for analysis.

NOTE: Generally, it is **NOT** acceptable to remove points from a calibration for the purposes of meeting calibration criteria. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems found must be fixed and documented in the run log or maintenance log. Then the calibration standards must be reanalyzed.

10.3 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious mis-injection or broken vial), then one point might be rejected but only if all of the following conditions are met:

10.3.1 The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and

10.3.2 The lowest remaining calibration point is still at or below the project reporting limit; and

10.3.3 The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and

10.3.4 The calibration must still have a minimum number of calibration levels required by the method, i.e., five levels for calibrations modeled with average calibration factors or linear regressions, or six levels for second order curve fits.

NOTE: Second order curves are not allowed for South Carolina work.

10.4 All initial calibration points must be analyzed **without any changes to instrument conditions and all points must be analyzed within 24 hours.**

10.5 Internal Standard Calibration

10.5.1 Internal standard calibration involves the comparison of an instrument response (e.g., peak area or peak height) from the target compound in the sample to the response of the internal standard compound, which is added to the sample or sample extract prior to injection. For this method, tributyl phosphate and tri-o-cresylphosphate are added to the sample and QC extracts just prior to analysis at a concentration level of 2.0 µg/mL. This same concentration of internal standard is added to each initial calibration standard.

10.5.2 Two internal standards (tri-o-cresyl phosphate and tributyl phosphate) are used for calibration. The area of the chromatographic peak for each analyte of interest is used as the instrument response. If matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute, but it would then have to be used consistently for all files and QC samples analyzed in the analytical batch.

10.6 Establishing the Calibration Function

Calibrations are modeled either as average response factors or as calibration curves, using a systematic approach to selecting the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until the calibration acceptance criteria are met.

10.6.1 Linear Calibration Using Average Response Factor

A calibration curve relates the instrument response, usually in terms of area of the chromatographic peak, to the concentration of the target analyte in each of the calibration standards. If linearity through the origin can be demonstrated, then the average response factor can be used to calculate the target analyte concentration in an unknown sample. The response factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small, the use of the straight line through the origin model is generally appropriate. The response factor is calculated as the ratio of the area response of the target analyte to the area response of the internal standard, as follows:

$$RF_i = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$ *Equation* 1

Where:

RF_i = Response factor for the i^{th} calibration level.
A_s = Area of chromatographic peak for the analyte of interest in the calibration standard.
A_{is} = Area of chromatographic peak for the internal standard.
C_{is} = Concentration of the internal standard, μg/mL.
C_s = Concentration of the analyte of interest in the calibration standard, μg/mL.

10.6.2 The average response factor and its associated relative standard deviation (RSD) are calculated as follows:

$$\overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$ *Equation 2*

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}} \qquad \textit{Equation 3}$$

$$\%RSD = \frac{SD}{\overline{RF}} \times 100 \qquad \textit{Equation 4}$$

Where:

$\overline{RF}$	=	Average response factor.
RF_i	=	Response *factor* for the i[th] calibration level.
n	=	Number of calibration levels.
SD	=	Standard deviation.
%RSD	=	Relative standard deviation, expressed as a percent.

10.6.3 Evaluation of the Average Response Calibration

Plot the calibration curve using the average RF as the slope of a line that passes through the origin. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

Acceptance Criteria: For Method 614, the %RSD must be ≤ 10%.

For Method 8141A/8141B, the %RSD must be ≤ 20%.

See Table 6 for DoD QSM 5.0 requirements.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

10.6.4 Linear Calibration Using Least-Squares Regression

Calibration using least-squares linear regression produces a straight line that does not pass through the origin. The calibration relationship is constructed by performing a linear regression of the instrument response (peak area or peak height) versus the concentration of the standards. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The weighting used is the reciprocal of the concentration or the reciprocal of the square of the concentration. The regression produces the slope and intercept term for a linear equation in the following form:

$$y = ax + b \qquad \textit{Equation 5}$$

Where:

y	=	Instrument response (peak area or height).
x	=	Concentration of the target analyte in the calibration standard.
a	=	Slope of the line.
b	=	The y-intercept of the line.

For an internal standard calibration, the above equation takes the following form:

$$\frac{A_s C_{is}}{A_{is}} = aC_s + b \qquad \textit{Equation 6}$$

To calculate the concentration in an unknown sample extract, the regression equations 5 and 6 are solved for concentration, resulting in the following equations, where x and C_s are now the concentration of the target analyte in the unknown sample extract:

$$x = \frac{y - b}{a} \qquad \textit{Equation 7}$$

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a} \qquad \textit{Equation 8}$$

10.6.5 Evaluation of the Linear Least-Squares Regression Calibration Function

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum "Clarification Regarding Use of SW-846 Methods", Attachment 2, Page 9, includes the statement "The Agency further recommends the use of this for weighted regression over the use of an unweighted regression."

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than the reporting limit (RL), and preferably less than the MDL.

Also examine the residuals, but with particular attention to the residuals at the low end of the curve. If the intercept or the residuals are large, a second-order regression should be considered.

The linear regression must have a correlation coefficient (r) ≥ 0.990. Some programs (e.g., DoD QSM 4.2) require a correlation coefficient (r) ≥ 0.995. DoD QSM 5.0 requires r^2>0.99.

Corrective Action: If the correlation coefficient falls below the acceptance limit, linear regression cannot be used and a second-order regression should be attempted.

10.6.6 Non-Linear Calibration

When the instrument response does not follow a linear model over a sufficiently wide working range, or when the previously described calibration approaches fail acceptance criteria, a non-linear, second-order calibration model may be employed. The second-order calibration uses the following equation:

$$y = ax^2 + bx + c \qquad \textit{Equation 9}$$

Where a, b, and c are coefficients determined using a statistical regression technique; y is the instrument response; and x is the concentration of the target analyte in the calibration standard.

10.6.7 Evaluation of Second-Order Regression Calibration

A minimum of six points must be used for a second-order regression fit.

Acceptance Criteria: The coefficient of determination (COD) must be (r^2) ≥ 0.990.

Second-order regressions should be the last option, and note that some programs (e.g., South Carolina) do not allow the use of second-order regressions. A second order model must not be used to avoid maintenance. Before selecting a second-order regression calibration model, it is important to ensure the following:

- The absolute value of the intercept is approximately < one-half of the lowest concentration standard reported.
- The response increases significantly with increasing standard concentration (i.e., the instrument response does not plateau at high concentrations).
- The distribution of concentrations is adequate to characterize the curvature.

Corrective Action: If the coefficient of determination falls below the acceptance limit and the other calibration models are unacceptable, the source of the problem should be investigated and the instrument recalibrated.

IMPORTANT: Third-order regressions are <u>not</u> allowed at TestAmerica Denver.

10.7 Second-Source Initial Calibration Verification (ICV)

A mid-level standard that is obtained from a source different from that of the calibration standards is used to verify the initial calibration (see Section 7.3). The ICV is analyzed immediately following the initial calibration (ICAL) at two different concentrations.

Acceptance Criteria: The result for any single target analyte in the ICV standard should be within ± 15% of the expected value. Method 8141B allows for ± 20%. However, the analysis is acceptable if the average of the percent difference (%D) values for all the analytes is within ± 15% and the %D for all individual analytes is within ± 30% (per Method 8000B).

NOTE: The grand mean of the %D is not allowed in Method 8000C.

NOTE: Anilazine and Naled are documented poor performers and are allowed a %D of ± 50%.

NOTE: As mentioned is section 7.3.1, two different second source ICVs are run. One result is reported per analyte.

Corrective Action: If this is not achieved, the ICV standard, calibration standards, and instrument operating conditions should be checked. Correct any problems and rerun the ICV standard. If the ICV still fails to meet acceptance criteria, then recalibrate the instrument.

10.8 Calibration Verification

10.8.1 12-Hour Calibration Verification

The 12-hour calibration verification sequence consists of, at a minimum, an instrument blank and the mid-level calibration standard. The 12-hour calibration verification sequence must be analyzed within 12 hours of the initial calibration and at least once every 12 hours thereafter when samples are being analyzed.

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.8.2 Continuing Calibration Verification (CCV)

10.8.2.1 The mid-level calibration standard is analyzed as the continuing calibration verification (CCV) standard (see Table 3). At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCSs, and method blanks. Some programs, such as DoD QSM 4.2 or 5.0, require a CCV after every 10 samples to minimize the number of samples requiring re-analysis when QC

limits are exceeded.

10.8.2.2 If 12 hours elapse, analyze the 12-hour standard sequence instead.

10.8.2.3 As recommended by method 8000, some programs, (e.g., Wisconsin and Arizona) require that any compound that uses a second order regression be checked with CCVs at two concentration levels, a midpoint and one near the RL. Check method comments and QASs in the public folders to verify project requirements for the two level verification.

10.8.3 RL Standard

It may also be appropriate to analyze a standard prepared at or very near the reporting limit (RL) for the method at the end of the analytical sequence (see Section 7.5). This standard can be used to rule out false negatives in client samples in cases where the %D for one or more of the analytes in a bracketing CCV falls below the lower acceptance limit. The results for the RL standard are not evaluated **unless** the previous CCV fails acceptance criteria.

10.8.4 Acceptance Criteria for Continuing Calibration Verification (CCV)

10.8.4.1 Detected Analytes (≥ RL)

10.8.4.1.1 For any analyte detected at or above the reporting limit (RL) in client samples, the percent difference (%D) for that analyte in the preceding and following CCVs (i.e., bracketing CCVs) or 12-hour calibration, on the column used for quantitation, must be within ± 15% and 10% for EPA 614. Method 8141B allows for ± 20% but does not allow the use of the grand mean that is explained in section 10.6.4.2 and Table 5.

NOTE: Anilazine and Naled are known poor performers and are allowed a %D of ± 30%.

10.8.4.1.2 In some cases, the nature of the samples being analyzed may be the cause of a failing %D. When the %D for an analyte falls outside acceptance limits in the CCV, and that analyte is detected in any or all of the associated samples, then those samples must be reanalyzed to prove a matrix effect. If the drift is repeated in the reanalysis, the analyst must generate an NCM for this occurrence to explain that the drift was most likely attributable to the sample matrix and that the samples may be diluted and reanalyzed to minimize the effect if so desired by the client.

10.8.4.1.3 Refer to Section 12 for which result to report.

10.8.4.1.4 DoD QSM 5.0 requires recalibration and reanalysis of all affected samples since the last acceptable CCV. As an alternative, the laboratory may analyze two additional consecutive CCVs within one hour of the failed CCV. If both pass, the affected samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate: then reanalyze all affected samples since the last acceptable CCV.

10.8.4.1.5 If a DoD client accepts TestAmerica's Technical Specifications for DoD QSM work, samples that have no detections when a CCV has recoveries that are above the project acceptance limits would be reported with a case narrative comment, in addition to applying any data qualifier flags required by the project.

10.8.4.1.6 The %D is calculated as follows:

$$\%D = \frac{\text{Measured Conc} - \text{Theoretical Conc}}{\text{Theoretical Conc}} \times 100$$ *Equation 10*

10.8.4.2 Analytes Not Detected (< RL)

For any analyte not detected in client samples, the %D for that analyte in the bracketing CCVs should also be within ± 15% (8141A), ± 10% (614) and ± 20% (8141B). However, the analysis is acceptable for Method 8141A if the average of the %D values for all the analytes is within ± 15% and the %D for any individual analyte is within ± 30%. The average %D is calculated by summing all the %D results in the calibration and dividing by the number of analytes. If an average %D is used and the %D for any individual analytes falls outside of ± 30%, then additional evaluation is needed as summarized in Table 5.

NOTE: Naled is a poor performer which breaks down into dichlorvos. Samples that are ND for both naled and dichlorovs can be reported with naled recoveries that are not within +/-30%. Document in a NCM. **A limit of +/- 80% is suggested in this case. **

10.8.4.3 See SOPs DV-QA-027P *Standardized CCV criteria for GC and HPLC* and CA-Q-P-004 *Reporting results form Methods that Require 2nd Column Confirmation* for further guidance.

10.9 Retention Time Windows

10.9.1 Retention time windows must be determined for all analytes.

10.9.1.1 Determine new RT windows each time a new column is installed, when RT drift indicates that a new window needs to be established, or annually, whichever is most frequent. The new windows must be

generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

10.9.1.2 Make an injection of all analytes of interest each day over a three-day period.

10.9.1.3 Calculate the mean retention time and associated standard deviation of the three retention times for each analyte, as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RT_i - \overline{RT}\right)^2}{n-1}} \qquad \textit{Equations 11 \& 12}$$

Where:

RT_i	=	Retention time for the i[th] injection.
n	=	Number of injections (typically 3).
SD	=	Standard deviation.

10.9.1.4 Set the width of the RT window for each analyte at ± 3 standard deviations of the mean RT for that analyte.

10.9.1.5 The center of the RT window for an analyte is the RT for that analyte from the last of the three standards measured for the 72-hour study.

10.9.2 If the RT window as calculated above is less than ± 0.03 minute, use ± 0.03 minute as the RT window. This allows for slight variations in retention times caused by sample matrix. The default RT window should be sufficiently wide to accommodate all levels of the calibration. This allows for slight variations in retention times caused by sample matrix.

10.9.3 The center of the window for each analyte is updated with the RT from the level 5 standard of the ICAL, or the CCV analyzed at the beginning of the analytical sequence. The width of each window remains the same until new windows are generated following the installation of a new column, annually, or in response to a RT failure.

10.9.4 The analyst must review peak assignments in standards, any time retention time windows are recalculated or when stock standards are replaced. Sample chromatograms are provided in the attachment for verification of elution order on the columns specified in Section 6.1.2.

11.0 Procedure

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory

Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

11.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.3 Sample Extraction

Instructions for extracting aqueous samples are detailed in SOP DV-OP-0006. Instructions for extracting solid samples are detailed in SOP DV-OP-0010. Instructions for concentrating extracts are detailed in SOP DV-OP-0007.

11.4 Gas Chromatography

Chromatographic conditions for this method are presented in Table 2. Use the ChemStation interface to establish instrument operating conditions for the GC. Raw data obtained by the ChemStation software is transferred to the Chrom database for further processing. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the Chrom software.

11.5 Instrument Troubleshooting and Maintenance

Before the start of any daily sequence the instrument system should be evaluated for possible maintenance.

11.5.1 If the previous run ended with a failing continuing calibration then the system should be maintained to bring it back into control.

11.5.2 The injector septum should be changed after about 200 injections have been completed.

11.5.3 Proper conditioning of the NPD bead is essential to obtain acceptable performance. Lowering the voltage level during periods of non-use may extend bead life.

11.5.4 If the last CCV that was analyzed indicated a high response then a simple liner change is typically sufficient to bring the system back into control.

11.5.5 Analysis of a few solvent blanks or a system bake out may be necessary to drive out any residual contamination on the column.

11.5.6 A reduced response may indicate that the system needs to be evaluated for leaks.

11.5.7 Poor peak shape may necessitate clipping a loop out of the analytical column. If this fails to solve the peak shape problem then replacement of the columns may be

indicated. The goal is to maintain the system as close to top condition as possible as was observed when new columns and injector parts were installed.

NOTE: This method has several closely eluting peaks. After column maintenance it is sometimes necessary to make adjustments to the instrument conditions (i.e. temperature program) to prevent peaks from co-eluting.

11.6 Bead Lighting Procedure

In order to protect the bead from damage and maximize bead lifetime a specific bead lighting procedure must be followed.

11.6.1 Begin by turning the hydrogen pressure in the detector to 3.0 (do not exceed 4). Turn the bead voltage to 2.5 (do not exceed 4 at any time during the lighting process or use).

11.6.2 Increase the voltage in increments of 0.1 units until the voltage reaches 3.0. If the bead indicates lighting (as evidenced by a sudden and significant increase in signal) at less than 3.0, for example when the bead is new, then slow the voltage increase increment to 0.02 prior to the anticipated voltage at which lighting should occur.

11.6.3 If lighting has not occurred by the time a voltage of 3.0 is reached then reduce the voltage increase increment to 0.02 (after you reach 3.0) until the bead lights.

11.6.4 After a sustained bead light up is obtained then increase the voltage an additional 0.01 units in order to insure that the bead stays lit. Increase the hydrogen at this time until the output signal reads a signal of 10.

11.7 Sample Introduction

11.7.1 Analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.7.2 Allow all extracts and standards to warm to room temperature before injection.

11.7.3 To prepare a sample for injection, transfer 250 µL of the sample extract to a conical vial. Then add 5 µL of the internal standard solution.

11.7.4 Cap the vial and invert it approximately 10 times to ensure a uniform mixture.

11.7.5 Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

11.8 Analytical Sequence

An analytical sequence starts with an initial calibration (Section 10.5) or a daily calibration verification standard and ends with a daily calibration verification standard.

11.8.1 The daily calibration includes analysis of the 12-hour calibration sequence (i.e., a mid-level calibration standard (CCV) and an instrument blank as described in Section 10.8.1) and updating the retention time windows (Section 10.9.2).

11.8.2 The CCV is analyzed after every 20 samples, including matrix spikes, LCSs and method blanks. Some programs require a CCV after every 10 samples. The CCV must be analyzed every 12 hours to maintain the 12-hour calibration sequence or at the end of the sequence if no further analyses are performed.

11.8.3 If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration. Any samples that were not bracketed by calibration verification standards must be reinjected with the appropriate bracketing standards.

11.9 Daily Retention Time Windows

The centers of the retention time (RT) windows determined in Section 10.8.4.3 are adjusted to the RT of each analyte as determined in the 12-hour calibration verification. The centers of the RT windows must be updated at the beginning of each analytical sequence, but not for any other calibration verification standards.

11.10 Upon completion of the analytical sequence, transfer the raw chromatography data to the Chrom database for further processing.

11.10.1 Review chromatograms online and determine whether manual data integrations are necessary.

11.10.2 All manual integrations must be justified and documented. See DV-QA-011P for requirements for manual integration.

11.10.3 Manual integrations may be processed using an automated macro, which prints the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature.

11.10.4 Alternatively, the manual integration may be processed manually. In the latter case, print both the both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram.

11.10.5 Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration.

11.11 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD.

11.11.1 Transfer the data to the LIMS system.

11.11.2 Perform a level 1 data review and document the review on the data review checklist, GC Data Review Checklist/Batch Summary. (See SOP DV-QA-0020.)

11.11.3 Submit the data package and review checklist for the level 2 review. The data review process is explained in SOP DV-QA-0020. Review of all manual integrations must be documented and the level 2 review is documented on the review checklist initiated at the level 1 review.

12.0 Calculations / Data Reduction

12.1 Qualitative Identification

12.1.1 Tentative identification occurs when a peak is found on the primary column within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmation column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times. If a RT shift greater than the RT window occurs for a reported compound then the situation must be explained in an NCM.

12.2 Dual-Column Quantitation and Reporting

12.2.1 Each sample is analyzed on two different columns at the same time. The laboratory designates a primary column based on optimal separation of the compounds of interest and other desirable chromatographic characteristics. The result from the primary column is normally reported. The result from the secondary (confirmation) column is reported if any of the following is true:

12.2.1.1 There is obvious chromatographic interference on the primary column.

12.2.1.2 The difference between the result for the primary column and the result for the secondary column is > 40% and chromatographic interference is evident on the primary column.

12.2.1.3 The continuing calibration verification, bracketing standard, or surrogate recovery fails on the primary column, but is acceptable on the secondary column. An NCM must be written to document the deviation. Corrective action (e.g., recalibration) must be performed for recurring incidents. If the difference between the primary column result and the secondary column result is > 40% and the primary column calibration fails, then the sample must be evaluated for reanalysis.

12.2.1.4 For DoD QSM 4.2 or QSM 5.0 work, calibration and QC criteria for the second column are the same as for the initial or primary column analysis. All instrument QC must pass on both columns.

12.2.2 Percent Difference Calculation

The RPD between two results is calculated using the following equation:

$$\%RPD = \frac{\left|R_1 - R_2\right|}{\frac{1}{2}\left(R_1 + R_2\right)} \times 100\% \qquad \textit{Equation 13}$$

Where R_1 is the result for the first column and R_2 is the result for the second column.

12.2.3 Dual Column Results With > 40% RPD

12.2.3.1 If the relative percent difference (RPD) between the responses on the two columns is greater than 40%, the higher of the two results is reported unless there is obvious interference documented on the chromatogram.

12.2.3.2 If there is visible positive interference, e.g., co-eluting peaks, elevated baseline, etc., for one column and not the other, then report the results from the column without the interference with the appropriate data qualifier flag, footnote, and/or narrative comment in the final report.

12.2.3.3 If there is visible positive interference for both columns, then report the lower of the two results with the appropriate flag, footnote, and/or narrative comment in the final report.

12.3 Surrogate Recovery

12.3.1 Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated as follows:

$$\%\text{Recovery} = \frac{\text{Measured Conc}}{\text{Theoretical Conc}} \times 100 \qquad \textit{Equation 14}$$

12.4 Calibration Range and Sample Dilutions

If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted with hexane (record the hexane lot number in the run sequence) and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for the analyte(s) that were found to be over the calibration range in the high sample, they must be reanalyzed to rule out carryover. It may also be necessary to dilute samples because of matrix interferences.

12.4.1 If the initial diluted run has no hits or hits below 20% if the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample must be

reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.4.2 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

12.4.3 Reporting Dilutions

Some programs (e.g., South Carolina) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported.

12.5 Interferences Observed in Samples

12.5.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

12.5.2 Suspected Negative Interferences

If peak detection is prevented by interferences, further cleanup should be attempted (see SOP DV-OP-0007). Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5.3 Suspected Positive Interferences

If no further cleanup is reasonable and interferences are evident that are suspected of causing false positive results, consult with the laboratory Project Manager to determine if analysis using additional confirmation techniques is appropriate for the project. Use of additional confirmation columns is another possible option. At a minimum, the Data Review Template prepared by the analyst should include the following comment for inclusion in the case narrative:

"Based on review of the chromatograms for samples _____, it is my opinion that the evident interferences may be causing false results.

Date _____ Analyst _____"

12.6 Calculation of Sample Results

12.6.1 Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10.6 for details on establishing the calibration function):

Average Response Factor: $$C_e = \frac{A_s C_{is}}{A_{is} \overline{RF}}$$ *Equation 16*

Linear Regression: $$C_e = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$ *Equation 17*

Non-linear Regression: $$C_e = f\left(\frac{A_s C_{is}}{A_{is}}\right)$$ *Equation 18*

Where:

C_e	=	Concentration of the analyte in the sample extract (µg/mL).
A_s	=	Peak area for the analyte in the sample extract injection.
C_{is}	=	Concentration of the internal standard in the sample extract (µg/mL).
A_{is}	=	Peak area for the internal standard in the sample extract.
b	=	y-intercept of the calibration fit.
a	=	Slope of the calibration fit.
$f( )$	=	Mathematical function established by the non-linear regression.

12.7 The concentrations of target analytes in the original aqueous sample are calculated as follows:

$$C_S = \frac{C_e V_e}{V_S} \times DF$$ *Equation 19*

Where:

C_S	=	Concentration of target analyte in the original sample, µg/L.
C_e	=	Concentration of the target analyte in the sample extract as determined by the calibration function, µg/mL.
V_e	=	The final volume of the sample extract, mL.
V_s	=	The volume of the original sample that was extracted, L.
DF	=	Dilution factor, if applicable.

12.8 The concentrations of target analytes in the original solid sample are calculated as follows

$$C_S = \frac{C_e V_e}{W_S} \times DF$$ *Equation 20*

Where:

C_S	=	Concentration of target analyte in the original sample, µg/kg.
C_e	=	Concentration of the target analyte in the sample extract as determined by the calibration function, µg/mL.
V_e	=	The final volume of the sample extract, mL.
W_s	=	The weight of the original sample that was extracted, kg.
DF	=	Dilution factor, if applicable.

12.9 LCS and Surrogate Spike Recovery Calculation

LCS and surrogate spike recoveries are calculated using the following equation:

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100\% \qquad \textit{Equation 21}$$

12.10 MS and MSD Recovery Calculation

Matrix spike recoveries are calculated as follows:

$$\text{MS or MSD } \%\text{Recovery} = \left(\frac{SSR - SR}{SA} \right) \times 100\% \qquad \textit{Equation 22}$$

Where:

SSR = Measured concentration in spiked sample.
SR = Measured concentration in unspiked sample.
SA = Concentration of spike added to sample.

12.11 MS/MSD RPD Calculation

The relative percent difference between the MS and MSD is calculated as follows:

$$\%RPD = \frac{|R_1 - R_2|}{\frac{1}{2}(R_1 + R_2)} \times 100\% \qquad \textit{Equation 23}$$

Where R_1 is the result for the MS and R_2 is the result for the MSD.

12.12 A second-level technical review of the organic data is performed prior to data reporting. This review is performed by a peer or supervisor using the guidelines and checklists detailed in SOP DV-QA-0020.

13.0 Method Performance

13.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

13.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency

must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

13.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

13.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

14.0 Pollution Control

Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

15.0 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

15.2 The following waste streams are produced when this method is carried out:

15.2.1 Vials containing sample extracts: Expired Extract Vials – Waste Stream A

15.2.2 Expired reagents and standards – Contact Waste Coordinator

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

16.0 References

16.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.1.1 Method 8141A, Organophosphorous Compounds by Gas Chromatography: Capillary Column Technique, Revision 1, September 1994.

16.1.2 Method 8141B, Organophosphorus Compounds by Gas Chromatography. Final Update IV, Revision 2, February 2007, Method 8141B.

16.1.3 Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

16.1.4 Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

16.1.5 Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

16.1.6 Method 3540C, Soxhlet Extraction, Revision 3, December 1996.

16.2 Title 40, Code of Federal Regulations (40CFR), Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A, -- Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 614, Organophosphorus Pesticides.

17.0 Method Modifications:

Item	Method No.	Modification
1	614	Method 614 specifies the use of packed columns, or any other columns that provide equivalent performance. The laboratory uses capillary columns for this analysis, which give superior performance.
2	614	This SOP requires a minimum of five calibration levels, whereas Method 614 requires at least three calibration concentrations.
3	614	Method 614 requires an RSD of <10% or the use of a calibration curve, with no stated linearity requirement. This SOP includes a linearity acceptance limit for a weighted or unweighted linear regression, $r \geq 0.990$.
4	614	Method 614 does not include any requirements for the agreement

Item	Method No.	Modification
		for dual-column results. This SOP requires that the difference must < 40%, or the result is qualified.
5	614	This SOP includes details for performing retention time studies. There are none in the source method.
6	8000B 8000C	These methods allow the use of third-order calibration curves. TestAmerica Denver does not allow third-order curves.
7	8141A/B 614	For calibration verification, Anilazine and Naled are documented poor performers and are allowed a %D of ± 50%.

18.0 Attachments

Table 1. Standard Analyte List and Reporting Limits
Table 2. Suggested Instrument Conditions
Table 3. Calibration Concentrations and Recipes
Table 4. LCS, MS, and MSD Spike Compounds
Table 5. Evaluation Criteria and Corrective Actions for Continuing Calibration Verification
Table 6. DoD QSM 5.0 QC Criteria for Gas Chromatography
Table 7. Analyte Number and Elution Order – Instrument D
Attachment 1 Example Standard Chromatogram – Instrument D & D2

19.0 Revision History

- Revision 12, dated 08 December 2017
  - Annual Review
- Revision 11, dated 30 September 2016
  - Removed Column RTX-OPP from Section 6,
  - Removed Table 7B and Attachment 2 as both Instrument D and D2 now use the same columns.
  - Revised Section 9.6.3 to reflect current policy
  - Revised Section 13 to reflect current practice
  - Updated Table 7A (now table 7) with additional coelution for Sulfotepp and Phorate
- Revision 10, dated 31 August 2015
  - Clarified language in Section 9.6 to rule out lab error before accepting MS/MSD results that are outside of limits
  - Updated reference to corporate SOP on calibration to reflect current document in Section 10.1.1
  - Added Section 10.8.4.3 referencing lab and corporate SOPs for CCV and sample result acceptance criteria for methods with two columns.
  - Revised Sections 10.9.2 and 10.9.3 to reflect current practice
  - Revised Section 13 to reflect current practice
  - Archived revision history prior to 2011
- Revision 9.0, dated 31 July 2014
  - Added statement in Section 4.11 regarding poor resolution between the two

mevinphos isomers.
  - Added supplies list to section 6.0
  - Moved Section 6.1.1 to Section 11.5.3 and moved Section 6.1.3 to Section 10.1.3.
  - Revised standards section to reflect current practice.
  - Added statement to Sections 7.2.3 and 7.3.4 to check methyl parathion and merphos, in particular, for degradation in standards.
  - Removed Section 9.9 as SOP references all required QC elements in 2012 MUR as required.
  - Added third note to Acceptance Criteria section in Section 10.7.
  - Added reference to DoD QSMs in section 10.8.3.
  - Added note to Section 10.8.7.2.
  - Added note to Section 11.5.6.
  - Removed chlorpyriphos-methyl and added dimethoate, benthiocarb and DEF to the appropriate tables.
  - Revised Tables 2, 3 and 4 to reflect current practice.
  - Added Table 6, DOD QSM 5.0 QC criteria for GC.
  - Added Table 7, Analyte number and elution order.
  - Replaced Attachments 1-6 with new Attachments 1 and 2, revised example chromatograms to reflect current data system output.
  - Formatting and grammatical changes throughout.
- Revision 8.0, dated 15 July 2013
  - Added use of second ICV solution in Sections 7.6, 10.8 and Table 3.
  - Updated Sections 9.1 and 11.1 to reflect current practice.
- Revision 7.0, dated 04 January 2013
  - Added section 9.9 for 2012 MUR QC requirements
  - Updated 10.9.4.1 and 10.9.4.2 to include EPA 614 CCV criteria.
- Revision 6.1, dated 16 May 2012
  - Annual Technical Review.
  - Revised Section 10.10.1.1 regarding frequency of new RT windows
  - Inserted paragraphs on instrument maintenance and bead lighting in Section 11.4
  - Formatting and grammatical corrections throughout SOP
- Revision 6, dated 16 May 2011
  - Added a Supelco standard to 7.1.6.
  - Acetone used as diluent in section 7.3.1.
  - Added standard preparation detail to 7.7 and 7.8.
  - Changed allowable MB concentration to ½ the RL and added detail to corrective action in section 9.4.
  - Added other acceptance criteria to section 9.8 and dilution details to the corrective action.
  - Specified that 8141A has +/-15% criteria in section 10.5.
  - Revised section 10.6.2 to include the method 8000 recommendation for two CCV levels.
  - Clarified that method 8141B does not allow the use of a grand mean for CCV in section 10.6.4.1.
  - Added a line indicating data transfer to LIMS to section 11.9.
  - Included a note in section 12.1.2 that RT shifts must be narrated.
  - Included a note to section 12.4 to use hexane and record the lot number.
  - Updated the RLs in table 1.

- Updated the instrument conditions in table 2.
- Updated the standard prep for L7 in table 3.
- Source methods review

Earlier revision histories have been archived and are available upon request.

Table 1.
Standard Analyte List and Reporting Limits

Compound	CAS Number	Reporting Limits	
		Water (µg/L)	Solid (µg/kg)
Azinphos methyl	86-50-0	2.5	13
Bolstar (Suprofos)	35400-43-2	1.0	13
Chlorpyrifos	2921-88-2	1.5	20
Coumaphos	56-72-4	1.0	13
Demeton, O and S	8065-48-3	3.0	39
Diazinon	333-41-5	0.5	22
Dichlorvos	62-73-7	0.5	23
Disulfoton	298-04-4	1.0	48
EPN	2104-64-5	1.2	13
Ethoprop	13194-48-4	1.5	15
Fensulfothion	115-90-2	2.5	25
Fenthion	55-38-9	2.5	33
Malathion	121-75-5	2.0	15
Merphos (Merphos A and DEF)	150-50-5	5.0	30
Methyl Parathion	298-00-0	4.0	20
Mevinphos (Mevinphos A and B)	7786-34-7	6.2	15
Naled	300-76-5	2.0	70
Phorate	298-02-2	1.2	20
Ronnel	299-84-3	10	46
Tetrachlorvinphos (Stirophos)	22248-79-9	3.5	15
Tokuthion	34643-46-4	1.6	20
Trichloronate	327-98-0	1.5	20
O,O',O"-Triethyl phosphorothioate	126-68-1	0.5	39
Thionazin	297-97-2	1.0	18
Sulfotepp	3689-24-5	1.5	20
Dimethoate	60-51-5	1.5	22
Ethyl Parathion (Parathion)	56-38-2	1.0	18
Famphur	52-85-7	1.0	13
Additional Compounds			
Anilazine	101-05-3	10	40
Atrazine	1912-24-9	10	67
Propazine	139-40-2	10	67
Simazine	122-34-9	10	67
Dimethoate	60-51-5	1.5	22
Azinphos ethyl	2642-71-9	0.7	33
Carbophenthion	786-19-6	1.0	33
Methyl carbophenthion	953-17-3	0.8	33
Phosmet	732-11-6	1.5	67
Benthiocarb (thiobencarb)	28249-77-6	3.0	33

Table 2.

Suggested Instrumental Conditions

Parameter	Recommended Conditions[1]
Injection Port Temp	250 °C
Detector Temp	325 °C
Initial Temp	80 °C (D) 75 °C (D2) then hold for 0.5 min
Temperature Program	(**ramp A**) 6°C/minute (D) 11°C/minute (D2) (**ramp B**) 12°C/minute (D and D2) (**ramp C**) 4°C/minute (D) 8°C/minute (D2) **(ramp D**) 2°C/minute (D) 30°C/minute (D2) (**ramp E**) 30°C/minute (D only)
Final Temp	(**A**) 160°C (D and D2) (**B**) 180°C (D) 185°C (D2) (**C**) 202°C (D) 210°C (D2) (**D**) 210°C (D) 305°C (D2) (**E**) 305° (D)
Final Hold Time	*(**A**) 0.00 minute (D and D2)* *(**B**) 0 minute (D) 1 minute (D2)* *(**C**) 0 minutes (D and D2)* *(**D**) 0 minute (D) 2 minutes (D2)* *(**E**) 2 minute (D)*
Column 1	Rtx®-OPP, 30 meter X 0.32 mm X 0.5 μm film or Rtx®-OPP2, 30 meter X .32mm X .0.32 μm film
Column 2	Rtx®-1MS, 30 meter X 0.32 mm X 0.25μm film
Injection Volume	2 μL
Carrier and Detector Gases	Helium and Hydrogen
Make-up Gas	Nitrogen

[1] D and D2 are Instrument IDs.

Table 3.

Calibration Concentrations and Recipes

Calibration Level	Conc.	Final Volume	Recipe
ICAL Level 7	5 µg/mL	10 mL	0.25 mL Restek 8140/8141 OP Pesticides Cal Mix A
			0.25 mL Restek 8141 Custom Spike Standard
			0.05 Restek 8141 Standard #2
			0.05 Restek 8141 Standard #3
			0.5 mL ChemService Carbophenothion Methyl
			0.05 mL Accustandard Chlormefos (surr.)
			0.05 mL Accustandard Triphenyl Phosphate (surr.)
ICAL Level 6	4 µg/mL	0.250 mL	0.200 mL of ICAL Level 7
ICAL Level 5	3 µg/mL	0.250 mL	0.150 mL of ICAL Level 7
ICAL Level 4	2 µg/mL	0.250 mL	0.100 mL of ICAL Level 7
ICAL Level 3	1 µg/mL	0.250 mL	0.050 mL of ICAL Level 7
ICAL Level 2	0.5 µg/mL	0.250 mL	0.025 mL of ICAL Level 7
ICAL Level 1	0.2 µg/mL	0.250 mL	0.010 mL of ICAL Level 7
Continuing Calibration (CCV)	2.5 µg/mL	10 mL	5.0 mL of ICAL Level 7
8141_SS_Acc	2 µg/mL	5 mL	0.050 mL Accustandard 8140 OPP Cal Mix A
			0.050 mL Accustandard 8141 Custom Spike Std.
			0.100 mL Accustandard Methyl Trithion
			0.100 mL Accustandard Benthiocarb
			0.010 mL Accustandard Chlormefos (surr.)
			0.010 mL Accustandard Triphenyl Phosphate (surr.)
8141_SS_Res	5 µg/mL	5 mL	0.125 mL Restek 8141 OP Pest Cal Mix A (sec. src.)
			0.025 mL Restek 8141 Standard #2
			0.125 mL Ultra Scientific custom standard
			0.100 mL Accustandard Methyl Trithion
			0.025 mL 8141 Standard #1 (second source)
			0.025 mL Triphenylphosphate (second source)

* All standards are brought to the final volume in Hexane:Acetone (90:10)
* Actual concentrations of each component in each standard is stored in the Reagent Module in the LIMS

Table 4.

LCS, MS, and MSD Spike Compounds

Spike Solution:			
Compound	**Concentration (μg/mL)**	**SW846 8141A Control Compound**	**EPA Method 614 Control Compound**
O, O', O"-Triethylphosphorothioate	4.0	X	
Thionazin	4.0	X	
Famphur	4.0	X	
Anilazine	4.0		
Atrazine	4.0	X	
Propazine	4.0		
Simazine	4.0	X	
Fenthion	4.0	X	
Merphos	4.0		
Methyl parathion	4.0	X	X
Mevinphos	4.0	X	
Naled	4.0		
Phorate	4.0	X	
Ronnel	4.0	X	
Tetrachlorvinphos (Stirophos)	4.0	X	
Tokuthion	4.0		
Trichloronate	4.0	X	
Azinphos-methyl	4.0	X	
Bolstar	4.0		
Chlorpyrifos	4.0	X	
Coumaphos	4.0	X	
Demeton	4.0	X	X
Diazinon	4.0	X	X
Dichlorvos	4.0	X	
Disulfoton	4.0	X	
Ethoprop	4.0	X	
Fensulfothion	4.0	X	
Dimethoate	4.0	X	
EPN	4.0		
Ethyl parathion (Parathion)	4.0	X	
Malathion	4.0	X	X
Sulfotep	4.0	X	
Surrogate Solution:			
Chlormephos	2.0	X	X
Triphenylphosphate	2.0	X	X

Table 5.
Evaluation Criteria and Corrective Actions for Continuing Calibration Verification

Evaluation Criteria for a Specific Analyte				Evaluation / Corrective Actions
Average %D	**Individual %D**	**RL Standard**	**Client Samples**	
N/A	± 15% ± 20% (8141B)	N/A	≥ RL	Calibration is verified for the analyte(s) detected in the sample; no action required.
N/A	Outside of ± 15% ± 20% (8141B)	N/A	≥ RL	Calibration is not verified for the analyte(s) detected in the sample. The sample must be re-analyzed using a verified calibration.
± 15%	± 30%	N/A	ND	Calibration is acceptable because analytes were not detected in the sample. An NCM is required.
Outside of ± 15%	N/A	N/A	N/A	Calibration is <u>not</u> verified and corrective action must be taken. **NOTE**: The exception to this may be those cases where the client has requested a small subset of the analytes typically measured by the method and the %D for each of those analytes is within ± 15%. Corrective action may include clipping the column, changing the liner, or other minor instrument adjustments, followed by reanalyzing the standard twice. If both results pass acceptance criteria, the calibration may be used to process samples. If the overall average %D still varies by more than ±15%, a new calibration curve must be prepared. Reanalyze any samples that were either preceded by or followed by the failed CCV using a verified calibration.
± 15%	< -30% (low)	Detected	ND	Sample results are acceptable because the RL standard indicates that the analyte would have been detected if present in the sample. Explain in an NCM. (**note:** If results are required to be reported to the MDL, client approval is required.)
± 15%	< -30% (low)	ND	ND	Analyte was not detected in the RL standard, possibly as the result of a calibration drift in the negative direction, and therefore one cannot be sure that the analyte would have been detected in the sample if present. Reanalyze samples with verified calibration. In the event that re-analysis substantiates that sample matrix is causing the drift, notify PM and discuss analytical approach with client.
± 15%	> +30% (high)	N/A	ND	Sample results are acceptable because the CCV failed high and the analyte was detected in the RL standard, so if the analyte were present in the sample, it would definitely have been detected. Explain in an NCM.

Table 6
DOD QSM 5.0 QC Criteria for Gas Chromatography

QSM 5.0 Table 1. Organic Analysis by Gas chromatography	
QC Element	**DoD QSM 5.0/DoE QSAS 3.0 Requirements**
Method 8081 (only) Endrin/DDT Breakdown Check	Performed prior to analysis of samples and at the beginning of each 12-hour shift. Degradation must be ≤15% each for both Endrin and DDT. Any problems must be corrected. Do not run samples until degradation is ≤15%.
Initial Calibration (ICAL) for all analytes including surrogates	Perform a minimum 5 point calibration for all analytes prior to sample analysis for linear and 6 levels for quadratic at instrument set-up and after ICV or CCV failure, prior to sample analysis. Acceptance Criteria options: 1. RSD for each analyte ≤ 20%. 2. Linear least squares regression: $r^2 \geq 0.99$ ($r>0.995$) 3. Non-linear regression: coefficient of determination (COD) $r^2 \geq 0.99$. This option is not used for Method 8082 or Method 8082A. Any problems must be corrected and ICAL repeated. Quantitation for multi-component analytes such as chlordane and toxaphene must be performed using a 5-point calibration. Results may not be quantitated using a single point. TestAmerica will analyze a single point for chlordane and toxaphene for pattern recognition and perform the 5-point calibration and reanalyze associated samples for the identified analyte. (10ICAL) For PCB analysis, a mixture of Aroclors 1016 and 1260 is normally used to establish detector calibration linearity using a 5-point calibration, unless project-specific data suggest the presence of other Aroclors. A single point calibration will be performed for the other Aroclors (10ICAL). If this specification is not accepted, 5-point calibration must be performed for all PCBs. No samples shall be analyzed until an ICAL has passed.
RT Window Position Establishment	Establish the RT window position for each analyte and surrogate once per ICAL and at the beginning of the analytical sequence. Set position using the midpoint standard of the calibration curve when an ICAL is performed. On days when ICAL is not performed the initial CCV is used.
Retention Time (RT) Window Width	Perform 72-hour study at method set-up and after major maintenance (e.g., column change) to calculate the RT window width for each analyte and surrogate. RT width is ± 3 times the standard deviation for each analyte RT from the 72 hour study.
Initial Calibration Verification (ICV)	Measure a second-source standard once after each ICAL prior to sample analysis. Acceptance limits for all reported analytes is ± 20% of expected value. All reported analytes must be within established RT window. Correct any problems and rerun second-source standard. If that fails, correct problem and repeat ICAL. No samples shall be analyzed until the second-source calibration verification is successful. For Method 8141, instability of standards is an issue. An acceptance criterion of ± 20% of the expected value for the mean of all compounds, with no individual compound to exceed a criterion of ± 30%. In addition, demeton will be evaluated as total demeton, and failures of the individual isomers will be allowed if the percent difference is in control for the total. (16OP)

Table 6
DOD QSM 5.0 QC Criteria for Gas Chromatography
(continued)

QSM 5.0 Table 1. Organic Analysis by Gas chromatography	
QC Element	**DoD QSM 5.0/DoE QSAS 3.0 Requirements**
Continuing Calibration Verification (CCV)	CCV concentration ≤ midpoint of calibration range. Run at beginning of day, after every 10 field samples, and at the end of the analysis sequence with the exception of CCVs for Pesticides multi-component analytes (i.e., Toxaphene, Chlordane), which are only required before sample analysis. All reported analytes must be within ± 20% of expected value (calculated from ICAL). All analytes must be within established RT windows. If the CCV is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project. (3HR) Recalibrate and reanalyze all affected samples since the last acceptable CCV; Or Immediately (within one hour) analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. (Passing criteria only has to apply to the analytes that failed in the bracketing CCV.) If either reanalyzed CCV fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. If a CCV fails to meet control limits, the routine corrective action process is to recalibrate and reanalyze all affected samples since the last acceptable CCV. TestAmerica will perform a single reanalysis. If it is determined through reanalysis that project samples are the cause of CCV failures, the client will be consulted before reporting (6CCVOrg) If reanalysis is not possible, apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV. Must be explained in the case narrative. For Method 8141, instability of standards is an issue. Acceptance criterion of ± 20% of the expected value for the mean of all compounds, with no individual compound to exceed a criterion of ± 30% is applied. In addition, demeton will be evaluated as total demeton, and failures of the individual isomers will be allowed if the percent difference is in control for the total. (16OP)
Method Blank (MB)	One per prep batch. No analytes detected > ½ LOQ (RL) or >1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater. For Method RSK-175, no common lab contaminants >LOQ (2CLC) If criteria not met, correct problem. If required, reprep and reanalyze MB and all samples processed with the contaminated blank. If reanalysis is not possible, apply B-flag to all results for the specific analyte(s) in all samples processed with the contaminated blank. Must be explained in the case narrative. Flagging is only appropriate when samples cannot be reanalyzed.
LCS	One LCS per prep batch. Include all analyte(s) in LCS that are required to be reported, including surrogates. For Method 8081, only single-component compounds are spiked (9Spik) Use DoD acceptance criteria if project limits are not specified. If analyte not listed by DoD, use in-house LCS limits if project limits not specified.

Table 6
DOD QSM 5.0 QC Criteria for Gas Chromatography
(continued)

QSM 5.0 Table 1. Organic Analysis by Gas chromatography	
QC Element	**DoD QSM 5.0/DoE QSAS 3.0 Requirements**
LCS (continued)	One LCS per prep batch. Include all analyte(s) in LCS that are required to be reported, including surrogates. For Method 8081, only single-component compounds are spiked (9Spik) Use DoD acceptance criteria if project limits are not specified. If analyte not listed by DoD, use in-house LCS limits if project limits not specified. If the LCS recovery is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project (3HR). Otherwise, correct any problems then re-prep and reanalyze the LCS and all associated samples for failed analytes. If insufficient sample, then apply Q-flag to specific analyte(s) in all samples in the associated prep batch. Flagging is only appropriate when samples cannot be reanalyzed unless 3HR is accepted by the client. Marginal exceedances are not allowed for critical chemicals of concern (risk drivers). Client must notify TestAmerica of these targets or if marginal exceedances will not be allowed. (1SME)
Matrix Spike	One per prep batch. Include all analyte(s) in LCS that are required to be reported, including surrogates. For Method 8081, only single-component compounds are spiked (9Spik) Use DoD-specific criteria for LCS. For failures, consult project-specific DQOs and contact client for additional measures to be taken. For specific analyte(s) in parent sample, apply J-flag if acceptance criteria are not met. Explain in the case narrative. The MS is for matrix evaluation only. If MS falls outside LCS limits, evaluate data to determine the source of the difference and to determine if there is a matrix effect or analytical error.
MSD or Sample Duplicate	One per prep batch. Include all analyte(s) in LCS that are required to be reported, including surrogates. For Method 8081, only single-component compounds are spiked (9Spik) Use DoD-specific criteria for LCS. For failures, consult project-specific DQOs and contact client for additional measures to be taken. RPD between duplicates ≤ 30%. For specific analyte(s) in parent sample, apply J-flag if acceptance criteria are not met. Explain in the case narrative. Data shall be evaluated to determine the source of the difference.
Surrogate Spike	Spike all field and QC samples with surrogates. Must meet DoD acceptance criteria, otherwise method-specified criteria or lab's in-house criteria. For QC and field samples, correct any problems, then re-prep and reanalyze all failed samples for failed surrogates in the associated prep batch. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary. If surrogate recoveries are above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project. For samples with ND results, a high bias as evidenced in these situations is typically not an issue (3HR).

Table 6
DOD QSM 5.0 QC Criteria for Gas Chromatography
(continued)

QSM 5.0 Table 1. Organic Analysis by Gas chromatography	
QC Element	**DoD QSM 5.0/DoE QSAS 3.0 Requirements**
Surrogate Spike (continued)	Apply Q-flag to all associated analytes if acceptance criteria are not met. Explain in the case narrative. All surrogates analyzed must be reported. For example, for Method 8082, if both surrogates TCMX and DCBP are analyzed and results are processed for both, then report both even if only one is included in the project work plan. A suitable surrogate has not been found for RSK-175. TestAmerica performs this analysis without a surrogate. (17RSK)
Confirmation of Positive Results (second column)	All positive results must be confirmed except for single column methods such as TPH by Method 8015 where confirmation is not an option or requirement. For Direct Aqueous Injection Methods (alcohols, acetates, and glycols) suitable second columns have not been identified. (15DIA) Calibration and QC criteria for the confirmation analysis are the same as for the primary column analysis. The RPD between results for the primary and secondary columns must be ≤ 40%. Apply J-flag if RPD > 40% and discuss in case narrative. Use project-specific reporting requirements if available; otherwise use method requirements if available; otherwise report the result from the primary column unless there is a scientifically valid and documented reason for not doing so and is approved by the client. If it is not possible to confirm a result due to interference, these unconfirmed results must be identified in the test report, using appropriate data qualifier flags and explained in the case narrative. Analyte presence is indicated only if both original and confirmation signals are positive or if confirmation signal cannot be discerned from interference.

Table 7 – Analyte Number and Elution Order – Instruments D & D2

Analyte	Analyte Number In Chrom[1]	Elution Order[2] - Column 1 (RTX-1MS)	Elution Order[2] - Column 2 (RTX-Opp2)
O, O', O"-Triethylphosphorothioate	1	1	1
Dichlorvos	2	2	2
Mevinphos Isomer A	3	3	5
Mevinphos Isomer B	4	4	4
Chlormefos (surrogate)	5	5	3
Thionazin	6	6	7
Demeton - O	7	7	6
Ethoprop	8	8	9
Naled	9	9	10
Tributyl phosphate (IS)	10	10	8
Sulfotepp	11	11	12
Phorate	12	12	11
Dimethoate	13	13	16
Demeton - S	14	14	13
Simazine	15	15	14
Atrazine	16	16	--
Propazine	17	17	--
Disulfoton	18	18	18
Diazinon	19	19	17
Methyl parathion	20	20	19
Ronnel	21	21	20
AtrazinePropazine (coeluting pair – Col 2)	22	--	15
Benthiocarb	23	22	21
Malathion	24	23	22
Fenthion	25	24	26
Ethyl parathion (Parathion)	26	25	25
Chlorpyrifos	27	26	23
Trichloronate	28	27	24
s-Triazine-2,4-dichloro-6-(o-chloroaniline) (Anilazine)	29	28	28
Merphos A	30	29	27
Tetrachlorvinphos (Stirophos)	31	30	29
Tokuthion	32	31	30
Merphos B (DEF)	33	32	31
Methyl carbophenthion	34	33	32
Fensulfothion	35	34	33
BolstarFamphur (coeluting pair – Col 1)	36	35	--
Carbophenthion	37	36	35
Triphenlyphosphate (surrogate)	38	37	37
Phosmet	39	38	39
EPN	40	39	38

Table 7 – Analyte Number and Elution Order (continued)

Analyte	Analyte Number In Chrom	Elution Order - Column 1 (RTX-1MS)	Elution Order – Column 2 (RTX-Opp2)
Azinphos-methyl	41	40	41
Bolstar	42	--	34
Tris (o-cresyl) Phosphate (IS)	43	41	40
Azinphos-ethyl	44	42	42
Famphur	45	--	36
Coumaphos	46	43	43
Mevinphos (Summary)[3]	47	--	--
Demeton, Total (Summary)[3]	48	--	--
Merphos (Summary)[3]	49	--	--
SulfoteppPhorate (coeluting Pair – Col 2)[4]	50	--	11

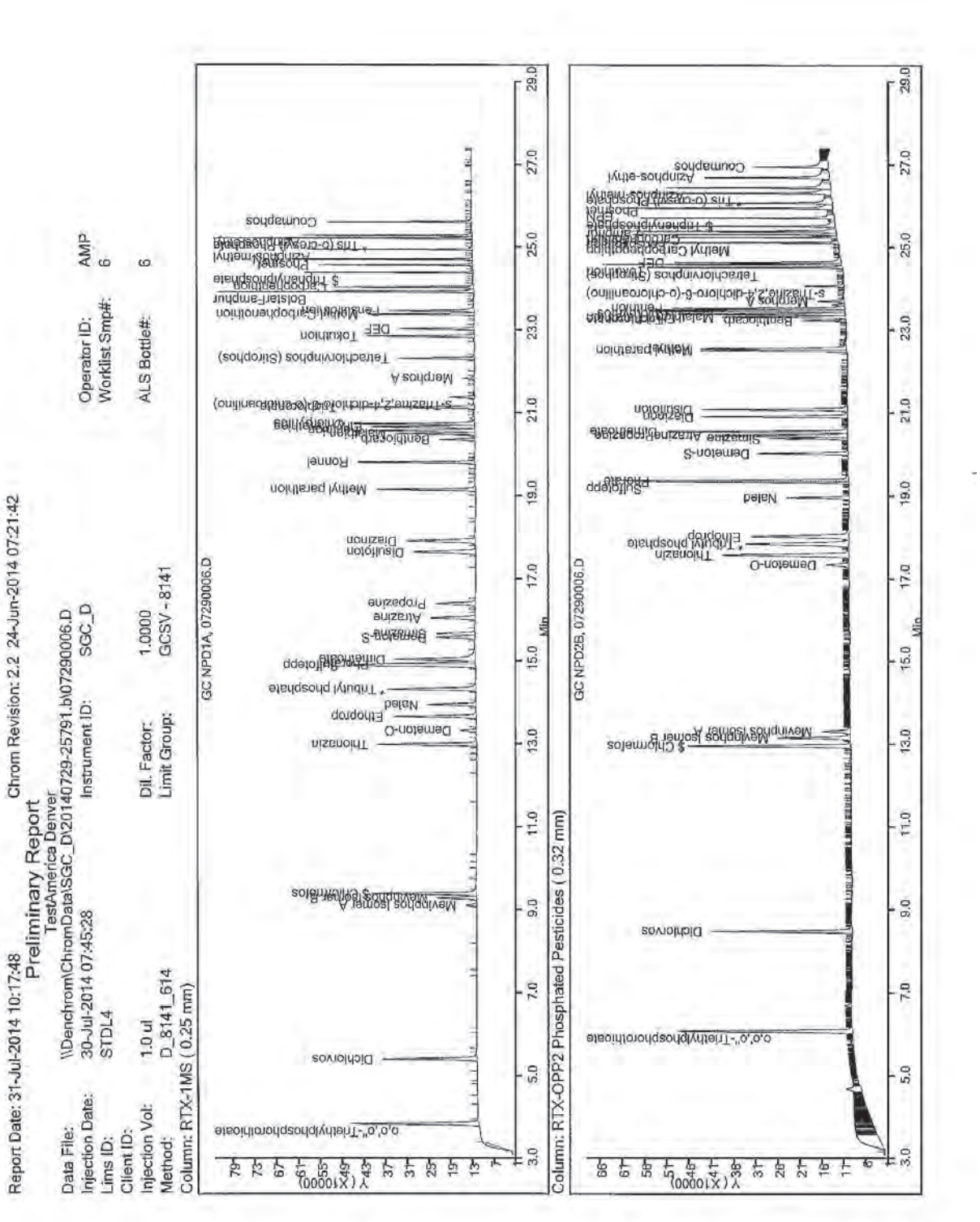
[1] Analyte number is the number assigned to the compound in Chrom, listed on the reports generate in Chrom.

[2] Elution order is assigned as the order in which the compounds elute on each column if all compounds are present.

[3] Summary compounds are determined by the sum of two results and are assigned an analyte number in Chrom for quantitation but are not distinct peaks in the chromatogram.

[4] Sulfotepp and Phorate can be separated on a new column, but as the column performance degrades they begin to coelute on Column 2. If this occurs they are reported as the coeluting pair only on Column 2 and are separate on column 2. When the compounds are separated the coelution analyte does not appear on the chromatogram.

Attachment 1
Example Standard Chromatograms
Instrument D & D2



Note: Absolute retention times may vary due to actual column length and condition.

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Electronic Copy Only

Title: Dissolved Gases in Water
Method: RSK-175

Approvals (Signature/Date):

Tegan Moore 12/7/17
Tegan Moore Date
Technical Specialist

Doug Gomer 12/7/17
Doug Gomer Date
Health & Safety Manager / Coordinator

Roxanne Sullivan 12/7/17
Roxanne Sullivan Date
Quality Assurance Manager

L.A.L. 12/7/17
William S. Cicero Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1. This document describes a procedure for the determination of methane, ethane, ethene, acetylene, propane, isobutylene, butane, and pentane dissolved in water using a static headspace autosampler connected to a gas chromatograph with dual flame ionization detectors (GC/FID). This SOP is based on the RSK-175 method described in EPA document EPA/600/J-89/186, 1994.

1.2. The most common application for this analysis is to assist in evaluating the biological activity in aquifers contaminated with petroleum hydrocarbons. It is also used by the fracking industry to establish baseline methane levels in groundwater monitoring.

1.3. Refer to Table 3 for a list of analytes and standard reporting limits.

2.0 Summary of Method

2.1 A water sample, with field blank and duplicate, is collected in a VOA vial with a screw cap fitted with a Teflon septum. The vial is completely filled so that there is no headspace. When the sample is received at the laboratory, 18 mL of the sample is transferred to a 22 mL headspace vial with a crimp septum cap. The sample is loaded onto the headspace autosampler and analyzed by dual column GC/FID.

2.2 The instrument is calibrated using a minimum of 5 of the 7 calibration levels shown in Table 2. Sample results are calculated using the external standardization method.

2.3 Unless extrapolating results to conditions different than those used for analysis, this procedure does not require calculation of the concentration in the headspace using Henry's Law and then using this result to calculate the concentration in the aqueous sample. Instead of calibrating with gas standards, the calibration standards are prepared in water to mimic the actual field samples. Therefore, the calibration incorporates the equilibration between the aqueous and gaseous phases in the sample vial. Continuing calibration verification standards are analyzed immediately prior to sample analysis to ensure that the same temperature and pressure exist for both standards and samples.

3.0 Definitions

3.1 Henry's Law

Henry's Law states that the equilibrium value of the mole fraction of gas dissolved in a liquid is directly proportional to the partial pressure of the gas above the liquid surface, and is expressed as follows:

$$P_g = X_g \times K_h$$

Where:

P_g = partial pressure in atmospheres

X_g = mole fraction of dissolved gas, which given a liquid volume and the gram molecular weight per mole can be converted to a concentration

K_h = Henry's law constant in atmospheres, the value of the constant is dependent on temperature

Henry's Law is applicable at low concentrations and low partial pressures of gas at or below one atmosphere of pressure.

3.2 Static Headspace Autosampler

The term "static headspace" means that the sample is not stirred, mixed, or bubbled during analysis. The autosampler described in Section 6.2 includes a heating block that holds the 22 mL vials and ensures a constant 40°C (± 1°C) temperature during analysis.

3.3 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, "Quality Assurance Program," for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Samples immediately following a high-level sample are re-analyzed if they exhibit any detection of target analytes. Typically carryover is not observed at sample concentrations that are within the calibration range.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual, and this document.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1 (as per the Environmental Health and Safety Manual), laboratory coat, and latex or nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.1.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

5.2.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating.

NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.

5.2.2 A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
Hydrogen Gas	Flammable High-Pressure Gas Asphyxiant	None established	Hydrogen gas can form explosive mixtures with air. May ignite if valve is opened to air. Burns with invisible flame. Inhalation effects are due to lack of oxygen. Moderate concentrations may cause headache, drowsiness, excitation, excess salivation, vomiting, and unconsciousness.
(1) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Supplies

6.1.1 Sample Collection Containers: 43 mL VOA vial with septum cap.

6.1.2 Sample Analysis Containers: 22 mL crimp cap vials.

6.1.2.1 Each lot of 22 mL headspace vials must have the volume confirmed by weighing ten vials and then filling to capacity and reweighing. The data are to be entered in the spreadsheet found at

R:\QA\Edit\FORMS\Support Equipment\Pipettes\(Att15) 22 mL vial Verification Sheet.

6.1.2.2 The file is stored at:

G:\GcVoa\Hidden\pipette and syringe calibration checks\Vial (22ml) Calibration Verification Spreadsheet.

6.1.3 Columns:

6.1.3.1 Restek Rt-U-Bond, 30 m x 0.32 mm ID x 10 µm

6.1.3.2 Restek Rt-S-Bond, 30 m x 0.32 mm ID x 10 µm

6.1.3.3 Columns giving equivalent performance may also be used.

6.1.4 Syringes: 5 µL – 20.0 mL gas-tight syringes.

6.1.5 Several 12" transfer cannulas, 20 ga.

6.1.6 Pressure relief valve (cannula or needle)

6.1.7 Source of N_2 gas regulated to provide a sample flow through the cannula at 14-20 mL per minute.

6.1.8 Balance to weigh to nearest 0.01 g.

6.1.9 Calibrated mechanical pipettes with pipette tips or Class A glass volumetric pipettes. Pipette calibration is checked in accordance with SOP DV-QA-0008.

6.2 Instrumentation

6.2.1 Instrumentation: Agilent Model 6890 GC with Dual FID detectors, or equivalent. Current instrument is instrument J.

6.2.2 Autosampler: Tekmar 7000 Headspace Autosampler

6.2.3 Data System: Chemstation for acquisition and Chrom for data processing, or equivalent.

6.3 Computer Software and Hardware

Refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

7.1 Gas cylinders of ultrahigh purity helium, hydrogen, air, and nitrogen, > 99.999% pure.

7.2 Standards Verification

All standards are subject to verification using a second-source standard before they are used for sample analysis. This process is described in SOP DV-QA-0015.

7.3 Gas Standards:

7.3.1 Expiration dates of primary gas standards will be the expiration date assigned by the vendor. If the vendor does not provide an expiration date, then the expiration date is set to the date of receipt plus two years. Standards should be replaced sooner than the assigned date if there is evidence of degradation of the standard. The gases are stored at room temperature.

7.3.2 Calibration Standards: The primary 7 gas standard is made by Matheson Tri-Gas as a special custom order. The stock calibration standard mix is composed of nominally 1% (mole fraction) methane, ethane, ethene, acetylene, propane, isobutylene, and butane in nitrogen. A secondary 99% methane stock is obtained from Scott specialty gases and is used for the higher level methane standards (levels 3, 5, and 6). Pentane (Chromasolv, HPLC grade) from Sigma-Aldrich is added via a dilute solution in acetone. This solution is prepared by adding 4 µL of neat pentane to 25 mL of acetone. The acetone is a high purity Ultra Resi Analyzed grade (99.4%) from Baker (other acetone solvents may be substituted as long as they do not contain interferences with the compounds analyzed with this method). This results in a stock concentration of 100 µg/mL.

7.3.2.1 The initial calibration (ICAL) standards are prepared fresh each time an ICAL is performed.

7.3.2.2 To prepare the ICAL standards, a gas-tight syringe is used to transfer the following volumes of the stock standard to 22 mL vials that contain 18 mL of deionized water and 4 mL of headspace:

ICAL Level	Vol of Stock Calib Mix (µL)	Vol Stock Methane (µL)	Vol of Pentane Reagent (µL)
1	2.5	0	0.5
2	5	0	1.0
3	40	400	5.50
4	200	0	25
5	400	200	50
6	800	50	100
7	1000	0	125

7.3.2.3 The resulting seven ICAL levels are shown in Table 2. An example calculation explaining the derivation of these concentrations is shown in Attachment 1.

7.3.3 Initial Calibration Verification (ICV) Standard:

A second lot of gas mix prepared by Matheson Tri-Gas Inc. at a 1% concentration for each compound is used to prepare the ICV. The standard is prepared by adding 400 µL of the gas standard mixture to 18 mL of water. A second source of pentane, Chem Services cat# f2414s (conc 1000 µg/mL), is used to prepare the ICV stock. The ICV stock is prepared at a concentration of 100 ug/mL by diluting 2.5 mL of the vendor stock to 25 mL final volume with acetone. The ICV standard for analysis is then prepared by adding 50 µL of the pentane ICV stock in addition to the 400 µL of gas to the 18 mL of water. Alternatively, a second source of the gas mix from Supelco, Scotty cat#23462 with just the methane, ethane, ethene and acetylene may be used for the ICV when only those compounds are being targeted for analysis. The concentrations of the gases in the ICV are as follows:

Concentration of Gases in ICV Standard

Gas	Concentration (µg/L)
Methane	146.0
Ethane	255.3
Ethene	273.7
Acetylene	237.0
Propane	401.4
Isobutylene	510.7
Butane	529.0
Pentane	278.2

7.3.4 Non-Routine Compounds

Other, non-routine compounds not listed in this section may be requested by a client and may be added to this procedure.

7.3.4.1 In these cases, all stock solutions will be obtained from commercial sources and will be verified with a second-source standard as described in Section 7.2 above.

7.3.4.2 Non-routine standards will be stored and treated as described in Section 7.3.1 above or as specified by the manufacturer.

7.3.4.3 Subsequent dilutions of specially requested compounds will be determined in a manner consistent with the client's recommendations for number of calibration points, inclusion of reporting limit, and concentration range adequate to represent the linearity of the instrument.

7.3.4.4 These specially requested, non-routine compounds either may be added to the dilution scheme used for routine compounds or

may be prepared as a separate calibration.

7.3.4.5 All standards preparation for non-routine compounds shall be documented using the same method that is used for routine compounds.

7.3.5 Continuing Calibration Verification (CCV) Standard:

CCV standards are prepared from the same Matheson Tri-Gas gas stock as the ICAL standards. The concentrations of the gases in the CCV are equivalent to the Level 4 standards shown in Table 2.

7.3.6 Laboratory Control Sample:

The LCS is fortified with the second source gas mix at the concentration of two times the level 4 calibration standard (see Table 2) using deionized water via cannula transfer in the same fashion as the samples.

7.3.7 Matrix Spike/Matrix Spike Duplicate:

The matrix spike (MS) and matrix spike duplicate (MSD) is created by fortifying a portion of an actual sample with the second source gas mix at two times the concentration of the level 4 calibration standard (see Table 2) in the same fashion as the calibration standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size[1]	Preservation[2]	Holding Time	Reference
Waters	VOA vial	40 mL	HCl, pH < 2; Cool, <6°C Not frozen	14 Days	Source Method (See Section 16.1)

[1] Care should be taken that no headspace is present in the sealed vials.

[2] Effervescing of carbon dioxide from alkaline waters will cause loss of the compounds of interest. Samples should be collected without acid if effervescence is observed. Exceptions such as this should be noted on the COC at the time of collection.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply. For SOPs that address only preparation, QC acceptance limits on the analytical results are not included. Refer to the appropriate SOP that describes the determinative method.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more

completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviation or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Method Performance Studies

An initial demonstration of capability (IDOC), retention time study, and a method detection limit study must be performed before using this method for the first time or if significant changes are made to the method. Afterward each new analyst must complete and IDOC and on-going proficiency must be demonstrated by each analyst on an annual basis. Current MDLs are found in the laboratory LIMS system. See Section 13 of this SOP for further details.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process. See QC Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

A method blank is prepared and analyzed with each batch of samples. The method blank consists of 18 mL of deionized water transferred via cannula. The method blank is subject to the entire extraction and analysis process. The acetone that is used to prepare the pentane stock solutions should be lot tested by preparing a solvent check. The solvent check is prepared by adding 125 µL of the acetone to 18 mL of the water that is used for the MB and is analyzed to the same specifications as listed here for the MB.

Acceptance Criteria: The method blank must not contain any analyte of interest at or above ½ the reporting limit or above one-tenth of the concentration found in the associated samples or >1/10 the regulatory limit whichever is greater.

Corrective Action: If the method blank exceeds allowable levels, the source of the contamination must be investigated and all associated samples re-prepared and reanalyzed. If the analyte was not detected in the samples, then the data may be reported with qualifiers (check project requirements to be sure this is allowed***)*** and it must be addressed in the project narrative.

9.5 Laboratory Control Sample (LCS)

An LCS is prepared and analyzed with each batch of samples. The LCS is prepared as described in Section 7.3.6.

Acceptance Criteria: In-house limits may be applied as described in Policy DV-QA-003P but must be no wider than 75-125%. For DoD QSM 5.0, limits are given in Appendix C of the QSM. Limits are stored in TALS.

Corrective Action: If LCS recoveries are outside of the established control limits, and the MS/MSD recoveries are also out of control limits then the system is out of control and corrective action must occur. If recoveries are above the upper control limit and the analyte(s) of interest is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.6 Matrix Spike Sample (MS) and Matrix Spike Duplicate (MSD)

One MS/MSD pair is required with each analytical batch. The MS and MSD samples are prepared as described in Section 7.3.7. For the DoD QSM 4.2 or QSM 5.0, the MS/MSD must be from the project site and if insufficient sample is available to analyze the MS/MSD pair, this is documented in an NCM but no LCSD is performed. Likewise the analyst should inform the project manager, through an NCM, if the MS/MSD is not specified by the client but is prepared using another sample from another client's project.

Acceptance Criteria: The MS/MSD recoveries and relative percent difference (RPD) between the two results must be within historical control limits, which are based on three standard deviations of past results, using a minimum of 20 points. QC limits are reviewed on an on-going basis as QC data are developed, and limits are updated annually. Current

control limits are in the TALS. The relative percent difference must be no wider than ± 20%.

Corrective Actions: The information obtained from MS data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If the MS and/or MSD recovery falls outside of the established control limits, the bracketing CCV and batch LCS recoveries must be within control limits in order to accept results for the associated samples. The following corrective actions are required for MS/MSD recovery failures to rule out lab error:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly (e.g., very low or very high recoveries);
- Consider objective evidence of matrix interference (e.g., heterogeneous sample, interfering peaks seen on chromatograms, or interference demonstrated by prior analyses);
- Flag the data for any results outside of acceptance limits.
- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample inhomogeneity; and flag the data.
- If both the parent sample and associated matrix spike results are over range the parent and the spikes shall be diluted by the same amount and the results from the reanalysis reported for both. If the analyte concentration in the parent sample is greater than four times the concentration of spike added, then spike recovery results are not compared to control limits, and the recovery is either reported as “NC” (not calculated) or with a qualifier flag to indicate that the spike was less than four times the analyte concentration in the sample. If the dilution will cause the spike to be less than two times the reporting limit, the MS/MSD do not need to be diluted and the recovery reported as “NC” (not calculated).
- For MS/MSD that serve as batch QC, if the parent sample result is within the calibration range and the MS/MSD results are above the calibration range, the results are reported with the MS/MSD result being flagged as an over-range measurement (e.g., the E-flag qualifier).

- If the MS/MSD are client requested, the parent sample result is within calibration range and the MS/MSD results are above the calibration range, the sample and spike should be diluted, keeping in mind that we need to assess whether or not the dilution will best serve the client's needs. Consult with the PM as needed. Both the parent sample and MS/MSD samples must have the same dilution factor. Some EDDs do not accept data that are at different dilution factors.
- If the native analyte concentration in the MS/MSD sample exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated) and the appropriate qualifier flags are added.

NOTE: See Denver Policy Memorandum P16-001 and Corporate Policy Memorandum CA-Q-QM-013 for more detail.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

9.7 Sample Duplicate (DU)

One sample duplicate is required with every 10 samples.

Acceptance Criteria: The duplicate relative percent difference (RPD) between the two results must be ≤20%.

Corrective Actions: If the RPD exceeds acceptance limits, the samples must be reanalyzed. If the RPD exceeds the limit upon reanalysis, report the data with the appropriate qualifier. In cases where the results are less than the RL and estimated this condition may be noted in an NCM and no further action is necessary.

10.0 Calibration and Standardization

10.1 TestAmerica Denver gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

10.1.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-P-003 *Calibration Curves and the Selection of Calibration Points* and under the public folder, *Arizona Calibration Training.*

10.1.2 Use the ChemStation chromatography data system to set up GC conditions for calibration. See Table 1 for typical operating conditions.

10.2 Initial Calibration (ICAL)

An initial calibration (ICAL) is performed after installing a new column and prior to analyzing samples. An ICAL is also performed whenever the initial or continuing calibration verification (ICV or CCV) analysis fails acceptance criteria, following major repair of the instrument, following maintenance that affects data quality, or when, in the judgment of the analyst, the GC performance is suspect.

10.2.1 The laboratory analyzes 7 calibration levels (as shown in Table 2) for the dissolved gases. The lowest point on the calibration curve is below the standard RL. The preparation of the calibration standards is described in Section 7.3.2.

10.2.2 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours. The ICV should be analyzed after the final calibration point is analyzed and accepted.

10.2.3 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious mis-injection explained in the run log), then one point might be rejected, but only if all of the following conditions are met:

10.2.3.1 The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and

10.2.3.2 The lowest remaining calibration point is still at or below the project reporting limit; and

10.2.3.3 The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and

10.2.3.4 The calibration must still have the minimum number of calibration levels required by the method, i.e., five levels for calibrations modeled with average calibration factors or linear regressions, or six levels for second-order curve fits.

10.2.4 Calibrations are modeled either as average response factors (RF) or as calibration curves, using a systematic approach to selecting the optimum calibration function in order as described in the following sections.

10.2.5 Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems found must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

10.3 External Standard Calibration

External standard calibration involves the comparison of instrument responses (e.g., peak area or peak height) from the target compounds in the sample to the responses of the target compounds in the calibration standards. The ratio of the detector response to the amount or concentration of target analyte in the calibration standard is defined as the calibration factor (CF), as follows:

$$CF = \frac{A_S}{C_S} \qquad \textit{Equation 3}$$

Where:

A_s = Peak area (or height) of the analyte or surrogate in the calibration standard.

C_s = Concentration of the analyte or surrogate, in ng/mL, in the injected calibration standard.

10.4 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors or as calibration curves, using a systematic approach to selecting the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until the calibration acceptance criteria are met.

10.4.1 Linear Calibration Using Average Calibration Factor

Tabulate the peak area response for each target analyte in each calibration level against the concentration injected. For each analyte in each calibration standard, calculate the calibration factor (CF) as shown in Equation 3 above. The calibration factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

For each target analyte, calculate the average calibration factor as follows:

$$AverageCalibrationFactor = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n} \qquad \textit{Equation 4}$$

Where:

CF_i = Calibration factor for the i^{th} calibration level.

n = The number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{CF}} \times 100\% \qquad \textit{Equation 5}$$

Where SD is the standard deviation of the average CF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)^2}{n-1}} \qquad \textit{Equation 6}$$

10.4.2 Evaluation of the Average Calibration Factor

The calibration relationship can be graphically represented as a line through the origin with a slope equal to the average calibration factor. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

Note: The use of grand average (evaluation of the average response over all the compounds) is no longer allowed. Each compound must meet the RSD criteria.

Acceptance Criteria: The RSD must be ≤ 20%.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

10.4.3 Linear Calibration Using Least-Squares Regression

Calibration using least-squares linear regression produces a straight line that does not necessarily pass through the origin. The calibration relationship is constructed by performing a linear regression of the instrument response (peak area or peak height) versus the concentration of the standards. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = ax + b \qquad \textit{Equation 7}$$

Where:

y = Instrument response (peak area or height).

x = Concentration of the target analyte in the calibration standard.

a = Slope of the line.

b = The y-intercept of the line.

For an external standard calibration, the above equation takes the following form:

$$A_s = aC_s + b \qquad \textit{Equation 8}$$

To calculate the concentration in an unknown sample extract, the regression equation (Equation 8) is solved for concentration, resulting in the following equation, where C_s is now C_e, the concentration of the target analyte in the unknown sample extract.

$$C_e = \frac{A_e - b}{a} \qquad \textit{Equation 9}$$

Where:

A_s = Area of the chromatographic peak for the target analyte in the calibration standard.

A_e = Area of the chromatographic peak for the target analyte in the sample extract.

a = Slope of the line as determined by the least-squares regression.

C_s = Concentration of the target analyte in the calibration standard.

C_e = Concentration of the target analyte in the sample extract.

b = Intercept of the line as determined by the least-squares regression.

10.4.3.1 Linear Regression Evaluation

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. The August 7, 1998 EPA memorandum “Clarification Regarding Use of SW-846 Methods”, Attachment 2, Page 9, includes the statement “The Agency further recommends the use of this for weighted regression over the use of an unweighted regression.”

Acceptance Criteria: To avoid bias in low level results, the absolute value of the intercept must be significantly less than the reporting limit, and preferably less than the MDL. Also examine the residuals (as discussed above), but pay particular attention to the residuals at the low end of the curve. If the intercept or the residuals are large, a second-order regression should be considered.

The linear regression must have a correlation coefficient ≥ 0.990. Some programs require r ≥ 0.995. DoD QSM 5.0 requires r^2 ≥0.99.

Corrective Action: If the correlation coefficient falls outside the acceptance limit, linear regression cannot be used and a second-order regression should be attempted

10.4.4 Second-Order Regression

Calibrations using second-order regression produce a calibration function in the following form:

$$y = ax^2 + bx + c$$

Where:

y	=	instrument response for analyte (area)
x	=	concentration of standard (ug/L)
a	=	factor for second-order term (curvature)
b	=	factor for linear term
c	=	intercept

NOTE: Second order curves are not allowed for South Carolina work.

10.4.4.1 Non-Linear Calibration Evaluation

A minimum of six points must be used for a second-order regression fit. Second-order regressions should be the last option. Note that some programs (e.g., South Carolina) do not allow the use of second-order regressions. Before selecting a second-order regression calibration model, it is important to ensure the following:

- The absolute value of the intercept is not large relative to the lowest concentrations being reported.
- The response increases significantly with increasing standard concentration (i.e., the instrument response does not plateau at high concentrations).

The distribution of concentrations is adequate to characterize the curvature.

Acceptance Criteria: The coefficient of determination must be ≥ 0.990.

Corrective Action: If the coefficient of determination falls below the acceptance limit and the other calibration models are

unacceptable, the source of the problem must be investigated and the instrument recalibrated. Third-order regressions are not allowed at TestAmerica Denver.

10.5 Initial Calibration Verification (ICV)

Analysis of an ICV is performed after each ICAL. The preparation of the ICV standard is described in Section 7.3.3.

Acceptance Criteria: The result for the ICV must be within ± 20% of the expected value on both columns.

NOTE: For West Virginia work, the acceptance criterion for the ICV is ± 15%.

Corrective Action: If the measured value of the ICV is more than 20% different from the expected value, the accuracy of the standards used for calibration should be re-verified. If a problem is found then correct the issue and reanalyze the ICV. The instrument must be recalibrated before analyzing samples.

10.6 Continuing Calibration Verification (CCV)

A CCV is analyzed after every 10 samples and at the end of the analytical sequence. Some programs require that the concentration of the CCV be analyzed at two concentrations (a mid point and one at the RL) when second order calibration fits are used.

Acceptance Criteria: Any analyte that is reportable as found must be bracketed by acceptable CCVs on both columns. A CCV result is acceptable if the absolute value of the difference between the result and the accepted value is ≤20%.

In some cases, the nature of the samples being analyzed may be the cause of the failing %D. When the %D for an analyte falls outside of ± 20% in the CCV, and that analyte is detected in any or all of the associated samples, then those samples must be reanalyzed (at a dilution if column damage is eminent) to prove a matrix effect. If the drift is repeated in the reanalysis, the analyst must generate an NCM for this occurrence to explain that the drift was most likely attributable to the sample matrix and that the samples may be diluted and reanalyzed to minimize the effect if so desired by the client.

NOTE: For West Virginia work, the acceptance criterion for the CCV is ± 15%.

Corrective Action: If the acceptance limit is exceeded on either column, corrective action must be taken. This may include clipping the column or other minor instrument adjustments, followed by reanalyzing the standard. If the criterion is still not met, a new calibration curve must be prepared and all samples analyzed since the last successful CCV must be reanalyzed.

As an alternative DoD QSM 5.0 allows the laboratory to analyze two additional consecutive CCVs within one hour of the failed CCV. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and recalibrate: then reanalyze all affected samples since the last acceptable CCV.

If a DoD client accepts TestAmerica's Technical Specifications for DoD QSM work, samples that have no detections when a CCV has recoveries above the project acceptance limits would be reported with a case narrative comment, in addition to applying any data qualifier flags required by the project.

10.7 Retention Time Windows

Retention time (RT) windows must be determined for all analytes.

10.7.1 Determine new RT windows each time a new column is installed, after a major adjustment to the instrument conditions, or annually, whichever is most frequent.

10.7.2 Make an injection of all analytes of interest each day over a 72-hour period.

10.7.3 Calculate the mean and standard deviation for the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RT_i - \overline{RT}\right)^2}{n-1}} \qquad \textit{Equations 12 \& 13}$$

Where:

RT_i = Retention time for the i^{th} injection.
n = Number of injections (typically 3).
SD = Standard deviation.

10.7.3.1 Set the width of the RT window for each analyte at ± 3 standard deviations of the mean RT for that analyte.

10.7.3.2 The center of the RT window for an analyte is the RT for that analyte from the last of the three standards measured for the 72-hour study.

10.7.4 Default RT windows may be used to accommodate variation in retention times caused by changes in peak shape due to concentration. These default windows, listed below, are used unless the calculated windows are wider.

Analyte	Default RT Window (min)
Methane	±0.03
AcetyleneEthane (coeluting pair)	±0.04
Ethene (Ethylene) Ethane Acetylene	±0.05
Propane	±0.06
Pentane	±0.15
Isobutylene Butane ButaneIsobutylene (coeluting pair)	±0.20

10.7.5 The center of the window for each analyte is updated with the RT from the level 4 standard of the ICAL or the CCV at the beginning of the analytical sequence. The width of each window remains the same until new windows are generated following the installation of a new column, or in response to an RT failure.

11.0 Procedure

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

11.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.3 Allow all samples and standards to warm to room temperature before transferring to vials for analysis.

11.4 Transfer 18 mL of the sample using a 12" cannula needle to a 22 mL headspace vial with a crimp septum cap that is marked to contain 18 mL. Insert a pressure relief valve (needle or cannula) through the septum about 3 mm into the 22 mL headspace vial. Insert a transfer cannula into the 40 mL VOA sample vial about three-quarters of the way down into the vial. Insert the other end of the cannula into the 22 mL headspace vial all of the way to the bottom of the vial. Pressurize the 40 mL VOA vial with a stream of N_2 gas with a flow of about 14-20 mL per minute. Remove the pressure gas after about 15 mL of volume has been transferred and pull the cannula out of the headspace vial when the 18 mL transfer is complete and allow the pressure to equilibrate through the pressure relief for a few seconds. Pull the cannula to above the liquid in the 40 mL VOA vial (to stop the flow of liquid). Remove the pressure relief valve. Shake the headspace vial vigorously for 10-15 seconds and store inverted until ready to load on the headspace analyzer.

NOTE: The volume of each lot of vials used in analysis must be verified as described in Section 6.1.2.

11.5 Measure the pH of the remaining sample using a pH strip and record it in the run log. Prepare an NCM for any samples with a pH $\geq$ 2.

11.6 Instrument Troubleshooting and Maintenance

Before the start of any daily sequence the instrument should be evaluated for possible maintenance. Generally the instrumentation used for this method does not require any routine maintenance.

11.6.1 If the previous run ended with a failing continuing calibration then system maintenance should be performed to bring it back into control.

11.6.1.1 A reduced response may indicate that the system needs to be evaluated for leaks.

11.6.1.2 Poor peak shape may be an indication that the columns need to be replaced.

11.6.1.3 The most common maintenance issues are typically related to a malfunctioning sample table and autosampling apparatus. If a malfunction is suspected then service the apparatus to restore it to normal operating condition.

11.6.1.4 Re-calibration should not be used to correct for maintenance related issues. Always document any maintenance procedure in the maintenance logbook.

11.7 Samples are automatically injected onto two columns. Samples, standards, and QC samples must be introduced into the GC using the same procedure.

11.7.1 TestAmerica Denver gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data. Use the ChemStation chromatography data system to set

up GC conditions for calibration. See Table 1 for typical operating conditions.

11.7.2 Prepare calibration standard solutions in headspace vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

11.7.3 Unprocessed calibration data are transferred to the Chrom database for processing. See Section 10 regarding selection of the appropriate calibration model. After processing the calibration data, print the calibration report and review it using the calibration review checklist (GC and HPLC Data Review Checklist - ICAL). Submit the calibration report to a qualified peer or the group leader for final review. The completed calibration reports are scanned and stored as Adobe Acrobat files on the Public Drive.

11.8 Load each sample, as well as the various standards and QC samples, into the autosampler.

11.9 The daily run sequence is documented in a bound log book, and should be as follows:

Primer (generally the primer is run twice)
Daily opening CCVs
LCS
LCSD
Method Blank
9 samples plus duplicate
CCVs
Followed by cycles of 9 samples, second duplicate, and CCVs as needed
Closing CCV

11.10 Daily Retention Time Windows

The center of the retention time (RT) windows determined in Section 10.7 are adjusted to the RT of each analyte as determined in the initial 12-hour calibration verification. The centers of the RT windows must be updated at the beginning of each analytical sequence and with each 12-hour calibration, but not for any other calibration verification standards.

11.11 Upon completion of the analytical sequence, transfer the raw chromatography data to the Chrom database for further processing.

11.11.1 Review chromatograms online and determine whether manual data manipulations are necessary.

11.11.2 All manual integrations must be justified and documented. See DV-QA-011P, *Acceptable Manual Integration Requirements.*

11.11.3 Manual integrations may be processed using an automated macro, which prints the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature.

11.11.4 Alternatively, the manual integration may be processed manually. In the latter case, print both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration. Manual integrations that are documented in this manner must be scanned into the documents section of the analytical batch.

11.12 Compile the raw data for all the samples and QC samples in a batch. The preparation batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD.

11.12.1 The data package should consist of the checklist, sequence(s), ICAL cover, ICAL summary and history used for data quantitation and the prep batch paperwork. The sequence(s) and ICAL summary should be scanned into the TALS database documents section.

11.12.2 Perform a Level 1 data review and document the review on the data review checklist, GC Data Review Checklist/Batch Summary (See SOP DV-QA-0020.)

11.12.3 Submit the data package and review checklist to the peer reviewer for the Level 2 review. All manual integrations must be evaluated by the peer reviewer and this review as well as the remainder of the Level 2 review must be documented by date and initial on the review checklist initiated at the Level 1 review. The data review process is explained in SOP DV-QA-0020.

12.0 Calculations / Data Reduction

12.1 Qualitative Identification

12.1.1 Tentative identification occurs when a peak is found on the primary column within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if qualified data (J flags) are to be reported. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmation column. Absolute retention times are adjusted according to the retention times of the daily opening CCV.

12.1.2 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2 Corrective Action for Retention Times

The retention times of all compounds in each continuing calibration must be within

the retention time windows established in Section 10.7. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed.

12.3 Dual-Column Quantitation

12.3.1 Each sample is analyzed on two different columns at the same time. The laboratory designates a primary column based on optimal separation of the compounds of interest and other desirable chromatographic characteristics. The result from the primary column is normally reported. If the continuing calibration verification fails on one of the columns, the appropriate corrective action must be taken. (See Section 10.6.) The result from the secondary (confirmatory) column may be reported if any of the following is true:

12.3.1.1 There is obvious chromatographic interference on the primary column.

12.3.1.2 The difference between the result for the primary column and the result for the secondary column is > 40% and chromatographic interference is evident on the primary column.

12.3.1.3 For DoD QSM 4.2 or QSM 5.0 work, calibration and QC criteria for the second column are the same as for the initial or primary column analysis.

12.3.2 Dual Column Results With > 40% RPD

12.3.2.1 If the relative percent difference (RPD) between the responses on the two columns is greater than 40%, the higher of the two results is reported unless there is obvious interference documented on the chromatogram.

12.3.2.2 If there is visible positive interference, e.g., co-eluting peaks, elevated baseline, etc., for one column and not the other, then report the results from the column without the interference with the appropriate data qualifier flag, footnote, and/or narrative comment in the final report.

12.3.2.3 If there is visible positive interference for both columns, then report the lower of the two results with the appropriate flag, footnote, and/or narrative comment in the final report.

12.3.2.4 The RPD between two results is calculated using the following equation:

$$\%RPD = \frac{\left|R_1 - R_2\right|}{\frac{1}{2}\left(R_1 + R_2\right)} \times 100\% \qquad \textit{Equation 14}$$

Where R_1 is the result for the first column and R_2 is the result for the second column.

12.4 Calibration Range and Sample Dilutions

12.4.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover.

12.4.2 If the samples have results at or above the RL for the analyte(s) that were found to be over the calibration range in the high sample, they must be reanalyzed to rule out carryover, unless other objective evidence indicates that the detection is not the result of carryover. Such evidence may include an observation where carryover was not observed when samples or blanks were analyzed after another sample with similar high compound recovery or when the detection in the sample with suspected carryover is much higher than the expected amount of carryover (i.e. the sample's concentration may be similar to or higher than the concentration found in the previous sample).

12.4.3 It may also be necessary to dilute samples because of matrix interferences.

12.4.4 If the initial diluted run has no hits or hits below 20% of the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.4.5 2X, 3X, and 4X dilutions are prepared using the same Cannula transfer technique, but with 9 mL, 12 mL, or 13.5 mL of reagent water added to the headspace vial before capping. For 3X and 4X dilutions, this will require an additional calibration check of the bottle-top dispenser. The same reagent water is used to prepare the MB and LCS. Using a cannula to transfer the sample targeted for dilution carefully fill the vial (and diluent) to the 18 mL mark with sample.

12.4.6 For transferring sample volumes that are less than 2 mL (greater than an approximately 10x dilution) it is recommended that the analyst use a gastight syringe to measure the sample volume. The gastight syringe should be filled using positive pressure in order to avoid degassing the sample as described here:

12.4.6.1 A 1 mL gas-tight syringe is inserted into a zero-headspace sample vial with the plunger loose in the top to avoid an airborne stream of sample from a pressurized sample but not air-tight so as to pull a vacuum on the sample on removing the plunger.

12.4.6.2 A 5 mL gas-tight syringe filled with air is inserted into the septum to pressurize the sample into the 1 mL syringe with the barrel removed. Keep the level of the pressurizing (5 mL)

needle above the level of the receiving (1 mL) needle. Dispose of the first fill to waste. Remove the 5 mL syringe and refill with air. Replace the 1 mL syringe without the barrel below the sample line, and insert the 5 mL syringe into the headspace to pressurize the sample into the receiving syringe.

12.4.6.3 If the sample is effervescing, the sample level should rise faster than the effervescence. Fill the receiving syringe to the top, so that there is no gap between the plunger and the sample. Wipe the receiving syringe with a paper towel and adjust the volume to the desired dilution.

12.4.6.4 Inject the sample into a sealed headspace vial that has been filled with the appropriate level of reagent water for the planned dilution and shake vigorously for 10-15 seconds. Rinse both syringes with deionized water.

12.4.7 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

12.4.8 Reporting Dilutions

12.4.8.1 Some programs (e.g., South Carolina) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported.

12.4.8.2 Some clients require use of dilution factors (“DF”) rather than initial and final volumes. This will be noted in the method comments.

12.5 Interferences Observed in Samples

12.5.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

12.5.2 If interferences are evident that are suspected of causing false positive results, consult with the laboratory Project Manager to determine if analysis using additional confirmation techniques is appropriate for the

project. Use of additional confirmation columns is another possible option, however caution is warranted in order to rule out false negatives. At a minimum, an NCM should be prepared by the analyst and should include the following comment for inclusion in the case narrative:

"*Based on review of the chromatograms for samples _____, it is my opinion that the evident interferences may be causing false results.*

Date _____ Analyst _____"

12.5.3 Sample dilution may be the only acceptable recourse to resolve detections when large amounts of non-target matrix are observed.

12.6 Calculations

12.6.1 Spike Recovery Calculation

LCS, MS, and MSD spike recoveries are calculated using the following equation:

$$\%\ Recovery = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

12.6.2 MS/MSD RPD Calculation

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)}$$

Where:

R_1 = result for the MS
R_2 = result for the MSD

12.6.3 Concentration of Analyte in Sample

The concentration of the analyte in the sample is calculated as follows:

$$C_S = C_C \times DF$$

Where:

C_s = concentration of analyte in sample (µg/L)
C_C = on-column concentration (ng/mL)
DF = Dilution Factor, post extraction dilutions

12.7 All data are subject to two levels of review, which is documented on a checklist (see SOP DV-QA-0020). See also Section 11.12.

13.0 Method Performance

13.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

13.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

13.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

13.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

14.0 Pollution Prevention

Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

15.0 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

15.2 The following waste streams are produce when this method is carried out:

15.2.1 Methanol Vial Waste – Waste Stream A

15.2.2 Liquid Methanol Waste – Waste Stream C

15.2.3 Acidified Water – Waste Stream W

15.2.4 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

16.0 References / Cross-References

16.1 RSK SOP-175 Revision 0, R.S. Kerr Environmental Research Laboratory; August 11, 1994.

16.2 Method 8000B, "Test Method for Evaluating Solid Waste", EPA SW-846, Update III; December, 1996.

16.3 Quality Systems Manual (QSM) for Environmental Laboratories, DoD Quality Systems Manual Version 5.0, July 2013.

17.0 Deviations From the Source Method

17.1 The method measures the concentration of the gases in the headspace and then calculates the concentration of the gas dissolved in the original water sample based on its partitioning properties, as indicated by its Henry's Law constant. This has been modified for this SOP by calibrating against the concentration of dissolved gases in water standards instead of the concentration of gases in the sample headspace.

17.2 The procedure for determination of retention time windows for SW 846, Method 8000B or 8000C is followed with the exception that default minimum windows that exceed the minimum window of ± 0.03 minutes is used, based on experience with the list of target compounds in this SOP and the use of headspace analysis.

17.3 The maximum allowable control limits for the LCS used in this SOP is 75-125%. Due to the addition of other compounds the source method criteria of 85-115% was extended. The limits study performed by DoD EDQW and published in DoD QSM 5.0 confirm that these wider limits are statistically supported.

17.4 The acceptance criteria for the CCV used in this SOP is 20% rather than the 15% stated in the source method. This is consistent with Method 8000C and DoD QSM 5.0. The state of West Virginia requires adherence to the source method criteria.

18.0 Attachments

Table 1 – GC Operating Conditions
Table 2 – Initial Calibration Levels
Table 3 – Standard Reporting Limits
Table 4 – Elution Order and Analyte Number

Attachment 1 – Example Calculation of ICAL Concentrations
Attachment 2 – Example Chromatograms

19.0 Revision History

- Revision 9, dated 08 December 2017
  - Annual Review
- Revision 8, dated 20 October 2016
  - Added note to ICV and CCV criteria to meet source method requirement of ± 15% for West Virginia work, Sections 10.5 and 10.6.
  - Revised corrective actions for failed MS/MSD to comply with current policy, Section 9.6
- Revision 7, dated 31 October 2015
  - Revised section 9.6 to reflect current practice
  - Revised Section 10.1.1 to reference new Corporate SOP number for calibration curves
  - Revised Section 10.4.2 to update RSD to method and DoD Requirements
  - Revised Section 10.7.5 to reflect minimum RT windows
  - Moved statement to warm samples to new Section 11.3 from original Section

11.6.
- Revised Section 11.11.3 to reflect current practice
- Revised Section 12.2 for corrective actions due to RT shifts outside established windows to reflect requirements of SW 846 and DoD QSM 5.0
- Added Section 12.4.6 to describe how to perform sample dilutions
- Added Sections 12.5.2 and 12.5.3 to address documentation of potential false positives.
- Revised Section 13 to reflect current practice
- Added Table 4 to document elution order for analytes on both columns
- Updated chromatogram to reflect current data system and revised list of attachments accordingly.
- Added reference to DoD QSM 5.0 to Section 16.
- Added Sections 17.2 -17.4.
- Removed references to AFCEE
- Archived revision history for revisions created prior to 2011.
- Formatting and editorial changes throughout

- Revision 6, dated 30 September 2014
  - Revised section 4.1 regarding carryover
  - Added information regarding location of electronic spreadsheet for pipette calibration in section 6.1.2
  - Added specification of instrument ID in section 6.2.1
  - Revised section 9.1 to reflect current practice
  - Added DoD QSM 5 QC and calibration criteria throughout
  - Added statement to Section 10.5 regarding corrective action for out of control ICV
  - Added information regarding frequency of determining RT window
  - Added new section 11.4, Instrument Troubleshooting and Maintenance
  - Added statement in Section 11.9.4 regarding documentation for manual integration processed manually.

- Revision 5, dated 31 July 2013
  - Added vial calibration information to section 6.1.2
  - Updated sections 7.3.2, 7.3.3, 9.4, 9.6, 9.7, 11.4.2, 11.9.1 and 12.4 to reflect current practices
  - Updated references to “Target” to “Chrom” through out document
  - Added Chrom example chromatogram (Attachment 2)
  - Added elution order and analyte number (table 3)

- Revision 4, dated 30 July 2012
  - Added references to new analytes throughout the SOP
  - Added reference to the fracking industry to Section 1.2
  - Updated Section 6 with new equipment/column information
  - Revised calibration standards to include new analytes and current concentrations
  - Expanded calibration section to include new analytes
  - Updated section 7.3.5 to current gas vendor.
  - Updated section 11.2 to reflect current practices
  - Updated tables to include new analytes
  - Added South Carolina requirements to Section 13.1

- Revision 3, dated 22 July 2011
    - Revised calibration standards
    - Expanded calibration section
    - Clarified requirement for calibration verifications to meet criteria on both columns, not just the primary column or column used for quantitation.

Earlier revision histories have been archived and are available upon request.

TABLE 1 – GC Operating Conditions

Parameter	Recommended Conditions
Injection Port Temperature	200° C
Detector Temperature	250° C
Oven Temperature	45°C held for 2.4 minutes, ramped at 19.33°/min to 74°, ramped at 1°/min to 77° and held for 0.25 minutes, ramped at 30°/min to 125° and held for 2.6 minutes.
Column 1	RT-U-Bond 30 m x 0.32 mm x 10 um
Column 2	RT-S-Bond 30 m x 0.32 mm x 10 um
Injection Volume	1 mL
Carrier Gas and Flow Rate	Helium 30 psi (~8.2 mL/min) held for 2.5 minutes, ramped at 10psi/min to 40psi and held for 1 minute (~11.3 mL/min), ramped at 15psi/min to 55psi (~18.5 mL/min, decreasing to ~15.2 mL/min at 125°)
Detector Gases and Flow Rates	Hydrogen/Air 40 mL/min, makeup nitrogen at 25 mL/min
Y Splitter	Yes

TABLE 2 – Initial Calibration Levels

	Concentration in Aqueous Phase (µg/L)[1]						
Compound	**Level 7**	**Level 6**	**Level 5**	**Level 4**	**Level 3**	**Level 2**	**Level 1**
Methane	365.0	2098	7373	73.00	14470	1.825	0.8125
Ethene	638.3	510.6	255.3	127.6	25.53	3.191	1.595
Ethane	684.2	547.4	273.7	136.8	27.37	3.421	1.710
Acetylene	592.5	474.0	237.0	118.5	23.70	2.962	1.481
Propane	1003	802.8	401.4	200.7	40.14	5.017	2.508
Isobutylene	1276	1021	510.7	255.3	51.07	6.384	3.192
Butane	1322	1058	529.0	264.5	52.90	6.613	3.306
Pentane	695.5	556.4	278.2	139.1	27.82	5.564	2.782

[1]These are estimated concentrations. Actual concentrations will vary slightly when the calibration standards are prepared.

TABLE 3 – Standard Reporting Limits

Compound	(ug/L)
Acetylene	5.0
Butane	5.0
Ethane	5.0
Ethene	5.0
Isobutylene	5.0
Methane	5.0
Pentane	5.0
Propane	5.0

TABLE 4 – Elution Order and Analyte Number

Analyte	Column A	Column B
Methane	1	1
Ethylene	2	2
Ethane	3	NA
Acetylene	5	NA
Acetylene/Ethane	NA	4
Propane	6	6
Butane/Isobutylene	8	NA
Butane	NA	9
Pentane	10	10
Isobutylene	NA	7

Attachment 1 – Example Calculation of ICAL Concentrations

This example is for methane at the 7th calibration level, where 1,000 µL of the stock standard (10,000 ppmV) is used..

The calculation is based on the Ideal Gas Law: PV = nRT

Where:

P	=	pressure in atmospheres (760 mm Hg = 1 atmosphere)
V	=	volume of gas in liters
n	=	number of moles of gas
R	=	gas constant, i.e., 08206 atm L / mol K
T	=	temperature in degrees Kelvin (T = °C +273.15)

Calculations for the standards are based on 22°C at 754 mm Hg, therefore

P	=	754/760 = 0.99211 atm
V	=	1 L of stock standard gas
R	=	0.08206
T	=	22 + 273.15 = 295.15 °K

Solving for n (number of moles),

$$n = \frac{PV}{RT} = \frac{0.99211\,atm \times 1L}{0.08206\,atm \bullet L/mole \bullet K \times 296.15K} = 0.04082 \text{ moles of methane in 1 L standard}$$

NOTE: Daily variations in laboratory temperature and pressure create less than 1% variation.

The following equation is used to calculate the concentration of methane in the Level 7 ICAL standard:

Methane concentration in Level 7 ICAL standard

$$= \frac{0.001\ L\ N_2}{0.018\ L\ H_2O} \times \frac{0.01\ L\ CH_4}{1.0\ L\ N_2} \times \frac{0.04082\ mole\ CH_4}{1.0\ L\ CH_4} \times \frac{16.04\ g\ CH_4}{1.0\ mole\ CH_4}$$

$$= 0.00036375\ g\ CH_4/L\ H_2O$$

$$= 363.8\ ug/L$$

Where:

0.001 L N_2	=	Volume of gas (in L) used to prepare the aqueous standard.
0.018 L H_2O	=	Volume of water in which the standards are prepared.
0.01 L CH_4	=	Volume of methane in 1.0 L of the gas standard, which is a 1% methane mixture in N_2
0.04082 mole CH_4	=	Number of moles of methane in 1.0 L of methane as determined above
16.04 g CH_4	=	Molecular weight of methane

Attachment 2
Example Chromatogram

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Semivolatile Petroleum Products Method for Soil and Water [Method NWTPH-Dx mod]

Approvals

Signatures on File

Ryan Zboralski Date
Semivolatile Organic Department Manager

Manjit Nijjar Date
Health & Safety Manager / Coordinator

Manjit Nijjar Date
Quality Assurance Assistant
For Terri Torres
Quality Assurance Manager

Dennis Bean Date
Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This SOP delineates the procedure for the identification and quantitation of semivolatile petroleum products using the WA DOE NWTPH-Dx method. This method is applicable to both soils and waters. Waters may be collected in either 1-liter or 250-ml sample jars.

1.1.2 This SOP does not include the procedures for extracting soil and water samples. Refer to the following SOPs for sample extraction procedures.

TA-OP-0301	Liquid-Liquid Extraction by Separatory Funnel, SW846 3510C
TA-OP-0323	Continuous Liquid-Liquid Extraction, SW846 3520C
TA-OP-0302	Sonication Procedure, SW846 3550B
TA-OP-0367	Microwave Extraction 3546

1.1.3 Reporting Limits

NWTPH_Dx	1L water RL (mg/L)	250mL water RL (mg/L)	Soil (mg/kg)
C10-C24	0.11	0.25	30
Motor Oil	0.25	0.5	100

1.2 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

This method is used to identify, by pattern matching (“fingerprinting”), and quantitate semivolatile petroleum products. These products include kerosene, jet fuels, diesel oils, fuel oils, lubricating oils, hydraulic fluids, mineral oils and insulating oils such as transformer oils. Soil samples are weighed, dried, surrogate is added and extracted with methylene chloride. Water samples (1-liter or 250-mL volume) are acidified, surrogate is added and extracted with methylene chloride. Extracts are then concentrated and an aliquot of sample is analyzed by GC-FID. The hydrocarbons are quantitated against diesel (nC10-nC24) and motor oil (>nC24-nC36) standards (default) used for calibration and identified by pattern matching to the calibration standard or appropriate library spectra.

3.0 Definitions

3.1 Diesel Range Organics (DRO): The sum of compounds producing chromatographic peaks, both resolved and unresolved, eluting between n-decane (C_{10}) and tetracosane (C_{24}).

3.2 Motor Oil (MO): The sum of the compounds producing chromatographic peaks, both resolved and unresolved, eluting between tetracosane (C_{24}) and n-hexatriacontane (C_{36}).

3.3 Jet Propellant-4 (JP-4): The range is determined by injecting a standard purchased from a vendor and choosing the retention times from the initial low point of the chromatographic

peaks to the end of the resolved and unresolved peaks. The hydrocarbon range for this fuel is typically from Toluene to C_{12}; however, LIMS defines this range as n-octane through n-octadecane.

3.4 Jet Propellant-8 (JP-8): The range is determined by the same method as used for JP-4. The hydrocarbon range for this fuel is typically from Toluene to C_{12}; however, LIMS defines this range as n-octane through n-hexadecane.

3.5 Mineral Oil (Transformer Oil): The sum of the compounds producing chromatographic peaks, both resolved and unresolved, eluting between dodecane (C_{12}) and tetratriacontane (C_{34}).

3.6 Bunker C (Fuel Oil 6): The sum of the compounds producing chromatographic peaks, both resolved and unresolved, eluting between n-decane (C_{10}) and n-hexatriacontane (C_{36}); however, LIMS defines this range as n-dodecane (C_{12}) through n-octatriacontane (C_{38}).

4.0 Interferences

4.1 Solvents, reagents, glassware, and other equipment coming in contact with the extract may yield interferences.

4.2 Non-petroleum hydrocarbons (non-polar) will also be extracted using this procedure. Hydrocarbons eluting in the ranges described above for fuel hydrocarbons will be detected and reported as false positives. All semi-volatile results must be reported; atypical results should be qualified appropriately.

4.3 Phthalate esters are found in many materials commonly found in the laboratory. In particular, plastics should be avoided because phthalates are routinely used as plasticizers and are easily extracted from the plastic materials.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.2 There are areas of high voltage in both the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents

and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Gas Chromatograph, Hewlett Packard 6890 or equivalent with autosampler equipped with a capillary split/splitless injector and an FID.
- Chromatographic column types:

6.1.1 Phenomenex ZB-1: 30 meters x 0.25 mm ID x 0.10 um film thickness cut in half to give two (2) 15 meter columns for dual column capable instruments.

6.1.2 Phenomenex ZB-1: 15 meters x 0.25 mm ID x 0.10 um film thickness.

These are the primary types of columns currently in use. Equivalent versions/types from a different vendor may be substituted. Note that elution chromatography may vary based on the actual column in place.

6.1.3 Analytical Balance, accurate to at least 0.0001g

6.2 Software

6.2.1 Data acquisition system: Agilent's ChemStation, is used for data acquisition and storage on machine-readable media. Since no processing is done by ChemStation and since there are no audit trail functions associated with data acquisition, the audit trail feature for ChemStation may be either enabled or disabled. The other component, Chrom, is used for data processing such as the measurement of peak area or peak height. By design, the audit trail feature for Chrom is always enabled.

6.2.2 Data processing: Chrom version 1.2 or higher

6.2.3 TestAmerica LIMS (TALS), current version

6.3 Supplies

- Volumetric Flasks, 10 mL, 25 mL, 50 mL, 100 mL, 250 mL, Class A, ground glass stoppered
- Scintillation vials with Teflon-lined screw caps
- Glass standard vials with screw caps and Teflon-lined septum
- Autosampler vials, 1.5 mL, crimp top or equivalent
- 20 mL scintillation vials, with Teflon-lined lids or equivalent
- Centrifuge
- Pasteur pipette, disposable

7.0 Reagents and Standards

7.1 Document reagents/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Methylene Chloride (CH_2Cl_2), analytical reagent grade or equivalent.

7.3 Sodium sulfate, anhydrous powder, reagent grade or equivalent.

Note: Sodium sulfate must be muffled at 400 °C for 4 hours prior to use to avoid phthalate contamination.

7.4 Sulfuric acid, concentrated, trace metals grade or equivalent.

7.5 Petroleum product standards, Accustandard FUEL-SET, 20 (50) mg/mL in CH_2Cl_2 or equivalent.

7.6 Check the Balance logbook to determine if the daily calibration check has been completed. If it has not, the analyst must perform this check according to SOP TA-QA-0014.

7.7 Surrogate Stock Standard. Approximately 0.2 g of o-Terphenyl (99%, Aldrich) and 0.2g n-triacontane-d62 (both weighed to the nearest 0.0001 g), and (0.2g neat 4-Bromofluorobenzene (Aldrich, catalog # 1127COV) are diluted to a final volume of 100 mL with an 80:20 mix of DCM:acetone, providing a stock spiking solution of approximately 2,000 mg/L.

Note: n-Triacontane tends to precipitate out of acetone; therefore, the vial of surrogate should be checked for this, and mixed on the vortex until all crystals are back in solution.

7.8 Reference/Stock Standards. Prepare individual petroleum product reference/stock standards; kerosene, JP-5, transformer oil, and bunker crude fuel oil.

7.8.1 Add 5 to 10 drops or the pure petroleum product to a tared 10 mL volumetric flask. Record the weight to the nearest 0.0001g and bring to volume in methylene chloride, stopper and mix by inverting several times. Calculate the concentration of the standard using the equation below.

7.8.1.1 Stock Conc., ug/ml = $\frac{\text{(final wt, mg)-(tare wt, mg)}}{\text{10 mL}} \times \frac{\text{1,000 ug}}{\text{mg}}$

7.8.1.2 These standards are also used to ensure the proper identification of petroleum products by chromatographic pattern matching.

7.8.2 The use of commercially available standards is an acceptable alternative to the above procedure.

7.9 Calibration Working Standards. Using the stock standards, prepare calibration working standards for the identified petroleum product(s) to be quantitated. Serially dilute the reference/stock standard(s) to prepare calibration curve(s). Calibration standards must, at a minimum, provide a minimum 5 (five) point calibration curve, include a sufficiently low standard to provide necessary detection limits, and define a linear working range of the instrument. A mid-range calibration standard should also be prepared for calibration curve verification. The mid-range calibration standard concentration is varied within the instrument calibration range.

7.9.1 In order to be acceptable, each calibration curve must have an average %RSD value ≤ 15%, or a linear correlation coefficient (r) of at least 0.990 and none of the standards may vary from their true value by more than ± 15%. #2 diesel oil and motor oil are the default petroleum product for reporting purposes.

7.10 Retention Time Window Standard. The retention time standard is prepared by appropriately diluting the EPH aliphatic stock standard (EPH AL calstk_0000X), and TPH surrogates (TPH_SURR_0000X) to a final concentration of 20 ug/mL each, with a final volume of 25 mL. The standard contains nC8-nC40 plus surrogates, sans nC39.

7.10.1 Establishing Retention Time Windows. The retention time window for each hydrocarbon range is established using the lower limit of the first eluting compound and the upper limit of the last eluting compound. The upper and lower limits are established by adding or subtracting 3σ from the absolute retention time of the appropriate compound. Alternatively a default standard deviation of 0.01 may be used for a retention time window of 0.03 minutes (EPA Method 8000C section 11.6)

7.11 Diesel and Motor Oil Spiking Solution. A 50,000 ug/mL #2 diesel fuel and motor oil composite standard is prepared and ordered as a custom standard from Restek, part number CS-13305, in a 5:1 DCM:acetone solvent mixture. This standard is logged into the LIMS system as “TPH Spike_RZ_0000X”.

7.12 Other spiking solutions may be prepared using different petroleum products by appropriately diluting a stock standard to a 5,000 ug/mL working solution. #2 diesel and motor oil will be the default spiked products if sample contaminant is unknown.

7.13 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples may be collected in 1-liter or 250 mL amber glass bottles. Soil samples are typically collected in 4-oz. or 8-oz. glass jars. All sample containers must have Teflon-lined caps.

8.2 All samples shall be stored at 0-6°C after collection. Water samples should be preserved with 1+1 HCl to a pH of ≤ 2.

8.3 Holding time, from the date of sampling to extraction, is 14 days for soil and 14 days for water. Holding time from extraction to analysis is 40 days.

8.4

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Glass	1000 or 250 mLs	1:1 HCl, pH < 2; Cool 0-6°C	14 Days, Extraction 40 Days, Analysis	40 CFR Part 136.3
Soil	Glass	10 grams	Cool 0-6°C	14 Days, Extraction 40 Days, Analysis	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in SOP TA-QA-0620, Quality Control Program.

9.1.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed together using the same reagents and standards. Each quality control batch must contain a method blank (MB), a laboratory control sample (LCS), matrix spike (MS), and duplicate (DUP) pair. Matrix spike/matrix spike duplicate pairs are only performed for Tier 4 projects or by client request. For more details see SOP TA-QA-0620.

9.3 Method Blank (MB)

One method blank is analyzed with every preparation batch or every 20 samples, whichever is more frequent. The method blank consists of either 1 liter or 250mL of organic-free water (for batches of aqueous samples) or 10 grams of Ottawa sand (for batches of soil samples). The method blank is processed exactly as samples in the batch, and is used to assess whether the laboratory processes have contaminated the samples in the batch.

Acceptance Criteria: Surrogate recoveries must fall within acceptance criteria and the results for the method blank must be less than or equal to the reporting limit concentration or less than 10% of the concentration found in the associated samples. DOD and BP LaMP require MB to be ≤ ½ RL.

Corrective Action: If the method blank acceptance criteria are not met, identify and correct the source of contamination, and re-prepare and reanalyze the associated samples.

9.4 Laboratory Control Sample (LCS)

One LCS is analyzed with every preparation batch or every 20 samples, whichever is more frequent. The LCS (and LCSD as appropriate) consists of either 1 liter or 250mL of organic-free water (for batches of aqueous samples) or 10 grams of Ottawa sand (for batches of soil samples), to which 100 µL of spike solution is added. See Table III for spike levels. The LCS is processed exactly as samples in the batch and is used to assess the accuracy of the analytical system. In the case where insufficient volume is provided for the extraction of an MS/MSD or duplicate sample, an LCSD will also be prepared.

Acceptance Criteria: The percent recovery of the analytes of interest must fall within the established control limits. For all other methods, the control limits are set at ± 3 standard deviations around the calculated mean of the historical LCS recovery data, unless project-specific control limits apply. Current control limits are stored in the laboratory LIMS. See SOP TA-QA-0620 for further details.

Corrective Action: If LCS acceptance limits are not met, the LCS should be reanalyzed once to confirm that the original analysis is reliable. If the results are still outside control limits, the associated samples must be re-extracted and reanalyzed. If the LCS recovery is above the upper control limit, and the associated samples are all below reportable concentrations, the deviation may be described in an NCM, if this is acceptable to the client or allowed by the specific program or project.

9.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

When specifically requested, one matrix spike (MS) and one matrix spike duplicate (MSD) are prepared by spiking replicate portions of the selected field sample with the same spiking standard that is used for the LCS. Field blanks and equipment rinses may not be used to prepare the MS and MSD. The MS and MSD are processed exactly as samples in the batch, and are used to assess the effects of sample matrix on the accuracy and precision of the analytical system.

Acceptance Criteria: The percent recovery of the analytes of interest must fall within the established control limits. The control limits are set at ± 3 standard deviations around the calculated mean of the historical MS recovery data, unless project-specific control limits apply. Current control limits are stored in the laboratory LIMS. See Policy QA-0620 for further details.

The relative percent difference (RPD) between the MS and MSD must be less than the established control limit, which is based on 3 standard deviations of the mean of the historical data. RPD control limits are maintained in the laboratory LIMS.

Corrective Action: If the analyte recovery in the MS and/or the RPD between the MS and MSD fails acceptance criteria, but all other QC criteria are met, the MS/MSD failure may be attributed to matrix effects and the associated sample results may be reported as qualified. However,

some programs (e.g., USACE) require reanalysis to confirm that presumed matrix effects are reproducible.

9.6 Duplicate Sample Analysis

A duplicate pair is required with each analytical batch. The RPD between samples should be ≤35%.

Corrective Action: If the RPD fails the acceptance criterion and the fuel pattern is inconsistent between chromatograms, the sample should be re-extracted and reanalyzed. If only the RPD value exceeds the acceptance criterion, the failure may be attributed to matrix effects or sample inhomogeneity and the associated sample results may be reported as qualified.

9.7 Surrogate Spikes

The o-terphenyl surrogate has chemistry similar to the analytes of interest, but is not expected to be found in environmental samples. 100-µL of the surrogate spike solution is added to each field and QC sample in the batch prior to sample extraction and all instrument blanks. See Table III for spike levels. Surrogate results are used to assess the performance of the analytical system for each field and QC sample and instrument blank.

Acceptance Criteria: The percent recovery of the surrogates must fall within 50-150% recovery.

Corrective Action: If surrogate recoveries are outside the established limits, verify calculations, dilutions, and standard solutions. Also verify that the instrument performance is acceptable. High recoveries may be due to co-eluting matrix interference and the chromatogram should be examined for evidence of this. Low recoveries may be due to adsorption by the sample matrix (e.g., clay particles, peat, or organic material in the sample). Recalculate the results and/or reanalyze the extract if the checks reveal a problem.

If the surrogate recovery is outside the established limits due to well-documented matrix effects, the results must be flagged and an explanation included in the report narrative. As with matrix spike failures, some programs (e.g., USACE) may require additional analyses to confirm suspected matrix interferences. The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to re-prepare / reanalyze a sample once to demonstrate that a matrix effect is reproducible.

NOTE: For LaMP samples, if the surrogate percent recovery fails, the recovery must be confirmed by re-extraction and reanalysis with the following exceptions:

- The lab has unequivocally demonstrated a sample matrix effect and informed the LaMP client representative.
- The recovery exceeds control limits and all target analytes in the sample are non-detect.

9.8 RT Reference Standard

The retention time window is established by injecting a mixture of n-alkanes from Toluene to n-hexatriacontane (C_{36}) three times over a 72 hour period. The mean and standard deviation for the three retention times are calculated. The width of the RT window is set at

±3 times the standard deviations of the mean RT. If the resulting RT window is less than 0.03 minutes, then a window of 0.03 minutes is used.

Acceptance Criteria: Toluene must be resolved from the solvent peak.

Corrective Action: If the acceptance criteria are not met, check instrument conditions and calibration materials, correct as necessary and repeat analysis of the reference standard before proceeding with the analysis of samples.

9.9 Instrument QC

9.10 Initial Calibration (ICAL)

9.10.1 A new calibration curve must be generated initially, after major changes to the system, or when continuing calibration criteria cannot be met. Major changes include installation of new columns and changing FID jets.

9.10.2 The ICAL is performed using the concentration levels described in Table II. A total of four separate initial calibration curves (ICALs) is required to calibrate for all the mixtures. An ICAL must always be analyzed for the diesel fuel as these standards contain the surrogate compounds. ICALs for the other mixtures are analyzed as needed, depending upon the requested parameters. Samples may be calculated as one or more mixtures, dependent upon the project requirements. The lowest calibration concentration is equal to the laboratory reporting limit (RL) concentration. The highest standard defines the highest sample extract concentration that may be reported without dilution. It is not acceptable to remove points from a calibration curve for the purpose of meeting criteria.

9.10.3 The external standardization method is used. Tabulate the area response for each calibration level against the concentration injected. The ratio of the response to the concentration injected, defined as the calibration factor (CF), is calculated for the standard at each concentration as follows:

$$CF_i = \frac{A_{fuel}}{C_{fuel}}$$

Where:

CF_i = Calibration factor for the i^{th} calibration level.
A_{fuel} = Total area of the fuel calibration standard peak.
C_{fuel} = Concentration of fuel calibration standard, mg/mL

9.10.4 If the percent relative standard deviation (%RSD) for the average (mean) of the calculated calibration factors is less than 15%, the average calibration factor can be used for sample quantitation.

$$\text{Average Response Factor} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where:

CF_i = Calibration factor for the i^{th} calibration level.
n = The number of calibration levels.

9.10.5 If %RSD for the mean calibration factor is greater than 15%, a linear least-squares regression may be used to fit the calibration data. The linear fit calculates the slope and intercept of a straight line that relates the concentration of each calibration standard to a chromatographic peak area, as follows:

$$A_s = mC_s + b$$

Where:

A_s = Area of the chromatographic peak for the target fuel.
m = Slope of the line as determined by the least-squares regression.
C_s = Concentration of the target fuel in the calibration standard, mg/mL.
b = Intercept of the line as determined by the least-squares regression.

9.10.6 The correlation coefficient of the fitted line must be ≥ 0.990. Note that some programs (e.g., AFCEE and USACE) require that the correlation coefficient is ≥ 0.995, unless approval is given in the project QAPP to use 0.990.

9.10.7 If the ICAL %RSD or correlation coefficient linearity criteria are not met, sample analysis cannot be performed using the calibration. Confirm that the instrument is performing properly, adjust as needed, and confirm that the standards are made correctly. After correcting the problem(s), prepare and reanalyze a new set of calibration standards.

9.10.8 See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

9.11 Second-Source Initial Calibration Verification (ICV)

A second-source initial calibration verification (ICV) standard is prepared and analyzed immediately after each ICAL. This standard can also be used as the continuing calibration verification (CCV) standard. The response for this standard must be within ± 15% of the response predicted from the ICAL. The percent difference between the measured ICV calibration factor (or the measured concentration of the ICV standard) and the ICAL calibration factor (or the known concentration of the ICV standard) is calculated as follows:

$$\text{Percent Difference} = \frac{\text{R1} - \text{R2}}{\text{R1}} \times 100\%$$

Where:

R1 = Average calibration factor from the calibration curve or the ICV known value.
R2 = Calculated calibration factor for the ICV analysis or the measured ICV value.

If the percent difference for the second-source verification falls outside of ± 15%, then sample analysis cannot be performed. Reanalyze the second-source verification standard to confirm the original result. If the second result fails, then re-prepare the verification standard, and/or re-prepare and rerun the ICAL.

9.12 Continuing Calibration Verification (CCV)

9.12.1 A CCV standard is analyzed at the beginning of the analytical sequence, every 10 samples, and at the end of the analytical sequence. The response for this standard must be within ± 15% of the response predicted from the ICAL.

In the event of calibration verification failure, corrective action must be taken prior to sample analysis. If routine corrective action procedures fail to produce a second consecutive (immediate) calibration verification within acceptance criteria, then either the lab has to demonstrate acceptable performance after corrective action with two consecutive calibration verifications (using fresh calibration solutions, at low and high concentrations) or, alternatively, a new initial calibration must be established according to Section 10.2. If one of these calibration verification injections fails, a new initial calibration curve must be processed. If a verification standard is not acceptable, all samples analyzed after the last acceptable verification standard must be reanalyzed. Any samples associated with failed closing calibration verifications where the response for an analyte in the calibration verification standard is above the acceptance limit and the analyte was not detected in any of the samples analyzed since the previous passing verification, do not need to be reanalyzed as the verification standard has demonstrated that the analyte would have been detected were it present (see Note below for information relative to DOD samples). Re-analysis is required for all other situations. If for some reason (i.e., lack of sample) re-analysis can't take place, a NCM needs to be initiated and the sample and QC results associated with the failing CCV need to qualified in the final report. Sample results associated with a CCV failure that are uploaded into the LIMS need to be qualified at the analyte level as appropriate. Additional information related to the CCV failure or corrective actions taken should be summarized in a NCM.

NOTE: For DOD samples, a high biased CCV with non-detects in the samples is only acceptable to report if approval is granted by the client. Otherwise, samples associated with a high failing CCV need to be re-analyzed.

9.13 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

10.1.1 **Note:** It has been noted that some petroleum products, i.e. heavy oils such as #6 fuel oil or bunker crude may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use standards that have undergone the cleanup technique to calibrate the GC.

10.2 Calibration

10.2.1 Refer to Table 2 for on-instrument calibration levels.

10.3 The gas chromatograph is set up as follows:

Injector: 300°C

Detector: 350°C

Oven ramping profile for 6890 GC systems with 15 meter column(s): Initial column temperature is set to 30-60°C, and held for 0.5 minutes, ramped to 340°C at 30°C/min and held for 2-3 minutes. Flow is set to constant flow at 1.5-3.5 mL/min. A post run is initialized at 340°C at a flow rate of 5.0 mL/min, and held for 2-4 minutes to clean out the system of contaminants.

Note: the oven ramping profile will vary from instrument to instrument, as each does not perform exactly like one another. In addition, actual column lengths and types vary as well.

Note: each instrument's run method parameters are printed out and stored in each appropriate instrument maintenance logbook.

10.3.1 The FID is allowed to stabilize at manufacturers recommended makeup and carrier gas flows prior to analysis.

10.3.2 Standard and surrogate solutions are allowed to come to room temperature prior to use.

10.4 Sample Analysis

10.5 Prior to analysis of any samples or QC samples, the analyst must prepare and analyze a mid-range calibration check standard (CCV) to insure that the instrument is functioning correctly and that the calibration is still valid.

10.5.1 Instrument response should be monitored daily by recording the absolute response of an individual peak. The surrogate o-Terphenyl is the peak chosen for these instruments. The absolute response for this peak in this standard needs to be documented in the maintenance log book on a daily basis.

10.6 The analyst shall use #2 diesel and motor oil as the default product for reporting purposes when no petroleum products were identified in any initial screening or when type(s) of petroleum products are unknown prior to analysis.

10.7 A portion of sample extract stored in an appropriately sized vial is transferred to 1.5 mL autosampler vials.

10.8 Extracts are analyzed by injection of 1 uL on the GC by an autosampler. **Note:** The use of GC/MS or GC/AED may be substituted for GC/FID as long as all other method parameters are met.

10.9 A mid-range calibration standard is analyzed, every 10 samples, and at the end of the analytical sequence.

10.10 If NWTPH-HCID has not been previously performed on the samples and/or the type of petroleum present is unknown, the analyst may prescreen the samples to determine the petroleum product.

10.11 When reporting results, the analyst should adhere to the following:

10.11.1 If detection is due to a typical fuel pattern other than diesel or motor oil, the analyst must add a “Pattern Recognition” NCM of the appropriate type.

10.11.2 If detection is not due to a typical fuel pattern, such as a single peak, the analyst must add a “DRO – Atypical” or “DRO – Discrete Peaks” NCM, explaining the particular detection.

10.12 For those surrogate compounds that elute within retention time ranges used for petroleum product integration, the analyst must subtract the area of the surrogate from the total area to yield a corrected area of the petroleum product.

10.13 For the default petroleum products, #2 diesel and motor oil, the calibration standard area of the components from decane (nC_{10}) and tetracosane (nC_{24}) (#2 diesel) and from tetracosane (nC_{24}) to hexatriacontane (nC_{36}) (motor oil) are integrated to the baseline as a group. The data system will automatically remove any surrogate areas that elute within the retention time windows. The samples are integrated in the same manner and the areas compared.

10.14 An example instrument analysis sequence is shown in Attachment 1.

10.15 Upon completion of the analytical sequence:

10.15.1 Create a worklist on Chrom that reflects the machine run sequence. The Chrom worklist will serve as the instrument sequence logbook. For the Rinse Blank before the opening CCV, add the solvent to the sample reagent tab. This will serve as the record of the solvent lot used to dilute the samples.

10.15.2 Review chromatograms via Chrom/Peak Review software and determine whether manual data manipulations are necessary.

10.15.3 All manual integrations must be justified and documented. See Corporate SOP CA-Q-S-002 for requirements for manual integration.

10.15.4 Manual integrations, if necessary, are performed in the Chrom/Peak Review software module, utilizing the appropriate integration type and reason. Before and after chromatograms with appropriate user information are automatically generated in Chrom and is uploaded into LIMS with each sample.

10.16 Open the analysis batch in the TALS/LIMS Analyst Desktop II module, and allow the system to perform the sample calculations.

10.16.1 Perform a level 1 data review, acknowledge any Data Review Checker (DRC) findings, and document the review on the data review checklist.

10.16.2 Submit the review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

10.17 GC Maintenance

10.17.1 Leak Checking. Leak checking after column installation is recommended. In order to avoid contamination when leak testing fittings and connections, direct a small jet of gas which can be detected by the detector, (for example methane for an FID) at the point to be tested, then use the detector at the maximum sensitivity to detect leakage of gas into the system. Response is rapid at points downstream of the column. Response time will be delayed by the elution time of the gas in the column. A quicker leak test can be performed by placing a drop of isopropanol on the point to be tested. If bubbles form, a leak is indicated. Alternatively, an electronic leak detector may be used.

10.17.2 Column Installation. Columns are replaced every six months or as needed. When a column will not hold its calibration for any length of time, replacement is needed. Poor peak shape and excessive baseline rise not attributed to sample contamination are other indication that the column may need replacement.

10.17.2.1 Remove the old column from the GC oven by loosening the injector and detector nuts with the appropriate wrench.

10.17.2.2 The injector end of the new column is installed first. Slide the column nut over the column end.

10.17.2.3 Install the appropriate ferrule onto the column. For the HP 6890/7890 GCs, the tapered end is placed towards the end of the column.

10.17.2.4 Cut 1 to 2 cm from the end of the column.

10.17.2.5 Uncoil approximately 20 cm of column.

10.17.2.6 Move the column nut and ferrule within 12-15 cm of the end of the column.

10.17.2.7 Cut 1 to 2 cm. off of the end of the retention gap. Insert the column end through the column nut, and then place a graphite ferrule onto the column and column nut. Using an old adaptable FID fitting, pre-crush the graphite ferrule to hold the column in place. For HP 6890/7890 GCs, measure 3 to 4 mm from the end of the column to the beginning of the ferrule.

10.17.2.8 Insert the retention gap into the injector while holding the column in place so it does not slide out of the ferrule. Tighten the column nut to finger tight. Make sure that the mark is visible and in the correct place for HP GCs. Tighten the column nut with a wrench approximately 1/4 turn or until the column cannot be pulled out of the injector.

10.17.2.9 For the detector end, insert the column end through the column nut, and slide a graphite ferrule over the column. Clip approximately 1 – 2 cm off the column end.

10.17.2.10 Partially insert the column into the lower end of the detector. For HP 6890/7890 GCs, the column is inserted 68 mm. CAUTION: The column can break or chip if it is forced into the detector!! Thread the column nut and ferrule until finger tight. For HP 6890/7890 GCs, pull the column back out of the detector approximately 1 mm. Tighten the ferrule and column nut with a wrench approximately 1/3 to 1/2 turn or until the column cannot be removed by pulling on it.

10.17.2.11 Install a ferrule onto the retention gap. For HP 6890/7890 GCs, the tapered end is placed towards the injector.

10.17.2.12 The gas flows are set to manufacturer or method recommended levels and are checked prior to each initial calibration:

Column flow: Approximately 1.5 -11 mL/min.
Make-up gas at the detector (Nitrogen): Column flow + X mL/min. = to 20 mL/min.
Hydrogen: 30 mL/min.
Air: 300 mL/min.
Total Flow: 360 mL/min.

10.17.2.13 Condition the column by heating the oven to 5-10 °C above its maximum operating temperature for approximately two hours, or until the baseline drops to its normal operating level. After the column is conditioned, the oven temperature is set at standby. At this point, the instrument is ready to be calibrated.

10.17.3 The injection port septa are replaced every 100-150 injections, or as needed under normal operating conditions.

10.17.4 The injection port should be cleaned and the liner replaced monthly, or as needed. The frequency is determined by the number of samples analyzed and the amount of contamination introduced into the system. The loss of detector response, particularly in early eluting peaks is an indicator that the liner or retention gap needs replacement. To replace the injection port:

10.17.4.1 Cool the column and injection port to ambient temperature to avoid burns.

10.17.4.2 Unscrew the septum nut from the top of the injector. Remove the septum. Unscrew the nut below the septum plate.

10.17.4.3 Using tweezers or needle nose pliers, remove the liner and the viton O-ring. If the O-ring is not damaged, it may be used again. Insert a clean liner into the O-ring with the tapered end up. Insert the liner into the injection port. Tighten the lower nut onto the injection port.

10.17.4.4 Replace the septum with a new septum. Tighten the septum nut until finger tight. Puncture the septum with a syringe. This will also indicate if the septum nut is tight enough.

10.17.5 The oven is heated to maximum operating temperature for approximately one hour to remove any residue or contamination introduced into the system during maintenance.

10.18 FID Maintenance

10.18.1 Maintenance of the FID involves cleaning deposits from internal parts, including the flame tip, and ferrule replacement. These maintenance procedures are performed every six months, or more frequently if there is degradation in the FID performance. “Spiking” signals and carbon build-up are indications that the detector needs cleaning.

10.18.2 Refer to the GC Operator’s Manual for proper disassembly and reassembly of the FID.

10.18.3 When removing the FID from the GC, inspect the O-ring at the base of the detector and replace as necessary.

10.18.4 Flame Tip and Internal Parts Cleaning.

10.18.4.1 Using Emery cloth, clean deposits from the bore of the collecting tube, the insulator, and the metal part of the flame tip.

10.18.4.2 If the flame tip is plugged, clear it by inserting a wire through the flame tip orifice.

10.18.4.3 Sonicate the detector parts in a methanol bath for ten to fifteen minutes.

10.18.4.4 Flush all components with methanol and dry in an oven at 100 °C for at

least 15 minutes.

10.18.4.5 Reinstall the detector.

10.18.5 Ferrule Replacement.

10.18.5.1 If a leak develops around the base of the flame tip assembly, replace the ferrule.

10.18.5.2 Note: A leak is evident by detector noise, instability, and loss of sensitivity.

10.18.6 Autosampler Maintenance

10.18.6.1 Check the wash solvent levels daily. Fill if needed. Empty the waste bottles if necessary.

10.18.6.2 The syringe may need replacement. Follow the procedure outlined in the HP 7673 Automatic Sampler Manual (pp 3-30 through 3-32).

10.18.6.3 Periodically clean the surface of the tray arm, gripper, gripper jaws, and the tray quadrants.

10.19 Spare Parts

10.19.1 Gas Chromatograph.

10.19.1.1 Septa, Merlin Microseal septum and column nut set

10.19.1.2 Injection Port Liners: HP 5890/6890 GCs: 4 mm ID straight

10.19.1.3 Column nut

10.19.1.4 Ferrules: 1/4 in. graphite 0.4 mm ID graphite

10.19.2 Autosampler

10.19.2.1 Syringes: HP7673: HP 10 uL 7673 Std. Plunger, or equivalent

10.19.2.2 Solvent and waste vials and septa

10.19.3 FID

10.19.3.1 FID jet

10.19.3.2 Column insulator

10.19.3.3 Collector tube

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., GC, autosampler, column) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, etc as may be the case).

If a column was replaced during maintenance procedures the specific make, model and serial numbers of the column installed needs to be entered in the instrument's maintenance logbook.

10.20 Troubleshooting

10.20.1 To ensure optimum performance of the FID, you must keep it clean and free of dust and deposits. Symptoms such as reduced sensitivity and increased noise indicate that detector needs cleaning.

10.20.2 Baseline noise:

10.20.2.1 Contaminated injector and or column. Clean the injector and solvent rinse the column.

10.20.2.2 The column is inserted into the flame of the FID. Reinstall the column.

10.20.2.3 Incorrect combustion gases or flow rates. Check and reset the gases at their proper values.

10.20.2.4 Physical defect in the detector. Clean or replace parts as necessary.

10.20.2.5 Defective detector board. Consult the instruction manual or contact the GC manufacturer.

10.20.3 Baseline spiking:

10.20.3.1 Particulate matter passing through the detector. Clean the detector.

10.20.3.2 Loose connections on cables or circuit boards (usually random spiking). Clean and repair the electrical connections as needed.

10.20.4 Baseline Drift (Upward):

10.20.4.1 GC or column contamination. Clean the injector. Solvent rinse the column.

10.20.4.2 Damaged stationary phase. Replace the column. Determine the cause of the damage to prevent future problems.

10.20.5 Baseline Drift (Downward):

10.20.5.1 Incomplete conditioning of the column. Condition the column until a stable baseline is obtained.

10.20.5.2 Unequilibrated detector. Allow the detector enough time to equilibrate.

10.20.6 Irregular Peak Shapes or Sizes

10.20.6.1 No peaks.

10.20.6.1.1 Plugged syringe. Clean or replace the syringe.

10.20.6.1.2 Broken column. Replace or reinstall the column.

10.20.6.1.3 Detector gases improperly set or not on. Check and reset the detector gases.

10.20.6.1.4 Very low or no carrier gas flow. Immediately lower the column temperature to 35-45C. Measure and verify the carrier gas flow rate. Check for leaks.

10.20.6.2 Tailing Peaks.

10.20.6.2.1 Active injector liner or column. Clean or replace liner. Replace the column if it is damaged.

10.20.6.2.2 Contaminated injector liner or column. Clean or replace the injector liner. Solvent rinse the column.

10.20.6.2.3 Poorly installed column, liner or union. Check and verify the installation of each fitting. Reinstall the column if needed.

10.20.6.2.4 Poorly cut column end. Re-cut and reinstall the column.

10.20.6.3 Rounded or Flat Topped Peaks.

10.20.6.3.1 Exceeding the range of the integrator. Dilute the sample.

10.20.6.4 Retention Time Shifts

10.20.6.4.1 Leak in the injector, especially the septum. Find and repair the leak. Change the septum.

10.20.6.4.2 Contaminated column. Solvent rinse the column.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\textbf{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\textbf{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.2 Precision (RPD)

$$\textbf{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.3 Concentration

$$\text{sample conc., mg/L} = \frac{(\text{area count} * \text{response factor}^{1}) * \text{extract volume}}{(\text{volume inj., uL}) * \text{sample volume, mL}}$$

$$\text{sample conc., mg/kg} = \frac{(\text{area count} * \text{response factor}^{1}) * \text{extract volume}}{(\text{volume inj., uL}) * (\text{sample weight, g}) * (\%\text{solids})}$$

1 = ng injected/area count

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

Instrumentation software must have each target limit set to the lowest MDL. CHROM (LOD)

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Acidic extracted sample and QC wastewater. After the extraction has been completed the spent water is neutralized and then collected into the organics

extraction water conical reservoir. The collected wastewater is then purged with air to remove any remaining methylene chloride. When the concentration levels are at or below local discharge limits, the wastewater can be discarded down the drain.

14.1.2 Solvent/Methylene Chloride waste. Any waste methylene chloride/solvent is collected in beakers and then poured into a 4-liter amber bottle labeled "Hazardous Waste" located in the hood. After the extraction has been completed, the $MeCl_2$ collected in the 4 L bottles is emptied into the $MeCl_2$ satellite waste barrel located next to the neutralization tank in lab hood #17. The funnel lid on the drum must be closed after each use. At or before the satellite waste reaches 55 gallons, the barrel is transferred to the waste disposal room from where it is sent out for recycling or fuel blending.

14.1.3 Vialed extract waste. Sample extracts that have been placed in vials for analysis are discarded into satellite waste buckets labeled "Hazardous Waste" located underneath the bench top. Once the buckets are full, the GC vials are bulked into the non-PCB GC vial waste barrel located in the waste room and sent out for incineration.

14.1.4 Extract waste. Unused sample extracts are held for at least 40 days, in case further testing is deemed necessary. After at least 40 days has passed, these extracts are transported to the waste room in racks of 100 were they are bulked into a flammable loose pack waste stream and sent out for incineration.

14.1.5 Expired primary and working standards. Expired standards are stored in a canister labeled "Hazardous Waste" at or near the point of generation. At or before the satellite waste reaches 55 gallons, it is removed to the waste warehouse where it is bulked into the non-PCB GC vial waste barrel and sent out for incineration.

15.0 References / Cross-References

15.1 Analytical Methods for Petroleum Hydrocarbons, WA DOE, Toxics Cleanup Program and the Ecology Environmental Laboratory, Publication No. ECY 97-602, June 1997.

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Methods 3510C, 3550B, 3540C, 3580A, 8000C, and 8015B.

16.0 Method Modifications:

Item	Method	Modification
1	NWTPH-Dx	For petroleum products eluting after #2 diesel, e.g. motor oils, hydraulic fluids, and heavy fuel oils, the reporting limit is approximately 50 mg/kg for soil as opposed to 100 mg/kg
2	NWTPH-Dx	Final sample extract volume is 5.0 mL instead of 10 mL for waters analysis.
3	NWTPH-Dx	Silica gel SPE tubes are used instead of silica gel 100/200 mesh.
4	NWTPH-Dx	A full liter of water or 100 mL of water is extracted instead of 400 mL.
5	NWTPH-Dx	Both #2 diesel and motor oil are used as default petroleum products when product is unknown or not identified.
6	NWTPH-Dx	Soil samples may be prepared using a validated modification of method 3550B.

17.0 Tables and Attachments

Table I: Aliphatic Hydrocarbon Standard
Table II: Calibration Levels
Table III: Special Hydrocarbon Ranges
Table IV: Spike Levels for Quality Control
Table V: Recommended GC Conditions

Attachment 1: Example Instrument Sequence
Attachment 2: n-Alkane Retention Time Standard Chromatogram

18.0 Revision History

- Revision 17, dated March 13, 2018
  - Updated approvals
  - Updated CCV criteria, section 9.12.1
  - Updated gas chromatograph setup, section 10.3
  - Updated sample analysis procedure

- Revision 16, dated April 6, 2017
  - Updated RLs in section 1.1.
  - Changed LVI volume to 250 mls, section 2.0.
  - Updated MB criteria to 10% of sample detection, section 9.3
  - Added LVI volume sections 9.3 and 9.4
  - Added Data Review Checker (DRC), section 10.19
  - Updated Table II

- Revision 15, dated April 22, 2016
  - Fixed section 9.2 to 20 samples per batch.
  - Updated section 10.13 to current practice.
  - Added section 10.18.1, Chrome worklist
  - Removed sections 10.18.4 and 10.19.3
  - Updated sequence and RT attachments 1 and 2
  - Updated table II.

- Revision 14, dated 6 January 6, 2015
  - Changed LVI volume in section 1.1.1 & 8.1.
  - Changed AccuStandard Fuel Set concentration from 20mg/L to 50mg/L in section 7.5.
  - Changed 4-BFB information in section 7.7.
  - Removed section 9.10 about PIBLK.
  - Removed part of section 10.13.1 about pattern recognition.
  - Added troubleshooting section 10.23.

- Revision 13, dated 16 May 2013
  - Updated preparation SOP's in section 1.1.2.
  - Removed Isopropanol reagent from table in section 5.2.
  - Added average response factor criteria for calibrations in section 7.9.1.
  - Updated average response factor %RSD criteria in sections 9.11.4 and 9.11.5.
  - Added section 10.2.1 to refer to Table 2 for on-instrument calibration levels.
  - Updated Table 2 to include new calibration levels to accommodate LVI analysis.

- Revision 12, dated 6 August 2012

- Updated preparation of stock surrogate standard in section 7.7.
- Updated GC model number types and re-arranged column installation procedures outlined in sections 10.20.2.3 through 10.20.2.10.
- Updated detector gas type in section 10.20.2.12.
- Updated waste streams, section 14.1

- Revision 11, dated 31 May 2011
  - Added references to applicable extraction procedures in section 1.1.2
  - Added RLs in section 1.1.3.
  - Updated carbon ranges for several fuels types discussed in section 3.
  - Incorporated ROMDs 00019 and 00026 in section 6.1
  - Added software descriptions in Section 6.2
  - Added more detail on the preparation of the sodium sulfate in section 7.3.
  - Revised surrogate composition (7.7), RT standard (7.10) and Diesel/Motor Oil Spike (7.11).
  - Incorporated ROMD 00025 in section 9.4.
  - Incorporated ROMD 00022 in section 9.11.8.
  - Incorporated ROMD 00024 in section 9.13
  - Incorporated ROMD 00020 in section 10.3.
  - Incorporated ROMD 00033 in section 10.5.2.
  - Added Item #6 to Method Mods in section 16.
  - Updated information in Tables II and V.

- Revision 10, dated 26 March 2010
  - Added documentation of reagent/standards and reagent/standard preparation Section 7.1.
  - Added removal of expired standards Section 7.13.
  - Added BP requirement for surrogates, Section 9.7.
  - Added criteria for additional QC, Section 9.13
  - Added daily balance check to Section 10.2
  - Added maintenance documentation requirements to the end of section 10.22

- Revision 9, dated 26 April 2008
  - Integration for TestAmerica and STL operations.
  - This SOP is the combination of SOPs 0339.9 and 0387.6.

Table I: Aliphatic Hydrocarbon Standard

Compound Boiling Points		
n-Alkane	**Name**	**B.P.$_{760}$ (°C)**
C_{10}	Decane	174
C_{24}	Tetracosane	391
C_{32}	Dotriacontane	468
C_{36}	Hexatriacontane	498

This Table can be used to get the estimated boiling point ranges of the hydrocarbons reported in a given sample.

Table II: Calibration Levels

ICAL Level	Surrogate	Fuel (mg/L)	Soil (mg/kg)[1]	1L Water (mg/L)[2]	250mL Water (mg/L)[3]
1	0.4	10	10	0.01	0.04
2	0.8	20	20	0.02	0.08
3	2	50	50	0.05	0.2
4	4	100	100	0.1	0.4
5 (CCV)	20	500	500	0.5	2
6	40	1000	1000	1	4
7	200	5000	5000	5	20
8	400	10000	10000	10	40

[1] Assumes 10g initial volume to 10mL final volume
[2] Assumes 1L initial volume to 1mL final volume
[3] Assumes 250mL initial volume to 1mL final volume

Table III: Special Hydrocarbon Ranges

Type	Carbon Ranges
Gasoline Range	Start of N-C8 through end of N-C12
Kerosene Range	Start of N-C8 through end of N-C20
Mineral Spirits Range	Start of N-C8 through end of N-C12
Jet Fuel A Range	Start of N-C8 through end of N-C16
Mineral (Transformer) Oil Range	Start of N-C12 through end of N-C24
Hydraulic Oil Range	Start of N-C19 through end of N-C36
Heavy Fuel Oil Range	Start of N-C12 through end of N-C38

Table IV: Spike Levels for Quality Control

Laboratory Control Samples (LCS) and Matrix Spike/ Spike Duplicate		
Analyte	**Spike Concentration**	
	Water (mg/L)	**Soil (mg/kg)**
Diesel Range Organics	5.0	500
Jet Fuel 8	5.0	500
Jet Fuel 4	5.0	500
Residual Range Organics (or Motor Oil)	5.0	500

Surrogate Control Samples		
Analyte	**Spike Concentration**	
	Water (mg/L)	**Low Soil (mg/kg)**
o-Terphenyl	0.2	20

Table V: Recommended GC Conditions

Hydrogen/Nitrogen Flow Rate	2.5 mL/min
Initial Column Temperature	45 ºC for 0.5 minutes
Temperature Ramp	30 ºC / minute
Final Column Temperature	330 ºC
Injector Temperature	300ºC
FID Temperature	350ºC

Attachment 1: Example Instrument Sequence

Report Date: 19-Apr-2016 14:31:03 Chrom Revision: 2.2 18-Apr-2016 13:22:42 Page: 1

TestAmerica Laboratories
Worklist Run Log Report

Worklist Name: 041516 TPH-Rear Worklist Num: 46903
Instrument: SEA012 Method: TPH-Rear_SEA012
Batch Directory: \\ChromNA\Seattle\ChromData\SEA012\20160415-46903.b
Anaylysis Type: SemiVOA Creator: Zalmai, Kayse 1
Inj Volume: 1.00 Inj Vol Units: ul
Run Reagents:
Methylene Cl_00002, Amount Added: 1.00 , Units: mL

Lab ID	Worklist ID	Sample Type	Inj Date/Time	File Name	Vial	Dil Factor	Client ID	Fract
BR	580-0046903-001	RB	15-Apr-2016 12:08:54	051B0101.D	51	1.0		sv
RTC	580-0046903-002	RTC	15-Apr-2016 12:30:28	052B0201.D	52	1.0		sv
CCVRT	580-0046903-003	CCVRT	15-Apr-2016 12:52:10	053B0301.D	53	1.0		sv
MB 580-214948/1-A	580-0046903-004	MB	15-Apr-2016 13:14:06	054B0401.D	54	1.0		sv
LCS 580-214948/2-A	580-0046903-005	LCS	15-Apr-2016 13:36:01	055B0501.D	55	1.0		sv
LCSD 580-214948/3-A	580-0046903-006	LCSD	15-Apr-2016 13:58:00	056B0601.D	56	1.0		sv
580-58712-G-2-A	580-0046903-007	Client	15-Apr-2016 14:20:09	057B0701.D	57	1.0	LS-GW-CDM22	sv
580-58712-G-3-A	580-0046903-008	Client	15-Apr-2016 14:42:10	058B0801.D	58	1.0	LS-GW-CDM10	sv
580-58712-G-4-A	580-0046903-009	Client	15-Apr-2016 15:04:15	059B0901.D	59	1.0	LS-GW-B28	sv
580-58712-G-5-A	580-0046903-010	Client	15-Apr-2016 15:26:39	060B1001.D	60	1.0	LS-GW-MW05	sv
580-58712-G-6-A	580-0046903-011	Client	15-Apr-2016 15:48:47	061B1101.D	61	1.0	LS-GW-B12	sv
580-58712-G-7-A	580-0046903-012	Client	15-Apr-2016 16:10:58	062B1201.D	62	1.0	LS-GW-MW10	sv
580-58712-G-8-A	580-0046903-013	Client	15-Apr-2016 16:32:56	063B1301.D	63	1.0	LS-GW-B02	sv
CCV	580-0046903-014	CCV	15-Apr-2016 16:54:58	064B1401.D	64	1.0		sv
580-58712-H-9-A	580-0046903-015	Client	15-Apr-2016 17:16:54	065B1501.D	65	1.0	LS-GW-B09	sv
580-58732-A-1-A	580-0046903-016	Client	15-Apr-2016 17:39:00	066B1601.D	66	1.0	MW1041316	sv
580-58732-A-2-A	580-0046903-017	Client	15-Apr-2016 18:01:02	067B1701.D	67	1.0	MW2041316	sv
580-58732-A-3-A	580-0046903-018	Client	15-Apr-2016 18:23:09	068B1801.D	68	1.0	MWDUP041316	sv
580-58755-D-1-A	580-0046903-019	Client	15-Apr-2016 18:44:58	069B1901.D	69	1.0	NDI16-W-AST-01	sv
580-58755-I-3-A	580-0046903-020	Client	15-Apr-2016 19:06:47	071B2001.D	71	1.0	NDI16-SW-PR-01	sv
580-58755-K-4-A	580-0046903-021	Client	15-Apr-2016 19:28:44	072B2101.D	72	1.0	NDI16-SW-DP-01	sv
CCV	580-0046903-022	CCV	15-Apr-2016 19:50:46	073B2201.D	73	1.0		sv

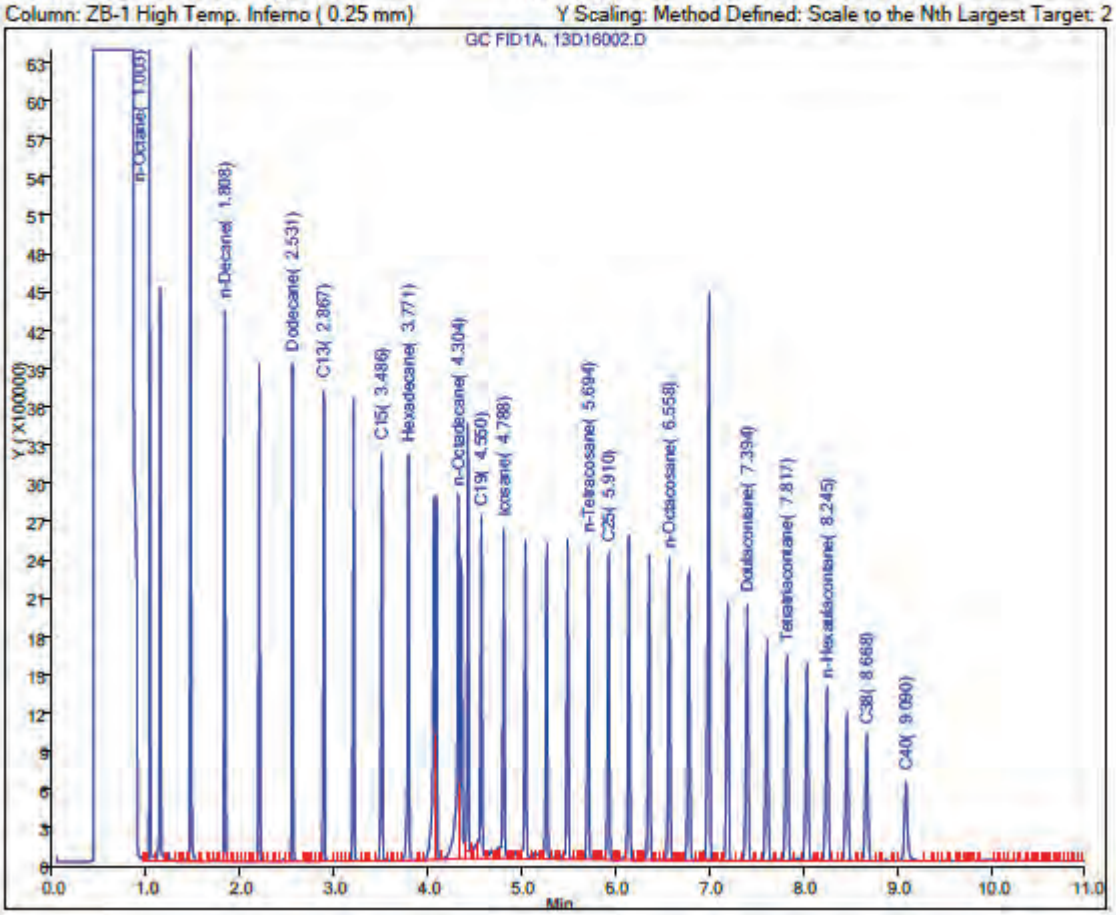
Attachment 2: n-Alkane Retention Time Standard Chromatogram

Report Date: 15-Apr-2016 16:26:07 Chrom Revision: 2.2 04-Mar-2016 14:36:24

Preliminary Report

TestAmerica Seattle

Data File: \\ChromNA\Seattle\ChromData\TAC020\20160413-46861.b\13D16002.D
Injection Date: 13-Apr-2016 10:41:30 Instrument ID: TAC020
Lims ID: RTC
Client ID:
Operator ID: kz ALS Bottle#: 2 Worklist Smp#: 2
Injection Vol: 1.0 ul Dil. Factor: 1.0000
Method: TPH-Front_TAC020 Limit Group: NWTPH-DX Standard list
Column: ZB-1 High Temp. Inferno (0.25 mm) Y Scaling: Method Defined: Scale to the Nth Largest Target: 2



Title: Chlorinated Herbicides by GC/MS [Method 8151A modified]

Approvals

Signatures on File	
Ryan Zboralski Date	Manjit Nijjar Date
Semivolatile Organic Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This SOP is used to determine the concentration of chlorinated herbicides in extracts prepared from all types of solid waste matrices, including soils, sediments, and aqueous samples.

1.1.2 This method can be used to quantify most chlorinated herbicide compounds that are soluble in diethyl ether, methanol and methylene chloride and capable of being eluted, after derivitization, as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. This method routinely provides qualitative and quantitative identification for the target analytes to the practical quantitation limits provided in Table 1.

1.1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 A measured volume of aqueous sample, typically 1 L, is brined with 200g sodium chloride and adjusted to pH 12.0 with sodium hydroxide. The sample is then acidified, and extracted with methylene chloride via SPE. A 15-gram volume of solid sample is extracted with methanolic NaOH, sonicated, and extracted into methylene chloride.

2.2 The extract is concentrated (typically) to a volume of 10.0 mL and derivatized using diazomethane. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of two or more characteristic masses (m/z). Quantitative analysis is performed using internal standard techniques with one or more characteristic m/z.

3.0 Definitions

The quality control terms used in this procedure are consistent with SW-846 terminology. Definitions are provided in the glossary of the TestAmerica Seattle Quality Assurance Manual (QAM)

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials are routinely demonstrated to be free from interferences under the conditions of the analysis by the analysis of method blanks.

4.2 Glassware must be scrupulously cleaned, following procedures described in SOP QA-0010, Use and Maintenance of Laboratory Glassware.

4.3 The use of high purity reagents and solvents helps to minimize interference problems.

4.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Ethyl Ether may form explosive peroxides on long standing or after exposure to air or light. To prevent formation of explosive peroxides this material must be disposed of within six months.

5.1.2 *Acidified $NaSO_4$ is used to dry water extracts after they have been eluted off the SPE cartridge. The creation of the Acidified $NaSO_4$ requires the use of both Ethyl Ether and Concentrated Sulfuric Acid. This MUST be done in a front-facing non-recirculating hood with a movable sash.*

5.1.3 Methylene chloride has been classified as a potential carcinogen by the state of California. Methylene chloride is harmful if inhaled, and may be fatal if swallowed. Use of this solvent should be relegated to a hood only.

5.1.4 Addition of NaOH or sulfuric acid to water is an exothermic reaction; exercise caution, use thermally resistant glassware, and perform additions in a cold water bath.

5.1.5 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. As a safety precaution, all standards, samples, and extracts are handled in an approved fume hood**.**

5.1.6 *Diazomethane is a toxic gas used to derivitize the extracted organochorine herbicides. Both the generation of the liquor and the volatized diazomethane are hazardous and highly reactive. Store the generated liquor in a amber-glass vial with a septum seal. When derivatization is to be done, it MUST be done in a non-re-circulating hood.*

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Ethyl Ether	Flammable Irritant Peroxide Former	400 ppm-TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of within six months.**
Methanol (MeOH)	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 *Agilent 6890 GC, Agilent 5975 MS*; 0.25 mm id, 30m, 0.1u film thickness DB-5MS capillary column or Phenomenex ZB-Semivolatiles 0.25mm id, 30m 0.25um or

equivalent; The serial number of the column used is documented in the instrument maintenance logbook; Varian 8400 auto sampler with 10uL sytinge; *Agilent Chemstation* Software Data System.

6.1.2 Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.

6.1.3 Data processing: Chrom version 1.2 or higher

6.1.4 TestAmerica LIMS (TALS), version 1.0 or higher

6.2 Supplies

- Heated Sonication Bath
- Analytical balance, capable of accurately weighing 0.0001 g
- Vacuum manifold for SPE
- Glass vials-40 mL, with Teflon-lined screw caps
- 20 mL glass vials with Teflon-lined screw caps
- Autosampler vials, 2.0 mL, with Teflon-lined screw caps or crimp caps
- Baker bond SPE disks H2O Phobic part no. 8109, or equivalent

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

Reagents

7.2 Sodium Hydroxide, reagent grade

7.3 Methylene Chloride, reagent grade.

7.4 Sulfuric (H2SO4) 95% acid, reagent grade.

7.5 Sodium Chloride, reagent grade.

7.6 *Baked Sodium Sulfate ($NaSO_4$), $NaSO_4$ baked at 400 degrees for a minimum or 4 hours, cooled, and stored in a 1L amber glass jar.*

7.7 *Acidified* Sodium Sulfate, *NaSO4 baked* at 400 degrees for a minimum of 4hours, cooled, *laid out on a large shallow baking pan, saturated with Ethyl Ether, add 100uL of Sulfuric Acid per 100g of $NaSO_4$, stir, allow to dry and place in appropriately sized amber glass container.*

7.8 6N NAOH, 24 grams of NAOH pellets dissolved into DI water in a 100ml volumetric flask. Fill to mark with water when cool.

7.9 12N Sulfuric acid, add 336 ml concentrated sulfuric into 500 ml water slowly in 1000ml volumetric flask. Fill to mark with water when cool.

7.10 Di water ASTM type II or better

7.11 Methanol, reagent grade.

7.12 Carbitol, reagent grade.

7.13 A 37% (w/v) KOH solution is prepared by dissolving 37g of KOH into 100mL of reagent water.

7.14 Methanolic KOH solution prepared by diluting 20ml of 37% KOH solution to 100mL with reagent methanol.

7.15 Diazald, reagent grade.

7.16 Diazald derivitization solution prepared by dissolving 10g of diazald in 50mL of 1:1MeCl2:Acetone.

Standards

7.17 Document standards and standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.18 100 ug/mL Custom Chlorinated Herbicides Standard, Restek # 569877, or equivalent.

7.19 1000 ug/mL 8151 Surrogate Standard, Restek # 32439, or equivalent. See Table 4.

7.20 10ug/mL 8151 ICAL Standard prepared by diluting 1mL of the 100ug/ml Custom Chlorinated Herbicides Standard and 100uL of the 1000 ug/mL 8151 Surrogate Standard to 10mL with methylene chloride. The Standard is then derivatized following section 10.4 of this document to convert the acid forms to the methyl ester forms.

7.20.1 After allowing sufficient time for the derivitization of the ICAL standard to occur, quench the reaction with silica gel and transfer the solution to a new vial.

7.21 Working 8151 ICAL Standards are prepared by diluting the 10ug/mL 8151 ICAL standard with methylene chloride as follows:

Volume of 10 ug/mL Stock Standard (µL)	Final Volume (mL)	Final Conc (µg/mL)
500	1.0	5.0
200	1.0	2.0
1000	10.0	1.0
500	10.0	0.5
200	10.0	0.2
100	10.0	0.1
50	10.0	0.05
20	10.0	0.02
10	10.0	0.01

7.22 10 ug/mL 8151 matrix spike solution prepared by diluting 1mL of the 100ug/mL purchased Custom Chlorinated Herbicides Standard to 10ml with Acetone.

7.23 100 ug/ml surrogate solution prepared by diluting 1ml of the 1000 ug/ml stock solution to 10 ml with Acetone.

7.24 Stock ICV Standard; 100ug/mL 8151 ICV Second Source Standard, Restek; Custom Phenoxy Herbicide 8151 Acids Mix, Cat No 569877.sec, or equivalent.

7.25 10.0 ug/mL 8151 ICV Standard is prepared by following the same procedures for the primary ICAL standards.

7.26 4000 ug/mL 8270 Internal Standard, Restek #31006, or equivalent.

7.27 100 ug/mL 8270 Internal Standard is prepared by diluting 1000uL of the 4000 ug/ml purchased internal Standard to 40 mL with methylene chloride.

7.28 1000ug/mL Restek DFTPP GC/MS Tuning Standard (w/ DFTPP, DDT, Benzidine and Pentachlorophenol), Restek # 31615, or equivalent.

7.29 *GC/MS Tuning Standard: A methylene chloride solution containing 25 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT should also be included in the Tuning Standard at 25 µg/mL. 2uL of this solution should be injected for an on column concentration of 50ng.*

7.30 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned, amber glass bottles fitted with a Teflon-lined cap. To achieve routine reporting limits, a full one liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Soil samples are collected in 8-ounce, pre-cleaned, wide-mouth jars with a Teflon-lined lid.

8.3 Samples and extracts are stored at 0-6℃.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	1 Liter	Cool 0-6°C	7 Days	40 Days from extraction	40 CFR Part 136.3
Soils	Glass	30 grams	Cool 0-6°C	14 Days	40 Days from extraction	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. The process of establishing control limits, and the use of control charts are described more completely in TA-QA-0620, Quality Control Program. Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.3 Method Blank (MB)

For aqueous sample batches, the method blank is reagent water; for solid sample batches, the method blank is clean sand. In either case, the method blank is free of the analytes of interest and is spiked with the surrogates. At least one method blank must be processed with each preparation batch.

Acceptance Criteria: The result for the method blank must be less than the reporting limit or less than 10% of the analyte concentration found in the associated samples, whichever is higher.

NOTE: Some programs (e.g., Navy and USACE) require that the maximum blank concentration must be less than one-half of the reporting limit or less than 10% of the lowest sample concentration.

Corrective Action: Re-preparation and reanalysis of all samples associated with an unacceptable method blank. If the analyte was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.4 Laboratory Control Sample (LCS)

The LCS is prepared using reagent water for aqueous methods and Ottawa sand for solid sample methods. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. The LCS is spiked with the compounds listed in Table 3 unless specified by a client or agency. The compounds must be spiked at a concentration equivalent to 1000 µg/L, depending on the analyte, unless special instructions state a specific level. Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. When preparing DOD or BP samples, an LCSD must be analyzed if there is not sufficient volume for a MS/MSD. The LCSD must pass the same control criteria as the LCS.

Acceptance Criteria: All analytes must be within established control limits. See QC SOP TA-QA-0620 for details on establishing control limits.

Corrective Action: If any analyte in the LCS is outside the laboratory-established historical control limits or project-specific control limits, as applicable, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS. This type of justification should be reviewed and documented with the client before reporting.
- If re-extraction and reanalysis of the batch are not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The matrix spike is a second aliquot of one of the samples in the batch. The matrix spike duplicate is a third aliquot of the same sample. The MS and MSD are spiked with the same analytes as the LCS (See Table 3). An MS/MSD pair is prepared and analyzed with every batch of samples when sufficient sample volume is available.

Acceptance Criteria: The percent recovery (%R) must fall within either historical limits or project-specific limits, as applicable. The relative percent difference (RPD) between the MS and MSD results should be less than or equal to the established historical or project-specific limit. See QC SOP TA-QA-0620 for details on establishing control limits

Corrective Action: If any individual recovery or RPD fails the acceptance criteria, then corrective action must occur. Initially check the recovery of the analyte in question in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is considered to be in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any analyte fails acceptance criteria for the LCS and/or LCSD, the laboratory operation is considered to be out of out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.
- If it is not possible to prepare both an MS and MSD due to limitations of sample amount, then a duplicate LCS should be prepared and analyzed. The RPD between the LCS and LCSD must be less than or equal to the RPD limit established for the MS/MSD.
- The MS/MSD pair must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted to concentrations below the calibration range.

9.6 Surrogates

9.6.1 Each sample, instrument blank, and QC sample is spiked with the surrogate standard. The surrogate compound is spiked at 100 µg/mL. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 4.

Acceptance Criteria: Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

Corrective Action:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem.
- Surrogate may be qualified if the chromatogram reveals obvious matrix interference eluting with the surrogate.
- Re-extract and reanalyze the sample or flag the data as “Estimated Concentration” if neither of the above resolves the problem.

NOTE: The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst

believes that the repeated out-of-control results are not due to matrix effect.

NOTE: For BP samples, if the surrogate percent recovery fails, the recovery must be confirmed by re-extraction and reanalysis with the following exceptions:

- The lab has unequivocally demonstrated a sample matrix effect and informed the BP representative.
- The recovery exceeds control limits and all target analytes in the sample are non-detect.

9.6.2 If the sample with failed surrogate recoveries was a sample used for an MS/MSD pair and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample and the MS and the MSD do not require reanalysis. This phenomenon indicates a possible matrix problem.

9.6.3 If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate).

9.6.4 If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effects.

9.7 Instrument QC is covered in sections 10.6 through 10.9.

9.8 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

Procedural variations are allowed only if deemed necessary in the professional judgment of the Analyst/Prep Technician to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The nonconformance shall be addressed in the case narrative, and the NCM shall be filed in the project file. The NCM process is described in more detail in SOP TA-QA-0610.

10.1 Sample Preparation

10.2 Aqueous Samples

10.2.1 The extraction of water samples using SPE technique as detailed immediately below should be employed. (If the water samples contain more than 1% of solids or cannot be filtered, procedures described in SOP OP-0301 may be employed.)

10.2.2 All samples and associated QC samples (approximately 1L initial volume) are spiked with 100uL of the surrogate spike solution; the LCS and matrix spikes are spike with 500uL of the matrix spiking solution. All samples and associated QC are brined with 200g NaCl; samples should be at ambient temperature (~20C to 30C) and periodic mixing will be required to completely dissolve the salt. All samples and associated QC are then hydrolyzed with 6N NaOH to a pH of >12

and allowed to sit for a minimum of 30 minutes. Document the lot number of the NaCl and the NaOH solution in the TALS batch information page.

10.2.3 The samples and associated QC samples are adjusted to a pH of 2.0 with 12N H2SO4 and allowed to sit for a minimum 30 minutes. Document the lot number of the H2SO4 solution in the TALS batch information page.

10.2.4 SPE disks DVB (H2O-Phobic) Baker Bond part no 8109 (or equivalent) are washed and conditioned on the vacuum manifold by washing 3x with MeOH. Add about 8 to 10mL MeOH on disk and acidify with 3 or 4 drops of H2SO4, stir, then saturate all layers of the disk by pulling acidified MeOH to down to about 5mL and let soak for 10min. Document the lot number of the HCl, disks, methanol, and MeCl2 in the TALS batch information page.

10.2.5 The methanol is drawn off under vacuum but not to dryness, and distilled water, taken to a pH of 2.0 with concentrated H2SO4, is added until the SPE and cup are full and drawn through, but not to dryness.

10.2.6 The water samples and QC are poured through under full vacuum and allowed to go to dryness, the vacuum should continue for at least 20 minutes drawing through the disk after dryness to remove all water retained on the disk.

10.2.7 40-mL vials should be placed under each disk.

10.2.8 10mL of methylene chloride is added to the disk and allowed to sit for at least 5 minutes before being pulled through the disk. This (10mL) is your Final Volume and should be recorded into your batching information. The sample can be further concentrated at this point if lower detection is desired.

10.2.9 Add approx 3g of *Acidified* Na2SO4 to each extract and shake by hand vigorously to remove any remaining H2O. The extract is then ready to be derivitized as in section 10.4.

10.3 Solid Samples

10.3.1 Check the Balance Logbook to determine if the daily calibration check was completed. If the balance requires a check, verify the calibration as detailed in SOP TA-QA-0014.

10.3.2 Weigh approximately 15 g of sample into a 40-mL pressure vial.

10.3.3 A 100-uL volume of surrogate standard solution is added to the sample.

10.3.4 A 500-uL volume of herbicide matrix spike standard is added to the sample volume chosen for matrix spike and matrix spike duplicate analysis. A blank spike of muffled sand can be used if additional method monitoring is desired.

10.3.5 See note below. A 20-mL volume of methanolic KOH solution is added to the soil and the sample is placed in the heated ultrasonic bath for 30 minutes.

10.3.6 **NOTE:** When the sample is dry, fine or powdery and especially if more than a 15g sample size is to be used, it will be necessary to pretreat the sample with an initial addition of 2-3 drops of 6N NaOH. This will ensure that there is adequate moisture to promote the hydrolysis of the herbicides and thus allow them to be extracted into the methanol.

10.3.7 Draw up exactly 10 mL's of the extract and place in a clean septa-top 40 mL VOA vial.

10.3.8 Add 5 mL MeCl2 and 20 mL 2%H2SO4.

10.3.9 Place in a foam 3x3 VOA vial rack, place another VOA vial rack on top, and shake vigorously for roughly 30 seconds.

10.3.10 Remove vials from VOA vial rack and place in separate tray upside down and let rest until the aqueous and organic layers have separated. The extract is the visible 5mL organic liquid layer resting on the bottom of the inverted vial. IMPORTANT: This (5mL) represents the "actual" final volume but 10mL is the "effective" final volume. Therefore, 10mL is the FV recorded in the prep batch info.

10.4 Diazomethane Generation and Extract Derivitization

10.4.1 Assemble Diazomethane Generator glassware on stir plate as pictured below:

10.4.2 Set up in fume hood with good face velocity flow,

10.4.3 **Do not add hot water to reaction side of vessel until hydrolysis is complete!**

10.4.4 (Reactor should be angled as pictured to minimize chance of liquids bumping or splashing over to collection side.)

10.4.5 Add crushed ice in brine to cooling well in condensing/receiving side of generator.

10.4.6 Fill beaker with enough ice/brine to cover 25mL round-bottom receiving flask.

10.4.7 Place stir bar in reaction side of generator.

10.4.8 Add the following to the reactor. Document the lot numbers in the TALS batch information page.

10.4.8.1 5g Diazald powder

10.4.8.2 15mL Carbitol

10.4.8.3 15mL Anhydrous EtOEt

10.4.9 Initial reaction is at ambient temperature, do not suspend vessel in warm water until hydrolysis is complete!

10.4.10 Stir and mix thoroughly for 1 minute.

10.4.11 With stopcock closed, charge addition funnel with 15mL 37% KOH(aq) and cover with 5mL EtOEt.

10.4.12 Add KOH dropwise to stirring Diazald solution. Reaction will be evident after a few drops of base. Wait for reaction to slow (less than 3-4mm of bubbles on surface of reaction) before adding more KOH. Drops of yellow liquid should form at the base of the cold-finger on the collection side of the vessel.

10.4.13 Continue adding KOH dropwise while monitoring reaction rate until hydrolysis is complete. Allow EtOEt to rinse remaining KOH into reaction, but retain 1 mL EtOEt in addition funnel to keep system closed.

10.4.14 With constant stirring, slowly add hot water (70-80C) to container surrounding reaction vessel. Distill DAM in EtOEt in a controlled manner: adjust water bath temperature and vessel submersion depth. If distillation boils over the procedure must stop and be repeated, keep bubbles/froth from boiling Ether under 5mm height.

10.4.15 Continue collection DAM until reaction side solution is light yellow or desired volume is collected. Store frozen away from light in 40mL VOA vial.

10.4.16 Transfer 1mL extract (XT) to 2mL autosampler (AS) vial.

10.4.17 Add 1 or 2 drops DAM liquor to XT. Cap XT as methylation takes place. Yellow color should remain in XT for at least 1 hour to ensure derivitization is complete, longer is preferable.

10.4.17.1 *This step **MUST** be done in a non-recirculating hood.*

10.4.18 Add 10uL IS to derivitized XT and run on GC/MS.

10.4.19 Derivitization is documented by adding the reagent: Diazomethane_000XX to the 'run reagents' tab in chrom's Worklist Editor by the vialing analyst when the worklist is generated immediately before/after vialing and derivitization.

10.5 Alternate Diazomethane Generation and Extract Derivitization

10.5.1 Add 5mL 37% NaOH solution, 5mL of Carbitol, and 30mL diazald reagent solution into the derivitization chamber. Document the lot number in the TALS batch information page.

10.5.2 Replace top on derivitization chamber.

10.5.3 Place clean Pasteur pipet on the end of the derivitization chamber.

10.5.4 Slowly bubbles nitrogen gas through the derivitization chamber.

10.5.5 Place tip of Pasteur pipet into the sample.

10.5.6 The nitrogen will slowly bubble through the sample. When the sample turns a yellow to pale orange color derivitization is complete.

10.5.7 Replace Pasteur pipet.

10.5.8 Repeat 10.4.2 – 10.4.8 until all samples have been derivitized.

10.5.9 Vial 1-mL of the derivitized extract into an autosampler vial.

10.5.10 Add 10uL internal standard per 1mL derivitized extract. This is the aliquot to run on the instrument.

10.6 Instrument Operating Conditions

10.6.1 Typical instrument operating conditions are provided in Table 2. Actual instrument operating conditions are posted in each maintenance logbook.

10.7 Instrument Tuning

10.7.1 A MS tuning compound (DFTPP) is analyzed every twelve hours during instrument operation, prior to analysis of standards, samples, or QC samples. Method tuning criteria must be met before sample analysis can proceed.

10.7.2 Tuning Procedure (Ion Trap): 3.0ul of the working GC/MS ion trap tuning standard (7.29) must be analyzed in a scanning mode of 40 - 450 m/z.

10.7.3 Inject the GC/MS tuning standard (Section 7.29) into the GC/MS system. Obtain a background-corrected mass spectrum of DFTPP and confirm that all the key m/z criteria are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. DFTPP Tuning Criteria are provided in Attachment I.

10.7.4 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. For non-DOD projects, the tailing factor for Benzidine must be less than or equal to 3, while the tailing factor for Pentachlorophenol must be less than or equal to 5. For DOD projects, the tailing factors for both compounds must be less than or equal to 2. Degradation of 4,4'-DDT to 4,4'-DDE and 4,4'-DDD for all projects must be less than 20%. Examples of column performance and degradation reports are provided in Attachment 2.

10.8 Calibration

10.8.1 A MS tuning compound (DFTPP) is analyzed every twelve hours during instrument operation, prior to analysis of standards, samples, or QC samples. See attached for DFTPP tuning criteria. Method tuning criteria must be met before sample analysis can proceed. There is also a breakdown done, where pentachlorophenol, benzidine and DDT are all examined, see attached for breakdown.

10.8.2 A 10-uL volume of internal standard solution is added to all calibration standards, QC samples, and samples prior to analysis. The autosampler injects 3-uL standard and extract volumes into the instrument for analysis.

10.8.3 The system is operated under a valid Initial Calibration. The initial calibration is a minimum of a five-point curve. If the percent RSD for the calibration points is less than 20% (15% for DoD), the curve is assumed to be linear through the origin and average RF is used to quantitate. If the percent RSD is greater than 20% (15% for DoD) a linear regression can be used as long as the correlation coefficient (r) is greater than or equal to 0.990 (0.995 for DoD Projects) or the coefficient of determination (r^2) is greater than or equal to 0.990.

10.8.4 If the initial calibration was not performed the same day as analysis, a continuing calibration is performed, using a mid-level standard. The continuing calibration

standard must have a percent difference of less than 20% for all compounds reporting. Otherwise data is appropriately qualified and/or the system must be recalibrated.

10.9 Initial Calibration

10.9.1 Internal Standard (IS) Calibration Procedure: Internal standards solutions are described in Sections 7.26 and 7.27. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation. 10-uL of internal standard solution is added to all calibration standards, QC samples, and samples prior to analysis. The autosampler injects up to 5-uL of standard and extract volumes into the instrument for analysis.

10.9.2 Compounds are assigned to the IS with the closest retention time.

10.9.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest when average response factors or linear regression curve fits are used. Six standards must be used for a quadratic least-squares calibration. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response.

10.9.4 Rejection of Calibration Points

10.9.4.1 Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

10.9.4.2 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious misinjection explained in the run log), then one point might be rejected, but only if all of the following conditions are met:

- The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and
- The lowest remaining calibration point is still at or below the project reporting limit; and
- The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and
- The calibration must still have the minimum number of calibration levels required by the method, i.e. five levels for calibrations modeled with average response factors or linear regressions, or six levels for second-order curve fits.

10.9.5 Add the internal standard mixture to result in a 1,000-µg/L final concentration. (For example, if the volume of the calibration standard used is 0.5 mL, add 5 µL of the 100 µg/L internal standard). The concentrations of all analytes are listed in Tables 11 and 12.

10.9.6 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against the concentration for each compound and internal standard. Calculate the response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12.

10.9.7 Initial Calibration Verification (ICV)

An initial calibration verification containing all components from a second source (an alternate vendor or a unique lot from the same vendor or the same source but prepared by an alternate analyst) must be analyzed after the initial calibration. Acceptance criteria for ICV percent recovery (%R) are 75-125% of all target analytes for commercial projects and 80-120% recovery for DoD projects (e.g., Navy and USACE).

10.9.8 Weighting of Calibration Data Points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.9.9 See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

10.9.10 If time remains in the 12-hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration, Section 10.10.

NOTE: Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.10 Continuing Calibration Verification (CCV)

10.10.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 25-ng injection of DFTPP must result in a mass spectrum for DFTPP, which meets the criteria given in Attachment I.

10.10.2 Following a successful DFTPP analysis, the continuing calibration verification (CCV) standard(s) are analyzed. The standard(s) must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the CCV.

10.10.3 The following criteria must be met for the CCV to be acceptable:

- The percent difference or drift (%D) of all compounds must be ≤ 20%.
- The internal standard response of the CCV must be within 50 - 200% of the response in the same level of the corresponding calibration.
- If any internal standard retention time in the CCV changes by more than 30 seconds from that of the same level of the corresponding initial calibration, the chromatographic system must be inspected for malfunctions and corrections made, as required.

- For DOD samples, a high biased CCV with non-detects in the samples is only acceptable to report if approval is granted by the client. Otherwise, samples associated with a high failing CCV need to be re-analyzed.

10.10.4 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample injected less than or equal to 12 hours after the DFTPP is acceptable.)

10.11 Sample Analysis

10.11.1 A MS tuning compound (DFTPP) is analyzed every twelve hours during instrument operation, prior to analysis of standards, samples, or QC samples. Tuning is performed following the procedure described in Section 10.6. The DFTPP breakdown must meet the method criteria before sample analysis can proceed.

10.11.2 A 10-uL volume of internal standard solution is added to all calibration standards, QC samples, and samples prior to analysis. The autosampler injects 3-uL standard and extract volume into the instrument for analysis.

10.11.3 The system is operated under a valid Initial Calibration.

10.11.4 If the initial calibration was not performed the same day as analysis, a continuing calibration is performed, using a mid-level standard (typically 500ppb for targets and surrogate).

10.11.5 Analyte identification is achieved using the retention time and the relative abundance of two or more characteristic masses (m/z). Relative retention times of identified compounds must fall within ± 0.06 minutes of the relative retention time of the authentic compound.

10.11.6 Analyte quantitation is achieved based on the initial calibration in accordance with Method 8000C.

10.12 Sample Analysis Sequence

See Attachment 3.

10.12.1 Create a worklist on Chrom that reflects the instrument run sequence. The Chrom worklist will serve as the instrument sequence logbook. For the Rinse Blank, add the solvent to the sample reagent tab. This will serve as the record of the solvent lot used to dilute the samples.

10.13 Maintenance Guide for IT/MS Systems

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., GC, autosampler, columns) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone non-routine maintenance or repairs, the system is evaluated using a CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, etc as may be the case).

10.13.1 The Varian 1093 SPI injector is used for all semivolatile GC/MS analyses. The schematics and part numbers for the injector are listed in Table 4-1 in the operator's manual.

10.13.1.1 Injector port maintenance is performed whenever the following conditions exist:

- High column bleed
- Peak broadening and/or tailing for polar analytes such as phenols
- Loss of sensitivity
- Calibration failures due to a loss of response
- Retention time drift
- Long or training solvent tail
- Overall loss of instrument response.

10.13.1.2 Turn the GC oven off and let the system cool to room temperature. Remove the column nut and column from the injector body. Remove the injector nut, removing the septum and liner from the injector body. (See Illustration 6-10 in the instrument manual).

10.13.1.3 Clean the inside of the injector body with a cotton swab containing a cleaning solvent such as methylene chloride. Allow to air dry, then replace the liner with a new or reconditioned liner that has been sonicated in solvent, solvent rinsed, and muffled at 400℃. Replace the septum and tighten the nut just past finger tight.

10.13.1.4 Using a ceramic column cutter, remove at least 0.5 meters of the column end, depending on the severity of the system contamination. Place a column nut and new ferrule over the end of the column and re-cut one inch from the column end to ensure that no ferrule fragments remain in the column. Feed the column into the tapered liner until seated, then hold pressure on the column while the nut is tightened to one turn past finger tight. At this point, the GC oven is turned on and brought up to operating temperature. The system should then be leak checked.

10.13.2 Column installation is performed when the following conditions are encountered;

- Heavy column bleed that cannot be eliminated by thermal conditioning.
- Loss of early eluting peaks due to column cutting.
- Inability to chromatographically resolve method performance compound peaks (i.e. chrysene from benzo(a)anthracene).
- Distortion of peak shapes i.e.; broadening, ghost peaks, split peaks that can't be resolved by injection port maintenance or flow control.

10.13.2.1 Turn the GC oven off and let the system cool to room temperature. Remove the column nut, liner, septum, and presstight inlet connector. Dispose of old column appropriately.

10.13.2.2 Cut approximately six inches off of the end of new columns (DB5-MS 30m, 0.1u film thickness or Phenomenex ZB-Semivolatiles 30m, 0.25um film or equivalent). Attach the column to the presstight inlet connector on the injector end and proceed as in 5.3.1.4 to connect to the injector.

10.13.2.3 Turn the GC on and set the injector temperature to 280℃, oven to 300℃ and condition for five minutes.

10.13.2.4 Perform a leak check on the system following the instructions contained in the operator's manual chapter on Miscellaneous Procedures of Operation. When the air water spectrum shows acceptable levels, proceed with the mass calibration procedure. For additional information of column replacement see the operator's manual chapter on Selected Routine GC Maintenance (pages 6-33 to 6-41).

10.13.3 Ion trap maintenance is required when these indicators appear:

- Inability to mass calibrate to FC43 (perfluorotributylamine) (see the operator's manual chapter on **Introduction to System Set Up,** tuning the mass spectrometer (Sections 2-10 to 2-15).
- Loss of sensitivity, even with the electron multiplier set at default of 3000ev.
- Inability to pass a DFTPP tune after all attempts adjusting the multiplier and target variables (see operator's manual, Sections 2-4 and 6-42 for details).
- The radio frequency cannot be balanced or the automatic systems check fails (see the operator's manual **Diagnostics Program** sections (6-6 to 6-10)).

10.13.3.1 Turn the GC/MS off using the pump down procedure described in the operator's manual, Routine Ion Trap Maintenance (Sections 4-5 to 4-6). After the instrument is shut down refer to Table 4-1 and Illustration Flow Chart 4-1 in the manual. This table and flow chart will list all parts and steps necessary to remove, replace and clean the ion-trap.

10.13.3.2 Routine ion-trap maintenance includes removal of the trap, its disassembling, cleaning with aluminum oxide, replacement of filaments, gold ring, ceramic spacers and installation of a new electron multiplier if necessary. The reassembling involves realignment of the above parts to instrument specifications. This procedure is described detailed in the operator's manual, Routine Ion Trap Maintenance, Chapter 4. These 70 pages are highlighted to emphasize the important or must do procedures.

10.13.4 Autosampler Maintenance

10.13.4.1 All moving mechanical parts are lubricated with a fine machine oil or equivalent as necessary.

10.13.4.2 All dust and debris is removed from the circuit boards and tubing replaced as necessary.

10.14 Troubleshooting

1. If a DFTPP tune fails spectra, replace vial with fresh tuning solution and reanalyze the tune sample
    a. If it fails a second time evaluate MS conditions
    b. Continued failures may result in re-auto tuning the instrument (10.13.5)
2. If tailing fails for either benzidine or PCP, minimum routine maintenance is required (see section 10.13.)
    a. Continued failure. Check column positioning into the inlet liner (most likely cause of problem) or the source on the MS side.

b. Replace column if all other options are exhausted

3. If DDT breakdown fails, minimum routine maintenance is required
   a. Continued failure. Check column positioning into the source
   b. Replace column if all other options are exhausted
4. IF CCV fails for TC target analytes, re-analyze a fresh CCV, if it fails a second time minimum routine maintenance is required. If the 2nd CCV is acceptable, the samples may be analyzed
   a. A second CCV failure requires additional instrument maintenance and generating a new ICAL if maintenance does not help.

11.0 Calculations/Data Reduction

11.1 Qualitative Identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST library**.** Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions.

NOTE: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.

11.1.1 The sample component retention time must compare to within ± 0.06 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

11.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

11.1.3 The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.1.4 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%).

11.1.5 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

11.2 Relative Response Factor Calculation

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound being measured
A_{is} = Area of the characteristic ion for the specific internal standard
C_x = Concentration of the compound being measured (µg/L)
C_{is} = Concentration of the specific internal standard (µg/L)

11.3 Calculation of TICs

The calculation of TICs (tentatively identified compounds) is identical to the above calculation (11.22) with the following exceptions:

A_x = Area of the total ion chromatogram for the compound being measured
A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference
RF = 1

11.4 Calculating the Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{RF} \times 100\%$$

Where:

RF = Mean of RFs from the initial calibration for a compound
SD = Standard deviation for the mean RF from the initial calibration for a compound

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}}$$

RF_i = RF for each of the calibration levels
n = Number of RF values

See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

11.5 Calculating the Continuing Calibration Percent Drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

Where:

C_{actual} = Known concentration in standard
C_{found} = Measured concentration using selected quantitation method

11.6 Calculating the Concentration in the Extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

11.6.1 Average Response Factor Calibration

If the average of all the RSDs of the response factors in the initial calibration is ≤15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

Where:

C_{ex}	=	Concentration in the extract, µg/mL
R_x	=	Response for the analyte
R_{is}	=	Response for the internal standard
C_{is}	=	Concentration of the internal standard
$\overline{RF}$	=	Average response factor

11.6.2 Linear Fit Calibration

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

Where:

C_{ex}	=	Concentration in the extract, µg/mL
R_x	=	Response for the analyte
R_{is}	=	Response for the internal standard
C_{is}	=	Concentration of the internal standard
A	=	Intercept of linear calibration line
B	=	Slope of linear calibration line

11.6.3 Quadratic Fit Calibration

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

Where:

C_{ex}	=	Concentration in the extract, µg/mL
R_x	=	Response for the analyte
R_{is}	=	Response for the internal standard
C_{is}	=	Concentration of the internal standard
A	=	Intercept
B	=	Factor for the linear term of the quadratic calibration function
C	=	Factor for the curvature term of the quadratic calibration function

11.7 Calculating the Concentration in the Sample

11.7.1 Calculation for Aqueous Samples

$$\text{Concentration, } \mu\text{g / L} = \frac{C_{ex}V_t}{V_o}$$

Where:

C_{ex} = Concentration in the extract

V_t = Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then V_t = 2,000.)

V_o = Volume of the sample that was extracted (mL)

Instrument software calculates the concentration of the analyte in the final extract in ug/L. This result is used in the following equation:

Water: Conc., (ug/L) = [extract conc., ug/L] x [final extract vol., mL] x [dilution factor]
[sample volume, mL]

11.7.2 Calculation for Sediment, Soil, Sludge, and Waste Samples

Results for sediments, sludges, and soils are usually calculated on a dry-weight basis, and for waste, on a wet-weight basis.

$$\text{Concentration, } \mu\text{g / kg} = \frac{C_{ex}V_t}{W_sD}$$

Where:

C_{ex} = Concentration in the extract

V_t = Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then V_t = 2,000.)

W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry-weight basis or 1 for a wet-weight basis

Instrument software calculates the concentration of the analyte in the final extract in ug/L. This result is used in the following equation:

Soil: Conc., (ug/kg) = [extract conc., ug/L] x [final extract vol., mL] x [dilution factor]
[sample weight, g] x [%solids]

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

11.8 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.9 MS/MSD Percent Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where:

S_{SR} = Spike sample result
S_R = Sample result
S_A = Spike added

11.10 Calculating the Relative Percent Difference (RPD) MS/MSD Pair

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

Where:

RPD = Relative percent difference
MS_R = Matrix spike result
MSD_R = Matrix spike duplicate result

11.11 Calculating the Peak Tailing Factor

$$TailingFactor = \frac{BC}{AB}$$

Where:

Peak width (AC) is measured at 10% peak height, and divided into two line segments at the peak centroid, so that

AC = AB + BC, with
AB = left-hand segment
BC = right-hand segment

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.1.1 Instrumentation software must have each target limit set to the lowest MDL. CHROM (LOD)

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Acidic extracted sample and QC wastewater. After the extraction has been completed the spent water is neutralized and then collected into the organics water conical reservoir. The collected wastewater is then purged with air to remove any remaining methylene chloride. When the concentration levels are at or below local discharge limits, the wastewater can be discarded down the drain.

14.1.2 Solvent/Methylene Chloride waste. Any waste methylene chloride/solvent is collected in beakers and then poured into a 4-liter amber bottle labeled "Hazardous Waste" located in the hood. After the extraction has been completed the $MeCl_2$ collected in the 4 L bottles is emptied into the $MeCl_2$ satellite waste barrel located next to the neutralization tank in lab hood #17. The funnel lid on the drum must be closed after each use. At or before the satellite waste reaches 55 gallons, the barrel is transferred to the waste disposal room from where it is sent out for recycling or fuel blending.

14.1.3 Vialed extract waste. Sample extracts that have been placed into autosampler vials for analysis are discarded into satellite waste buckets labeled "Hazardous Waste" located underneath the bench top. Once the buckets are full the GC vials are bulked into the non-PCB GC vial waste barrel located in the waste room and sent out for incineration.

14.1.4 Extract waste. Unused sample extracts are held for at least 40 days, in case further testing is deemed necessary. After at least 40 days have passed these extracts are transported in to the waste room in racks of 100 were they are bulked into a flammable loose pack waste stream and sent out for incineration.

14.1.5 Expired primary and working standards. Expired standards are stored in a canister labeled "Hazardous Waste" at or near the point of generation. At or before the satellite waste reaches 55 gallons, it is removed to the waste warehouse

where it is bulked into the non-PCB GC vial waste barrel and sent out for incineration.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Methods 3510C, 3550B, 8000C, and 8151A.

16.0 Method Modifications:

Item	Method	Modification
1	8151A	The detector used is Ion Trap MS, instead of ECD.
2	8151A	SPE extraction replaces ethyl ether LL extraction as primary technique..
3	8151A	One mid-range concentration calibration standard is used for daily calibration.
4	8151A	Methanol replaces acetone to remove aldol condensation products

17.0 Attachments

Table 1 Chlorinated Herbicide Target Analyte List RLs
Table 2 Typical Instrument Operating Conditions
Table 3 Working LCS and MS/MSD Standard
Table 4 Working Surrogate Standard

Attachment 1: DFTPP Tuning Criteria
Attachment 2: Breakdown and Tailing Factor Reports
Attachment 3: Example Instrument Sequence
Attachment 4: DoD QC Tables
Attachment 5: Summary of QC Requirements

18.0 Revision History

- Revision 19, dated 20 April 2017
  - Added Acidified NaSO4 and Diazomethane hazard awareness to section 5.1
  - Added Sodium Sulfate, Acidification process for Sodium Sulfate and updated Tuning Standard, section 7.
  - Added requirement for derivatization to be performed in a hood, section 10.4

- Revision 18, dated 19 April 2017
  - Incorporated ROMD 00065..
  - Removed PIBLK requirement, section 9.3.

- Revision 17, dated 11 May, 2016
  - Updated section 2.1.
  - Updated standards and concentrations in sections 7.17 through 7.30
  - Updated procedures in section 10.2.8
  - Updated section 10.3.9 to shaker table instead of wrist shaker.
  - Added section 10.4.19 to describe where and how the derivatization is documented.
  - Added section 10.12.1 to describe the requirements for the Chrom worklist.

- Revision 16, dated 27 March, 2015
  - Added new Diazomethane Generation and Extract Derivitization procedure to section 10.4.

- Revision 15, dated 20 February, 2015
    - Changed supply list in section 6.2
    - Added SPE disk conditioning instructions to section 10.2.4
    - Added additional prep instructions to sections 10.2.8, 10.2.9 and 10.2.10
    - Additional dervitization instructions added to sections 10.4.1 through 10.4.3.
    - Added maintenance and troubleshooting, sections 10.12 and 10.13

- Revision 14, dated 22 August 2013
    - Changed sonic bath to be used unheated. Section 10.3.5
    - Changed hydrolization time to 30 minutes. Section 10.2.2
    - Added additional soil prep details in sections 10.3.7 through 10.3.9
    - Added additional detail under Safety section 5.1

- Revision 13, dated 7 May 2012
    - Incorporated ROMD 00044 in Section 10.3.5
    - Updated reagents and preparation of reagents, section 7
    - Updated standards making and vendors, section 7
    - Added a few more details in the procedure, section 10
    - Added requirement for documenting lot numbers, temperatures, and thermometer ID in the TALS batch information page, section 10
    - Added details for using a reference vial, section 10
    - Updated waste streams, section 14.1

- Revision 12, dated 16 May 2011
    - Incorporated ROMDs 00019 and 00026 in Section 6.1
    - Replaced methylated chlorinated herbicide standards in sections 7.15 and 7.17.
    - Added reference to derivatization procedure in section 7.18.
    - Updated tuning standards and included preparation of a working tune standard, sections 7.25 – 7.29 (ROMD 00027).
    - Incorporated ROMD 00020 in Section 10.5.1.
    - Incorporated ROMD 00033 in section 10.5.2.
    - Revised tuning procedures, sections 10.6.2, 10.6.3 and 10.6.5 (ROMD 00027).
    - Added section for monitoring raw instrument response of 1 compound for every CCV analysis.
    - Revised section 9.5 to include requirement of LCSD in the absence of MS/MSD (ROMD 00025).
    - Added bullet point to section 9.7 discussing corrective actions for surrogate failure.
    - Removed paragraph in section 9.7.1 regarding acceptance of 1 acid and 1 base surrogate failure. Not applicable to this method.
    - Added reference to corporate SOP for Initial calibration models and algorithms, section 10.8.9 (ROMD 00022).
    - Added bullet point in section 10.9.3 regarding procedure for high failing CCV's in DOD samples (ROMD 00024).
    - Added maintenance, data reduction and data review sections, 10.12, 10.13 and 10.14.
    - Added section 11, containing equations associated with calculating extract concentration.
    - Added Table 2 with general instrument operating conditions.

- Revision 11, dated 26 March 2010
    - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
    - Added removal of expired standards Section 7.19.
    - Added criteria for rinse blank evaluation Section 9.3
    - Updated surrogate spike level to 100 µg/mL Section 9.7.1
    - Added requirement for setting Section target limit set to lowest MDL Section 11.1.1

- Revision 10, dated 7 April 2009
    - Updated DoD QC Tables
    - Added Attachment 5: Summary of QC Requirements
    - Corrected minor typographical errors.

- Revision 9, dated 17 June 2008
    - Integration for TestAmerica and STL operations.

Table 1

Chlorinated Herbicide Target Analyte List RLs[1]

Analyte	Water RL (ug/L)	Soil RL (mg/kg)
Dalapon	0.5	3.33
Dicamba	0.25	1.33
Dichloroprop	0.25	1.33
2,4-D	0.25	1.33
Pentachlorophenol	0.25	1.33
Silvex (2,4,5-TP)	0.25	1.33
2,4,5-T	0.25	1.33
Dinoseb	0.25	3.33
2,4-DB	0.25	1.33
Mecoprop	0.25	3.33

1 - TestAmerica performs MDL studies and MDL verifications, so these values are subject to change please contact TestAmerica Seattle for current RLs.

Table 2

Typical Instrument Operating Conditions[1]

Parameter	Recommended Conditions
Injection Port Temperature:	250 °C for 1 min, then 300 °C at 200 °C/min for 15.75min
Temperature Program:	40 °C for 2.7 minutes 25 °C/min to 310 °C for 3.00 minutes 35 ℃/min to 320 ℃ for 0.22 minutes
Column 1:	Phenomenex Zebron ZB-5MS (30 m X 0.25 mm ID X 0.25 um)
Injection:	1 µL
Carrier Gas:	Helium

1 – Instrument conditions can be changed. See maintenance log for current instrument conditions.

TABLE 3

Working LCS and MS/MSD Standard

Compound	Concentration (µg/mL)
2,4,5-T	10
2,4-D	10
2,4,-DB	10
Dalapon	10
Dicamba	10
Dichlorprop	10
Dinoseb	10
MCPA acid	10
MCPP acid	10
Silvex	10

TABLE 4

Working Surrogate Standard

Compound	Concentration (µg/mL)
2,4-dichlorophenylacetic acid	100

Attachment 1: DFTPP Tuning Criteria

Report Date: 11-May-2016 16:05:29 Chrom Revision: 2.2 20-Apr-2016 13:59:46

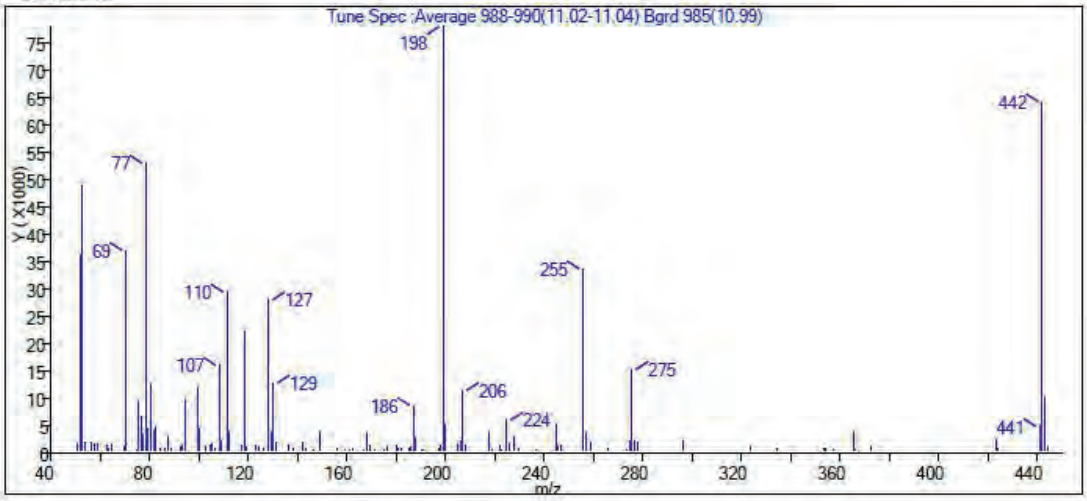
Preliminary Report

MS Tune Report

TestAmerica Seattle

Data File:	\\ChromNA\Seattle\ChromData\TAC039\20160509-47257.b\dftpp003.d		
Injection Date:	09-May-2016 15:22:56	Instrument ID:	TAC039
Lims ID:	dftpp		
Client ID:			
Operator ID:		ALS Bottle#:	0 Worklist Smp#: 1
Injection Vol:	1.0 ul	Dil. Factor:	1.0000
Method:	8151TAC039	Limit Group:	8151_GCMS
Tune Method:	DFTPP Method 525.2, BP 198		

29 DFTPP



m/z	Ion Abundance Criteria	% Relative Abundance
198	base peak, or >50% of 442	100.0 (121.6)
51	10-80% of the base peak	62.2
68	<2% of mass 69	0.7 (1.5)
69	Present	47.1
70	<2% of mass 69	0.0 (0.0)
127	10-80% of the base peak	35.4
197	<2% of mass 198	1.0
199	5-9% of mass 198	6.0
275	10-60% of the base peak	19.0
365	>1% of the base peak	4.1
441	Present and < mass 443	5.5 (44.2)
442	base peak, or >50% of 198	82.3
443	15-24% of mass 442	12.4 (15.1)

Report Date: 11-May-2016 16:05:29 Chrom Revision: 2.2 20-Apr-2016 13:59:46

Data File: \\ChromNA\Seattle\ChromData\TAC039\20160509-47257.b\dftpp003.d\8151TAC039.rslt\spectra.d
Injection Date: 09-May-2016 15:22:56
Spectrum: Tune Spec :Average 988-990(11.02-11.04) Bgrd 985(10.99)
Base Peak: 198.00
Minimum % Base Peak: 0
Number of Points: 117

m/z	Y	m/z	Y	m/z	Y	m/z	Y
49.00	1129	101.00	357	168.00	712	244.00	4728
50.00	35464	103.00	646	170.00	4	245.00	404
51.00	48088	104.00	1115	174.00	41	246.00	674
52.00	1223	105.00	274	175.00	365	255.00	33024
55.00	1281	107.00	15390	179.00	633	256.00	3081
56.00	1003	108.00	1521	180.00	217	258.00	1253
57.00	987	110.00	28784	181.00	103	265.00	139
61.00	835	111.00	3219	184.00	55	273.00	15
62.00	130	116.00	812	185.00	384	274.00	1512
63.00	964	117.00	21600	186.00	8084	275.00	14644
68.00	560	118.00	585	187.00	2225	276.00	1684
69.00	36376	122.00	667	189.00	11	277.00	1205
73.00	14	123.00	338	190.00	2	296.00	1450
74.00	8782	125.00	265	196.00	199	323.00	547
75.00	5894	127.00	27352	197.00	760	334.00	186
76.00	2634	128.00	3316	198.00	77264	353.00	50
77.00	52328	129.00	12157	199.00	4646	354.00	89
78.00	3688	130.00	1258	204.00	957	357.00	2
79.00	11797	135.00	757	205.00	1482	365.00	3133
80.00	3527	137.00	98	206.00	10808	366.00	5
81.00	3983	141.00	1351	207.00	741	372.00	463
83.00	130	142.00	216	217.00	3364	423.00	1859
85.00	286	145.00	37	218.00	13	424.00	171
86.00	2398	148.00	3260	221.00	798	441.00	4234
87.00	51	155.00	314	222.00	40	442.00	63560
91.00	365	158.00	22	224.00	5401	443.00	9589
92.00	750	160.00	17	225.00	885	444.00	531
93.00	9077	161.00	112	227.00	2414		
98.00	11340	166.00	2	229.00	130		
99.00	3706	167.00	2894	236.00	18		

Attachment 2: CCV and Breakdown and Tailing Factors

Report Date: 11-May-2016 16:05:29 Chrom Revision: 2.2 20-Apr-2016 13:59:46

Preliminary Report

Peak Tailing Report

TestAmerica Seattle

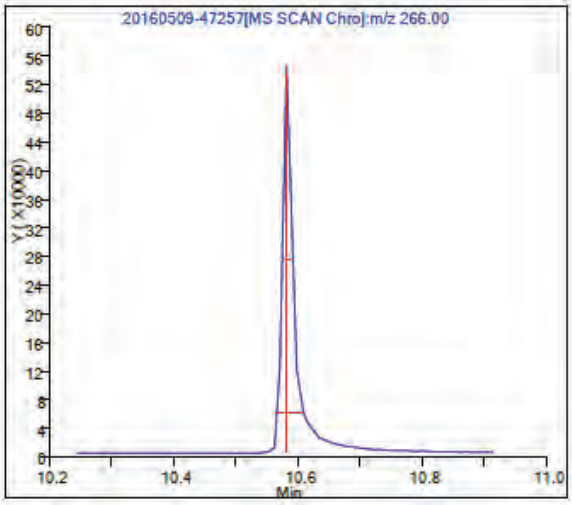
Data File: \\ChromNA\Seattle\ChromData\TAC039\20160509-47257.b\dftpp003.d
Injection Date: 09-May-2016 15:22:56 Instrument ID: TAC039
Lims ID: dftpp
Client ID:
Operator ID: ALS Bottle#: 0 Worklist Smp#: 1
Injection Vol: 1.0 ul Dil. Factor: 1.0000
Method: 8151TAC039 Limit Group: 8151_GCMS

53 Pentachlorophenol_T. Detector: MS SCAN

Peak Tailing Factor =
BackWidth/FrontWidth @ 10% Peak Height

Back Width = 0.028 (min.)
Front Width = 0.016 (min.)

Tailing Factor = 1.8, Max. Tailing < 5.00
Passed

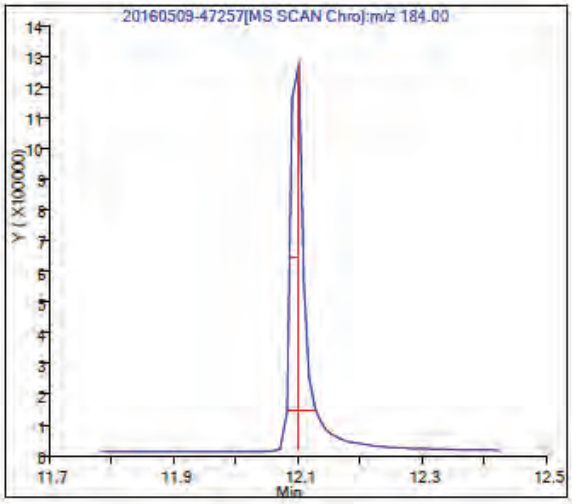


55 Benzidine_T. Detector: MS SCAN

Peak Tailing Factor =
BackWidth/FrontWidth @ 10% Peak Height

Back Width = 0.028 (min.)
Front Width = 0.019 (min.)

Tailing Factor = 1.4, Max. Tailing < 3.00
Passed



Report Date: 11-May-2016 16:05:29 Chrom Revision: 2.2 20-Apr-2016 13:59:46

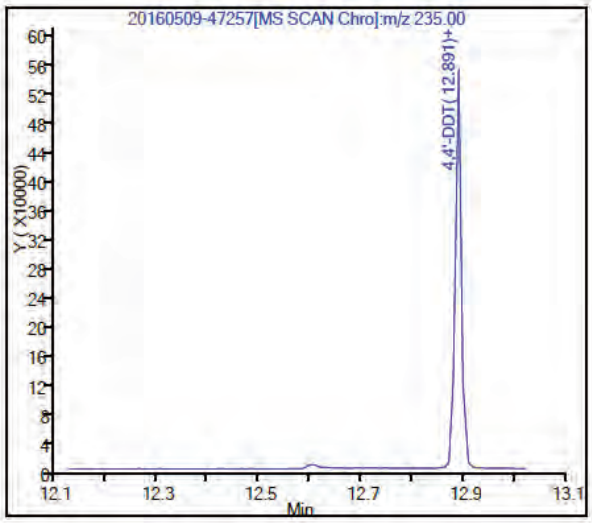
Preliminary Report

Breakdown Report

TestAmerica Seattle

Data File: \\ChromNA\Seattle\ChromData\TAC039\20160509-47257.b\dftpp003.d
Injection Date: 09-May-2016 15:22:56 Instrument ID: TAC039
Lims ID: dftpp
Client ID:
Operator ID: ALS Bottle#: 0 Worklist Smp#: 1
Injection Vol: 1.0 ul Dil. Factor: 1.0000
Method: 8151TAC039 Limit Group: 8151_GCMS

51 4,4'-DDT, Detector: MS SCAN

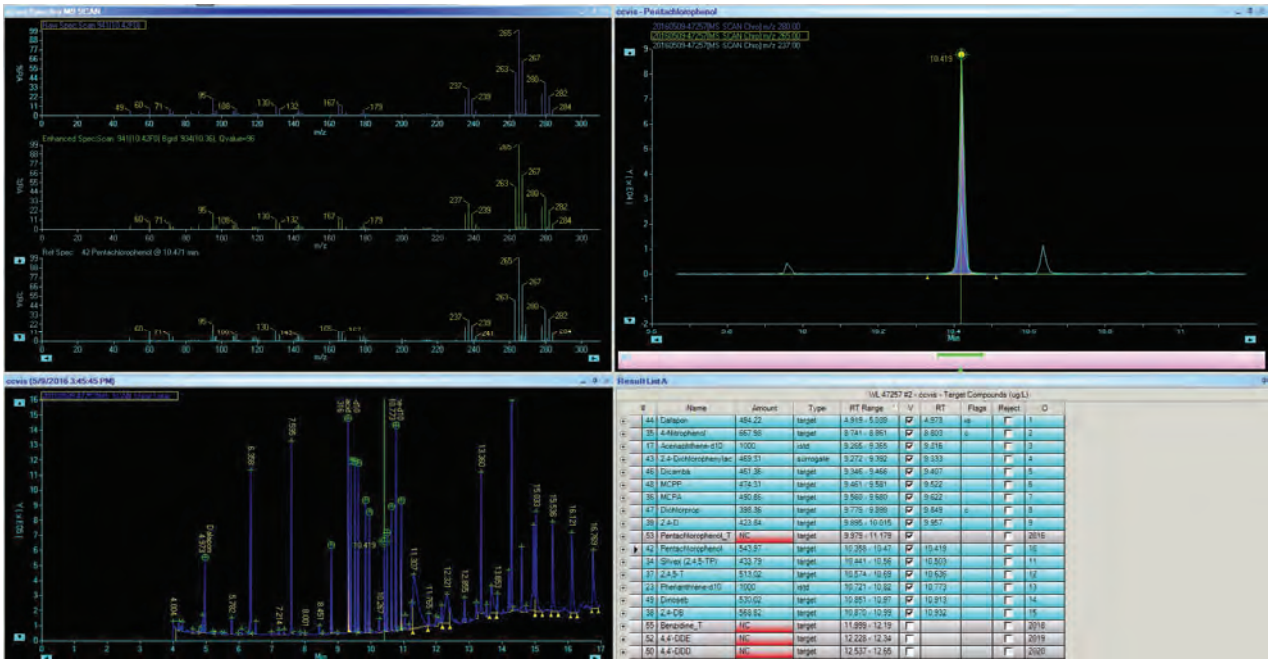


SW-846 Method

%Breakdown =
(Area Breakdown Cpnds/
Total Area Breakdown Cpnds) * 100

51 4,4'-DDT, Area = 446796
50 4,4'-DDD, Area = 8941
52 4,4'-DDE, Area = 0

%Breakdown: 1.96%, Max Limit: 20.00%
Passed



Report Date: 11-May-2016 16:13:20 Chrom Revision: 2.2 20-Apr-2016 13:59:46

Preliminary Report

TestAmerica Seattle
CCVIS, Cal Verification ISTD Check Report

Data File: \\ChromNA\Seattle\ChromData\TAC039\20160509-47257.b\ccvis003.d
Lims ID: ccvis
Client ID:
Sample Type: CCVIS
Inject. Date: 09-May-2016 15:45:45 ALS Bottle#: 0 Worklist Smp#: 2
Injection Vol: 1.0 ul Dil. Factor: 1.0000
Sample Info:
Operator ID: Instrument ID: TAC039
Sublist: chrom-8151TAC039*sub1

Method: \\ChromNA\Seattle\ChromData\TAC039\20160509-47257.b\8151TAC039.m
Limit Group: 8151_GCMS
Last Update: 10-May-2016 09:59:02 Calib Date: 22-Oct-2015 20:50:01
Integrator: RTE ID Type: RT Order ID
Quant Method: Internal Standard Quant By: Initial Calibration
Last ICal File: \\ChromNA\Seattle\ChromData\TAC039\20151022-44687.b\std1.d

Column 1 : Det: MS L28671D
Process Host: XAWRK018

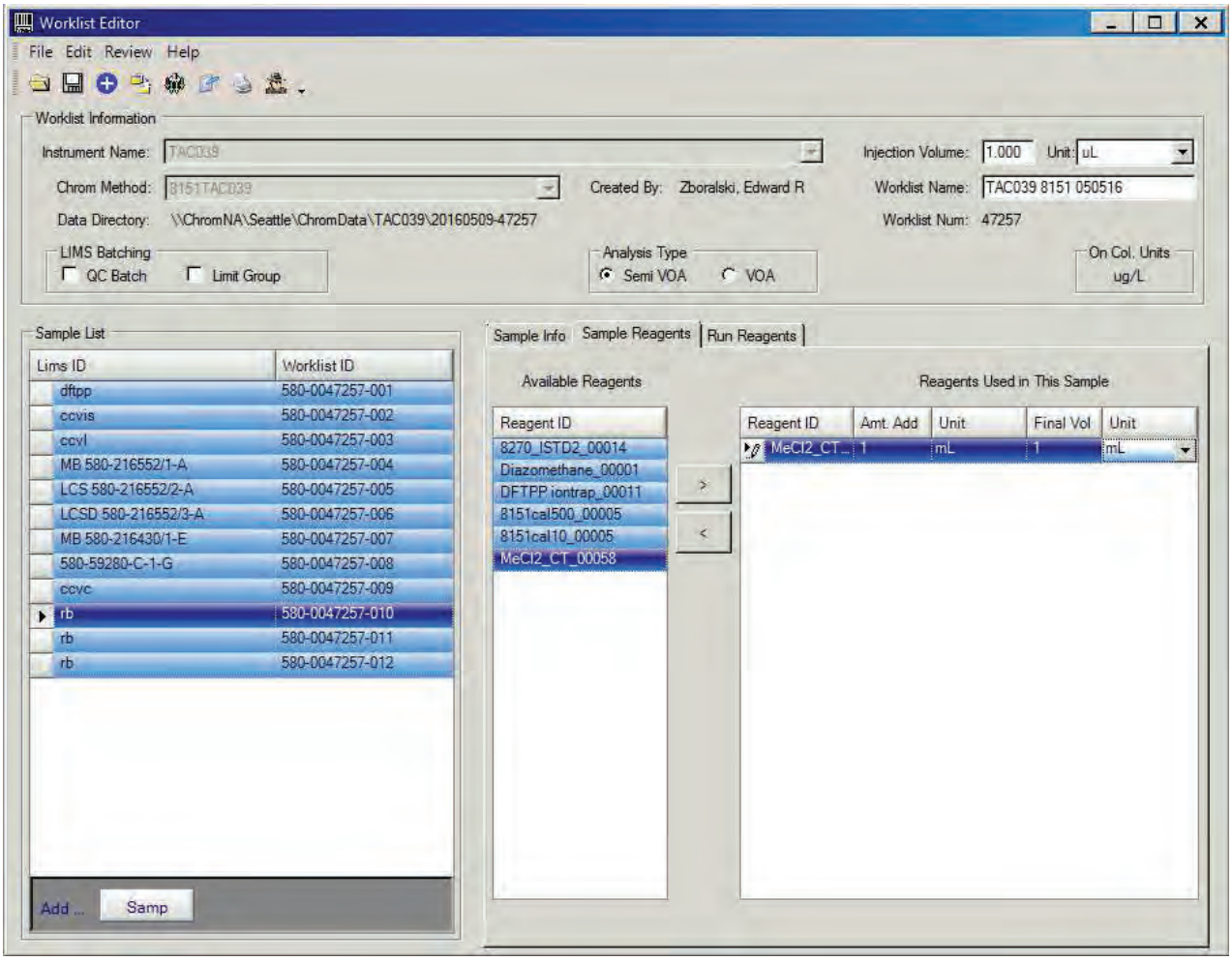
First Level Reviewer: bittene Date: 10-May-2016 08:20:27

Start Cal Date: 22-Oct-2015 17:25:10
End Cal Date: 22-Oct-2015 20:50:01

Compound	Standard RRF/Amt	DLT RT	Ccal Amt	Ccal RF	Min. RRF	%D	Max. %D	%Rec
44 Dalapon	(I) 0.910442	-0.006		0.899918	0.000	-1.2	20	99
35 4-Nitrophenol	500.0	0.002	668.0	1.227444	0.050	*33.6	20	134
$ 43 2,4-Dichlorophenylaceti	1.199958	0.001		1.126313	0.000	-6.1	20	94
46 Dicamba	1.131868	0.001		1.044390	0.000	-7.7	20	92
48 MCPP	0.733160	0.001		0.695483	0.000	-5.1	20	95
36 MCPA	0.547126	0.002		0.537121	0.000	-1.8	20	98
47 Dichlorprop	500.0	0.010	398.4	0.348511	0.000	*-20.3	20	80
39 2,4-D	500.0	0.002	423.8	0.539535	0.000	-15.2	20	85
42 Pentachlorophenol	500.0	0.001	544.0	0.377680	0.000	8.8	20	109
34 Silvex (2,4,5-TP)	0.224337	0.002		0.194632	0.000	-13.2	20	87
37 2,4,5-T	0.485944	0.002		0.498598	0.000	2.6	20	103
49 Dinoseb	500.0	0.002	530.0	0.254706	0.000	6.0	20	106
38 2,4-DB	505.0	0.002	568.8	1.249609	0.000	12.6	20	113

(I) Fails an Initial Calibration Test

Attachment 3: Example Instrument Sequence



Attachment 4: DoD QC Tables

Table G-7. LCS Control Limits for Chlorinated Herbicides SW-846 Method 8151 Water Matrix

Analyte	Median	Lower Control Limit	Upper Control Limit
2,4,5-T	94.8	42	147
2,4,5-TP (Silvex)	92.9	51	134
2,4-D	98.4	45	152
2,4-DB	94.1	35	153
2,4-Dichlorophenylacetic Acid	85	32	138
Dalapon	79	19	139
Dicamba	95.3	50	141
Dicloroprop	102	46	159
MCPA	89.2	35	144
MCPP	95.2	33	157

Table G-8. LCS Control Limits for Chlorinated Herbicides SW-846 Method 8151 Solid Matrix

Analyte	Median	Lower Control Limit	Upper Control Limit
2,4,5-T	84.6	31	138
2,4,5-TP (Silvex)	86.1	43	129
2,4-D	86	28	144
2,4-DB	88.2	34	142
2,4-Dichlorophenylacetic Acid	74	27	122
Dicamba	85.2	38	132
Dichloroprop	91.4	28	155
MCPA	81.5	28	135
MCPP	88.7	35	143

Attachment 5. Summary of QC Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
DFTPP Tune	Prior to ICAL and at the beginning of each 12-hour period.	See Section 10.5	Retune instrument and verify. Rerun affected samples.
Breakdown Check	At the beginning of each 12-hour period and prior to analyzing samples.	Degradation ≤ 20% for DDT. Benzidine tailing < 3.0 and PCP tailing < 5.0. **For DoD:** Benzidine and PCP should be present at their normal responses, and should not exceed a tailing factor of 2.	Correct problem then repeat breakdown check. No samples can be run until degradation is acceptable.
Minimum 5-point Initial Calibration	Initial calibration prior to sample analysis	Option 1: RSD for each analyte ≤ 20% Option 2: Linear regression r ≥ 0.990 Option 3: Non linear regression r^2 ≥ 0.990 and 6 points must be used. **For DoD:** 1. Average Response Factor for SPCCs: ≥ 0.050 2. RSD for RFs for CCCs: ≤ 30% and one option below: Option 1: RSD for each analyte ≤ 15% Option 2: Linear regression r ≥ 0.995 Option 3: Non linear regression r^2 ≥ 0.990 and 6 points must be used.	Terminate analysis; correct the problem; recalibrate. Problem must be corrected. No samples may be run until ICAL has passed.
ICV	Following initial calibration.	75-125% recovery **For DoD:** 80 - 120% recovery	Terminate analysis; correct the problem; recalibrate.
Relative Retention Times (RRT)	With each sample	RRT of each target analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL. Laboratory may update RTs based on the CCV to account for minor performance fluctuations or after routine system maintenance (e.g.

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
			column clipping).
CCV	Daily before sample analysis and every 12 hours of analysis time; and at the end of the analytical batch run	%D/Drift ≤ 20%D %D/Drift ≤ 50%D for end of analytical batch CCV.	Correct problem, rerun CCV. If that fails, then repeat ICAL. Reanalyze all sample since last successful CCV.
Internal Standards (IS) verification	Every field sample, standard, and QC sample	Retention time ± 30 seconds from RT of the midpoint standard in ICAL; EICP area within -50% to +100% of ICAL midpoint standard.	
Method Blank	One per batch of 20 field samples or fewer.	The result must be < RL or < 1/10 the amount measured in any sample or 1/10 the regulatory limit. **For DoD:** No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit. For common laboratory contaminants no analytes detected > RL.	Re-extract and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.
LCS	One per batch of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must contain all analytes to be reported and must be within QSM control limits.	See Section 9.4 for additional requirements.
Surrogate	All field and QC samples.	Must be within laboratory control limits, however, 1 acid or 1 base/neutral surrogate may fail before requiring corrective action. **For DoD:** must be within QSM control limits.	See Section 9.6 for additional requirements.
Matrix Spike/Laboratory Fortified Matrix	One per lot of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must contain all analytes to be reported and must be within QSM control limits.	See Section 9.5 for additional requirements.

Title: Semivolatile Organic Compound (Base/Neutrals and Acids) Analysis by GC/MS [Method 8270D]

Approvals

Signatures on File	
Ryan Zboralski Date	Manjit Nijjar Date
Semivolatile Organic Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 This method is based upon standard method SW846 8270D, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices.

1.1.1 Direct injection of a sample may be used in limited applications.

1.1.3 Refer to Table 1 for the list of compounds applicable for this method. This method may be amenable to additional compounds. If non-standard analytes are required, they must be validated by the procedures described in section 12 before sample analysis.

1.2 The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method. They are reported as 3- and 4-methylphenol.
- Hexachlorophene and famphur analysis are not quantitatively reliable by this method.

1.3 The reporting limit (RL) of this method for determining an individual compound is approximately 10 ug/kg to 4,000 ug/kg for soil/sediment samples and 0.02 µg/L to 15 µg/L for water samples. Some compounds have higher reporting limits. The current reporting limits are all updated in TALS. Reporting limits will be proportionately higher for sample extracts that require dilution.

1.4 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 Aqueous samples are extracted with methylene chloride using a continuous extractor or Separatory Funnel.

2.2 Solid samples are extracted with methylene chloride / acetone using sonication or microwave extraction. The extract is dried, concentrated, and analyzed by GC/MS.

2.3 Waste dilution is used for samples that are miscible with the solvent.

2.4 Extraction procedures are detailed in the following SOPs:

TA-OP-0302	SONICATION EXTRACTION PROCEDURE, SW846 3550B
TA-OP-0323	CONTINUOUS LIQUID-LIQUID EXTRACTION, SW846 3520C

2.5 Additional extraction procedures are detailed in the following SOPs. They may be subject to having complete MDL studies so check with QA before using.

TA-OP-0301 Separatory Funnel Extraction (3510C)

TA-OP-0367 Microwave Extraction (3546)

2.6 Qualitative identification of the analytes in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3.0 Definitions

3.1 Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / matrix spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the TestAmerica Seattle SOP TA-QA-0620 Quality Control Program for further details of the batch definition.

3.2 Method Blank (MB) - An analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.3 Laboratory Control Sample (LCS) - A blank matrix (reagent water or Ottawa Sand) spiked with the analytes of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked analytes demonstrates that the laboratory techniques for this method are acceptable.

3.4 Matrix Spike (MS) – An aliquot of a matrix (water or soil) fortified (spiked) with known amounts of specific analytes and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.5 Matrix Spike Duplicate (MSD) - A second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method by measuring the relative percent difference (RPD) between the MS and MSD results.

3.6 Surrogates - Organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, MS, and MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

4.0 Interferences

4.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample. Cleanup procedures may help to eliminate select interferences, as follows:

- Method 3640A, Gel-Permeation Chromatography - Removes higher molecular weight hydrocarbons by size exclusion chromatography, which is most frequently used for biological samples.

- Other, more aggressive cleanup procedures listed in SW-846 may be used for select compounds listed in this procedure, but may cause degradation of some of the more reactive compounds. Consult with a technical expert in the laboratory for more difficult interference problems.

4.2 Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause method interferences. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section (Section 9.0). Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If interference is detected, it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.3 The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum. Cut resistant gloves must be worn when using sharp tools or when washing glassware.

5.1 Specific Safety Concerns

5.1.1 Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

NOTE: LATEX AND VINYL GLOVES PROVIDE NO PROTECTION AGAINST THE ORGANIC SOLVENTS USED IN THIS METHOD. NITRILE OR SIMILAR GLOVES MUST BE USED.

5.1.2 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.4 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power before performing any maintenance.

5.1.5 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Materials with Significant or Serious Hazard Rating

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Gas chromatograph/mass spectrometer system: an analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source
- Mass Spectrometer: Capable of scanning from 35 to 500 u (previously “amu”) every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) that meets all of the criteria in Table 3 when 25 ng of the GC/MS tuning standard is injected through the GC
- Autosampler: LEAP Technologies CTC A200S, HP7683 Autosampler or equivalent
- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used
- Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the NIST Mass Spectral Library is recommended. Agilent (Hewlett Packard) ChemStation for Windows 95 (version G1701AA) or equivalent. Agilent’s ChemStation, is used for data acquisition and storage on machine-readable media. Since no processing is done by ChemStation and since there are no audit trail functions associated with data acquisition, the audit trail feature for ChemStation may be either enabled or disabled. The other component, Chrom, is used for data processing such as the measurement of peak area or peak height. By design, the audit trail feature for Chrom is always enabled.
- Data processing: Chrom version 1.2 or higher.
- LIMS system: TALS version 1.0 or higher

6.2 Supplies

- Column: 30 m x 0.25 mm I.D., 0.25-µm film thickness fused-silica capillary column (Phenomenex ZB-SemiVolatiles, Restek Rxi-5SilMS, or equivalent).

  Note: Other columns may be used. This was the column in place at the time the SOP was prepared. The serial number of the column used is documented in the instrument maintenance logbook.
- Gas-tight syringes (Hamilton 1700 Series, or 1000 Series or equivalent).
- 10 ml scintillation vials with polypropylene closures or 10, 20, 40 or 60 ml VOA vials with Teflon-lined silicone septa enclosures (or equivalent).
- Analytical balance, capable of reading to 0.0001g. Analysts must verify calibration has been preformed on the balance before using it. The calibration must bracket the weights to be determined.
- Class A volumetric flasks; 10 mL, 25 mL, 50 mL, 100 mL, 250 mL.
- Carrier gas: Ultra high-purity helium

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 A minimum five-point calibration curve is prepared when average response factors or linear regression curve fitting is used. Six calibration points are required for second-order curve fits. The low point should be at or below the reporting limit. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2.1 Initial calibration stock standards 8270

7.2.1.1 1000 ug/ml 8270 List 1 / Std#1 MegaMix – Restek 571995

2000 ug/ml 8270 List 1 / Std#9 - Restek 569730

2000 ug/ml 8270 List 1 / Std#10 - Restsk 569731

2000 ug/ml 8270 List 1 / Std#11 - Restek 569732

5000 ug/ml Surrogate stock – Phenova AL0-130068

7.2.2 Intermediate calibration standard 8270

7.2.2.1 Dilute 1.0-mL of stock solutions listed in section 7.2.1.1. For the surrogate standard, dilute 200 uL. Mix to a final volume of 10-mL to make a 100-500 µg/mL intermediate stock solution.

7.2.3 Working calibration standards 8270

7.2.3.1 Dilute the intermediate calibration stock solution (section 7.2.3) as follows to make working calibration standards:

Note: Calibration points may be added on an as-needed basis when wider calibration ranges are needed.

Calibration Level	Volume of Intermediate Stock (µL)	Final Volume	Concentration (µg/L)
1	5	50	10
2	10	50	20
3	25	50	50
4	50	50	100
5	100	50	200
6	250	50	500
7	500	50	1000
8	1000	50	2000
9	2500	50	5000
10	5000	50	10000

7.2.4 ICV Standard 8270

7.2.4.1 8270 List 1 / Std#1 MegaMix – Restek 571995.SEC

8270 List 1 / Std#9 - Restek 569730.SEC

8270 List 1 / Std#10 - Restsk 569731.SEC

8270 List 1 / Std#11 - Restek 569732.SEC

7.2.4.2 1.0 ug/mL ICV Working Solution is prepared by diluting 100 µL of each standard in section 7.2.4.1 to a final volume of 100-mL with methylene chloride.

7.3 An internal standard (IS) solution is prepared. Compounds in the IS Mix are acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.3.1 2000 ug/ml 8270 Internal Standard Restek #567684. A 100 ug/ml 8270 Internal Standard is prepared by diluting 5.0 ml of the 2000 ug/ml Restek Standard to 100 ml with methylene chloride.

7.3.2 Internal standards are added to all standards and extracts to result in a final concentration of 1000 µg/L for full scan and 100 µg/L for SIM. For example, if the volume of an extract aliquot used was 1 mL, 10 µL of a 100 µg/mL internal standard solution would be added to the aliquot.

7.4 GC/MS Tuning Standard: A methylene chloride solution containing 25 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT should also be included in the Tuning Standard at 25 µg/mL. 2uL of this solution should be injected for an on column concentration of 50ng.

7.5 Laboratory Control Spiking Solution, Matrix Spike Solution, and surrogate spike solutions: Prepare as indicated in the extraction SOPs.

7.6 The standards listed in sections 7.1 to **Error! Reference source not found.** must be refrigerated at 0-6°C. Stock standards expire 1 year after preparation.

7.7 ICAL reagents should be replaced after one month if the vials have been opened frequently (more than 5 times in a month).

7.8 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned, amber glass bottles fitted with a Teflon-lined cap. To achieve routine reporting limits, a full one-liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Alternatively, water samples can be collected in a pre-cleaned, amber 250mL bottle with a Teflon-lined cap. Currently, LVI volumes are only used for 8270 SIM PAH analysis.

8.3 Soil samples are collected in 8-ounce, pre-cleaned, wide-mouth jars with a Teflon-lined lid.

8.4 Samples and extracts are stored at 0-6℃.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	250mL for LVI or 1 Liter for non LVI	Cool 0-6°C	7 Days	40 Days from extraction	40 CFR Part 136.3
Soils	Glass	30 grams	Cool 0-6°C	14 Days	40 Days from extraction	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section and in Table 6. The process of establishing control limits, and the use of control charts are described more completely in TA-QA-0620, Quality Control Program. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in SOP TA-QA-0620, Quality Control Program.

9.1.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via instructions in the LIMS.

9.1.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed together using the same reagents and standards. Each quality control batch must contain a method blank (MB), a laboratory control sample (LCS), matrix spike (MS), and/or matrix spike duplicate (MSD) or duplicate (DUP) pair. For more details see SOP TA-QA-0620.

9.3 Method Blank (MB)

For aqueous sample batches, the method blank is reagent water; for solid sample batches, the method blank is clean sand. In either case, the method blank is free of the analytes of interest and is spiked with the surrogates. At least one method blank must be processed with each preparation batch.

Acceptance Criteria: The result for the method blank must be less than the reporting limit or less than 10% of the analyte concentration found in the associated samples, whichever is higher.

NOTE: Some programs (e.g., DOD and BP) require that the maximum blank concentration must be less than one-half of the reporting limit or less than 10% of the lowest sample concentration.

Corrective Action: Re-preparation and reanalysis of all samples associated with an unacceptable method blank. If the analyte was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.4 Laboratory Control Sample (LCS)

The LCS is prepared using reagent water for aqueous methods and Ottawa sand for solid sample methods. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. For DOD and BP, an LCSD must be analyzed if there is not sufficient volume for a MS/MSD. The LCSD must pass the same control criteria as the LCS. Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

Acceptance Criteria: All analytes must be within established control limits. See QC SOP TA-QA-0620 for details on establishing control limits.

Corrective Action: If any analyte in the LCS is outside the laboratory-established historical control limits or project-specific control limits, as applicable, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the LCS recovery is high and there are non-detect samples. An NCM is initiated. The non-detect samples are flagged and reported.

  NOTE: DOD programs do not allow reporting data from high LCS's with sample non-detects. If data is to be reported, it must be authorized by the client via a variance on a site by site basis.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the

project records and the report. An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS. This type of justification should be reviewed and documented with the client before reporting.

- If re-extraction and reanalysis of the batch are not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The matrix spike is a second aliquot of one of the samples in the batch. The matrix spike duplicate is a third aliquot of the same sample. The MS and MSD are spiked with the same analytes as the LCS. An MS/MSD pair is prepared and analyzed with every batch of samples when sufficient sample volume is available.

Acceptance Criteria: The percent recovery (%R) must fall within either historical limits or project-specific limits, as applicable. The relative percent difference (RPD) between the MS and MSD results must be less than or equal to the established historical or project-specific limit. See QC SPP TA-QA-0620 for details on establishing control limits

Corrective Action: If any individual recovery or RPD fails the acceptance criteria, then corrective action must occur. Initially check the recovery of the analyte in question in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is considered to be in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any analyte fails acceptance criteria for the MS, MSD, and the LCS, the laboratory operation is considered to be out of out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.
- If it is not possible to prepare both an MS and MSD due to limitations of sample amount, then a duplicate LCS should be prepared and analyzed. The RPD between the LCS and LCSD must be less than or equal to the RPD limit established for the MS/MSD.
- The MS/MSD pair must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted to concentrations below the calibration range.

9.6 Surrogates

9.6.1 Each sample, blank, and QC sample is spiked with the surrogate standards. Surrogate compounds are spiked at 100 µg/mL. The compounds routinely included in the surrogate spiking solution, along with recommended standard

concentrations, are listed in Table 4.

Acceptance Criteria: Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

Corrective Action: For particular sublists, such as PAH only, acid surrogates may fail with no corrective action required. However, the failure must be documented in an NCM if the surrogates are reported. Otherwise, if any surrogates are outside of the limits, then the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem.
- Re-extract and reanalyze the sample or flag the data as “Estimated Concentration” if neither of the above resolves the problem.

Note: For BP LaMP samples, if the surrogate %R fails, the recovery must be confirmed by re-extraction and reanalysis with the following exceptions:

- The lab has unequivocally demonstrated a sample matrix effect and informed the BP representative.
- The recovery exceeds *upper* control limits and all target analytes in the sample are non-detect.

NOTE: The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/ reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

9.6.2 If the sample with failed surrogate recoveries was a sample used for an MS/MSD pair and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample and the MS and the MSD do not require reanalysis. This phenomenon indicates a possible matrix problem.

9.6.3 If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate).

9.6.4 If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effects.

9.7 **Instrument QC**

9.8 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The nonconformance shall be addressed in the case narrative, and the NCM shall be filed in the project file. The NCM process is described in more detail in SOP TA-QA-0610.

10.1 Sample Preparation

Samples are prepared according to the following organic preparation SOPs, as applicable:

TA-OP-0302 SONICATION EXTRACTION PROCEDURE, SW846 3550B

TA-OP-0323 CONTINUOUS LIQUID-LIQUID EXTRACTION, SW846 3520C

Additional extraction procedures are detailed in the following SOPs.

TA-OP-0301 Separatory Funnel Extraction (3510C)

TA-OP-0367 Microwave Extraction (3546)

TA-OP-0314 Waste Dilution (3580A)

10.2 Instrument Operating Conditions

10.2.1 Typical instrument operating conditions are listed in Table 2. Actual instrument operating conditions are posted in each maintenance logbook.

10.2.2 The instrument is tuned for DFTPP, calibrated initially with a minimum of a five levels, and verified each 12-hour shift with one or more continuing calibration standard(s).

10.2.3 All standards and extracts are allowed to warm to room temperature before injecting.

10.3 8270 SIM

10.3.1 SIM (selective ion monitoring) is an alternative to analyzing samples under full scan mode. SIM selects specific target ions for analysis. SIM can be up to ten times more sensitive. In order to achieve maximum sensitivity the selected ions should be broken up in to several groups. Each of the target analytes should have 1 ion used for quantitation and 2 qualifier ions. The suggested SIM groupings and ion are in Table 7. Other parameters can be used as long as sufficient sensitivity is achieved.

10.3.1.1 SIM can also be extended to other 8270 target analytes not listed in Table 7.

10.3.1.2 The internal standards and surrogates do not need to have 2 qualifier ions.

10.4 Instrument Tuning

10.4.1 A MS tuning compound (DFTPP) is analyzed every twelve hours during instrument operation, prior to analysis of standards, samples, or QC samples. Method tuning criteria must be met before sample analysis can proceed.

10.4.2 Tuning Procedure (Ion Trap): 2.0 ul of a 2.5 ng/uL solution of decafluorotriphenylphosphine (DFTPP) must be analyzed in a scanning mode of 40 - 450 m/z. The tuning solution must also contain 4,4'-DDT, Pentachlorophenol, and Benzidine at the same concentration.

10.4.3 Tuning Procedure (Quadrapole): 2.0 ul of a 25 ng/uL solution of decafluorotriphenylphosphine (DFTPP) must be analyzed in a scanning mode of 40 - 450 m/z. The tuning solution must also contain 4,4'-DDT, Pentachlorophenol, and Benzidine at the same concentration.

10.4.4 Inject the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. DFTPP Tuning Criteria (per EPA method 525.1):

Mass	Ion Abundance Criteria
51	10 - 80% of base peak
68	< 2% of mass 69
69	present
70	< 2% of mass 69
127	10 - 80% of base peak
197	< 2% of mass 198
198	Base peak or > 50% of 442
199	5 - 9% of mass 198
275	10 - 60% of base peak
365	> 1% of base peak
441	Present, but less than mass 443
442	Base peak or > 50% of mass 198
443	15 - 24% of mass 442

10.4.5 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Column performance and Injector Inertness Acceptance Criteria:

- Benzidine tailing factor of $\leq$ 2.0
- Pentachlorophenol tailing factor of $\leq$ 2.0
- Degradation of 4,4'-DDT to 4,4'-DDE and 4,4'-DDD < 20%.

10.5 Initial Calibration

10.5.1 Internal Standard (IS) Calibration Procedure: Internal standards are listed in Section 7.6. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation. 10 uL of internal standard solution is added for every 1 mL of extract to all calibration standards, QC samples, and samples prior to analysis. The autosampler injects up to 5 uL of standard and extract volumes into the instrument for analysis.

10.5.2 Compounds are assigned to the IS with the closest retention time.

10.5.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest when average response factors or linear regression curve fits are used. Six standards must be used for a quadratic least-squares calibration. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response.

10.5.4 Rejection of Calibration Points

10.5.4.1 Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

10.5.4.2 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious misinjection explained in the run log), then points may be rejected, but only if all of the following conditions are met:

- The rejected point(s) are the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and
- The lowest remaining calibration point is still at or below the project reporting limit; and
- The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and
- The calibration must still have the minimum number of calibration levels required by the method, i.e. five levels for calibrations modeled with average response factors or linear regressions, or six levels for second-order curve fits.

10.5.5 Add the internal standard mixture to result in a 1,000-µg/L final concentration. (For example, if the volume of the calibration standard used is 0.5 mL, add 5 µL of the 100 µg/L internal standard).

10.5.6 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against the concentration for each compound and internal standard. Calculate the response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12 and Corporate SOP CA-Q-S-005. No sample analysis may be performed unless these criteria are met.

Resolution check.

Isomeric pairs need have greater than >50% resolution. Benzo(b)fluoranthene and benzo(k)fluoranthene are usually the most likely failure. This isomeric pair must have >50% resolution. This needs to be checked on the mid point ICAL and the CCV. If the combined peak “benzofluoranthenes “ is being requested, the 50% resolution check is not applicable, but all other isomers that are in the list must also be >50% resolution.

10.5.7 If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with RSD > 20% (>15% for DOD)for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve fit, then the appropriate curve should be used for quantitation.

10.5.8 If the RSD for a compound in the initial calibration is > 20%(>15% for DOD), then calibration using a curve fit, must be used. Linear or quadratic curve fits may be used. Use of 1/Concentration2 weighting is recommended to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response.

10.5.9 If a linear regression equation is used, the correlation coefficient (r) must be greater than 0.990 for commercial projects and greater than 0.995 for DoD projects, and r squared (r2) greater than 0.990.

10.5.10 Use of second-order equations (quadratic) may be used on rare occasions and must consist of a minimum of six data points. In these cases, the intercept and degree of curvature should be examined to be sure that results will be reliable throughout the working range, and the coefficient of determination (r2) must be greater than 0.990.

10.5.11 Weighting of Calibration Data Points

10.5.12 In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. 1/Concentration2 weighting (often called 1/X2 weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.5.13 In addition to meeting %RSD requirements, each analyte must meet a minimum RF requirement. The minimum RF requirements are defined in table 8.

10.5.14 See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

10.5.15 An initial calibration verification containing all components from a second source (an alternate vendor or a unique lot from the same vendor) must be analyzed after the initial calibration. Acceptance criteria for ICV percent recovery (%R) are 80-120% of all target analytes for DoD (e.g., Navy and USACE) and BP LaMP projects; 70-130% for non-DoD projects (e.g., 8270D HSL components); and 50-150% for poor performers (see Table 5).

10.5.16 If the percent difference for the second-source verification falls outside acceptance criteria, then sample analysis cannot be performed. Reanalyze the second-source verification standard to confirm the original result. If the second result fails, then re-prepare the verification standard, and/or re-prepare and rerun the ICAL.

10.5.17 If time remains in the 12-hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration, Section 10.6.

NOTE: Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.5.18 If a calibration is in use for greater than 3 months a check at the low and high ends of the calibration will be performed once per month of continued use and the %D and evidence of saturation for the high end check will be used to evaluate the continued effectiveness of the calibration.

10.6 Continuing Calibration Verification (CCV)

10.6.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 25-ng injection of DFTPP must result in a mass spectrum for DFTPP, which meets the criteria given in Table 3.

10.6.2 Following a successful DFTPP analysis, the continuing calibration verification (CCV) standard(s) are analyzed. The standard(s) must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the CCV.

10.6.3 The following criteria must be met for the CCV to be acceptable:

- For DOD samples, the percent difference or drift (%D) must be within ± 20% for all reported analytes. Any samples associated with a continuing calibration verification standard where the response for an analyte in the verification standard is above the acceptance limit and the analyte is not detected in any of the samples analyzed in the 12-hour window, do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected if it were present (for DOD samples this requires client pre-approval). If a compound in the CCV fails low, the analyst may elect to analyze a RL (CCVL)standard immediately after the CCV. If the compounds of concern are detected in the RL standard, it demonstrates that they would be detected in the samples, if present. This allows for the reporting of non detect sample results. Any compounds using a linear calibration fit in the initial calibration must undergo a low level readback on the CCVL. The readback concentration must be within 30% of the true value unless the analyte has been identified as a poor performer in which case the readback value must be within 50% of the true value. Compounds failing the readback value must be re-analyzed. For situations where the failed compound is present in a sample, the results must be qualified or the problem must be fixed and the CCV and affected samples must be re-analyzed. Possible problems include standard mixture degradation, column contamination and active sites.

  If the subsequent calibration verification injection fails, a new initial calibration curve must be processed. (i.e., no more than two consecutive injections of the calibration verification may be processed.

- Analysis of DOD samples also requires a closing CCV to be analyzed at the end of the analytical run. Closing CCV requirements are 50%D for all analytes.
- For non-DOD samples, all compounds listed in Table 1 must meet 20%D except those listed as poorly performing compounds in Table 5 which must be within ± 50%D. (See Section 12 for calculations)
- For SIM PAH analysis of samples analyzed under the BP Lamp program, all target analytes must meet ± 15% D. See above for corrective actions.
- For non BP SIM samples, the percent drift must be ± 20% for all compounds.

NOTE: Some analytes are included in both Tables 1 and 5. Those analytes that are in Table 1 will be controlled to ± 20% for projects reported under the DoD QSM and will be controlled to ± 50%D for commercial projects.

- The internal standard response of the CCV must be within 50 - 200% of the response in the same level of the corresponding calibration.
- If any internal standard retention time in the CCV changes by more than 30 seconds from that of the same level of the corresponding initial calibration, the chromatographic system must be inspected for malfunctions and corrections made, as required.

10.6.4 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample injected less than or equal to 12 hours after the DFTPP is acceptable.)

10.7 Sample Analysis

10.7.1 Calibrate the instrument as described in Section 10.5. Depending on the target compounds required by the client, it may be necessary to use more than one set of calibration standards.

10.7.2 All samples must be analyzed using the same instrument conditions as the preceding continuing calibration verification (CCV) standard.

10.7.3 Add internal standard to an aliquot of the extract to result in a 1000-µg/L concentration (for example, 10 µL of internal standard solution at 100 µg/mL in 1000 µL of extract). Mix thoroughly before injection into the instrument. The internal standard response must be within 50-*200*% of the response in the daily CCVIS.

10.7.4 Inject the aliquot into the GC/MS system using the same injection technique as used for the standards.

10.7.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 11. Quantitation is based on the initial calibration, not the continuing calibration verification.

10.7.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst (see Corporate SOP CA-Q-S-002) or automatically by the data system. Chrom generates a report of the before and after chromatograms.

10.7.7 Target compounds identified by the data system are evaluated using the criteria listed in Section 11.1.

10.7.8 Library searches of peaks present in the chromatogram that are not target compounds, i.e., Tentatively Identified Compounds (TIC), may be performed if required by the client. They are evaluated using the criteria in Section 11.2.

10.8 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the midrange of the calibration range. Samples may be screened to determine the

appropriate dilution for the initial run. If the initial diluted run has no hits and the matrix allows for analysis at a lesser dilution, the sample may be reanalyzed at a lesser dilution.

10.8.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are significantly less than two times the height of the internal standards, the sample may be reanalyzed at a more concentrated dilution. **This requirement is approximate and subject to analyst judgment.** For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

10.8.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will be reported only at client request.

10.9 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at 0-6°C, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

10.10 Retention Time Criteria for Samples

If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.11 Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP TA-WC-0125 for determination of percent moisture.

10.12 Procedural Variations

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.13 Maintenance Guide for GC/MS systems

10.13.1 Routine Instrument Maintenance

In addition to the schedules listed in Appendix A, the following activities constitute routine maintenance procedures and are performed as necessary.

- Clip Column;
- Install new injection port liner;
- Install new septum;
- Install new gold seal and washer, or equivalent;

10.13.2 Injector port maintenance is performed whenever the following conditions exist:

- High column bleed
- Peak broadening and/or tailing for polar analytes such as phenols
- Loss of sensitivity
- Calibration failures due to a loss of response
- Retention time drift
- Long or training solvent tail
- Overall loss of instrument response

10.13.2.1 Turn the GC oven off and let the system cool to room temperature. Remove the column nut and column from the injector body. Remove the injector nut, removing the septum and liner from the injector body. (See Illustration 6-10 in the instrument manual).

10.13.2.2 Clean the inside of the injector body with a cotton swab dipped in methanol. Follow with a wash of methanol, collecting the washings below at the column inlet port. Allow to air dry, and then replace the liner with a new or reconditioned liner that has been boiled in mineral acid, solvent rinsed, and muffled at 400℃. Replace the septum and tighten the nut just past finger tight.

10.13.2.3 Using a ceramic column cutter, remove at least 4 cm of the column end, depending on the severity of the system contamination. Place a column nut and new ferrule over the end of the column and re-cut one inch from the column end to ensure that no ferrule fragments remain in the column. Feed the column into the tapered liner until seated, then hold pressure on the column while the nut is tightened to one turn past finger tight. At this point, the GC oven is turned on and brought up to operating temperature. The system should then be leak checked.

10.13.3 Column installation is performed when the following conditions are encountered;

- Heavy column bleed that cannot be eliminated by thermal conditioning.
- Loss of early eluting peaks due to column cutting.
- Inability to chromatographically resolve method performance compound peaks (i.e. chrysene from benzo(a)anthracene).
- Distortion of peak shapes i.e.; broadening, ghost peaks, split peaks that can't be resolved by injection port maintenance or flow control.

10.13.3.1 Turn the GC oven off and let the system cool to room temperature. Remove the column nut, liner, septum, and presstight inlet connector. Dispose of old column appropriately.

10.13.3.2 Cut approximately six inches off of the end of new columns (DB5-MS 30m, 0.1u film thickness). Attach the column to the presstight inlet connector on the injector end and proceed as in 5.3.1.4 to connect to the injector.

10.13.3.3 Turn the GC on and set the injector temperature to 280℃. Allow helium to flow through the column for a couple minutes, and then turn the oven to 310℃ and condition for at least an hour.

10.13.3.4 Perform a leak check on the system following the instructions contained in the operator's manual chapter on **Miscellaneous Procedures of**

Operation. When the air water spectrum shows acceptable levels, proceed with the mass calibration procedure. For additional information of column replacement see the operator's manual chapter on **Selected Routine GC Maintenance** (pages 6-33 to 6-41).

10.13.4 Major Maintenance

A new initial calibration is necessary following certain maintenance procedures. These maintenance procedures include changing the column, cleaning the ion volume or repeller, cleaning the source, replacing the multiplier, and replacing the "top board" or RF-related electronics. Refer to the manufacturer's manual for specific guidance.

10.13.5 Autotune the MS

After major maintenance an autotune of the MS must be performed. Using an Agilent 5973 or 5975 MS, Select Autotune and run a tune to tune the MS.

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., GC, autosampler, column) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a tune, CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, tune, etc as may be the case).

If columns were replaced during maintenance procedures the specific make, model and serial numbers of the columns installed need to be entered in the instruments maintenance logbook.

10.14 Troubleshooting

1. If a DFTPP tune fails spectra, replace vial with fresh tuning solution and reanalyze the tune sample
    a. If it fails a second time evaluate, MS conditions
    b. Continued failures may result in re-auto tuning the instrument (10.13.5)
2. If tailing fails for either benzidine or PCP, minimum routine maintenance is required (see section 10.13.)
    a. Continued failure. Check column positioning into the source
    b. Replace column if all other options are exhausted
3. If DDT breakdown fails, minimum routine maintenance is required
    a. Continued failure. Check column positioning into the source
    b. Replace column if all other options are exhausted
4. IF CCV fails for TC target analytes, re-analyze a fresh CCV, if it fails a second time minimum routine maintenance is required. If the 2nd CCV is acceptable, the samples may be analyzed
    a. A second CCV failure requires additional instrument maintenance and generating a new ICAL

10.15 Examples of Analytical Sequences:

Example 1
RB
DFTPP
STD IC 10 8270
STD IC 20 8270
STD IC 50 8270
STD IC 100 8270
STD IC 200 8270
STD IC 500 8270
STD IC 1000 8270
STD IC 2000 8270
STD IC 5000 8270
STD IC 10000 8270
ICV
QC and Samples (up to a 12 hour time limit)

Example 2
RB
DFTPP
CCV
QC and Samples (and CCVC if DOD) up to a 12 hour time limit

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST library**.** Two criteria are used to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions.

NOTE: Sometimes extract matrix and high targets can cause the analytes to shift outside the retention time found in the CCV. Identification can still be determined using the characteristic ions. Also, dilutions to lessen the matrix effects may be necessary to verify the identification.

NOTE: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.

11.1.1 Full Scan Analysis

11.1.1.1 The sample component retention time must compare to within ± 0.06 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

11.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

11.1.1.3 The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.1.1.4 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%).

11.1.1.5 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

11.1.2 SIM Analysis

The reference mass spectrum must be generated using the conditions of this method on the same instrument used for sample analysis. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions >30% relative intensity, if less than three such ions occur in the reference spectrum. The mass spectrum of the peak is evaluated to confirm the presence of the compound. Spectra are compared against the reference spectra of each compound by an analyst competent in the interpretation of mass spectra. The following requirements must be met:

11.1.2.1 DFTTP tune (run in SCAN mode) runs before a 12 hour clock.

11.1.2.2 The quantitation and qualifier ions must be used for the identification of target compounds. Characteristic ions for the target compounds are presented in Table 7. The monitoring ions must agree within 20% of the relative intensities of the same ions in the reference standard.

11.1.2.3 The RT of the secondary ion must elute within 2 seconds of the primary ion in the sample.

11.1.2.4 The relative RT (RRT) of the compound in the sample must be within ±0.006 RRT of the standard compound. Matrix may affect the RT and the analyst should use their technical judgement for identification. Further dilutions may be necessary to verify identification.

11.1.2.5 A result should be reported as non-detect if, after careful review and in the technical judgment of the mass spectral interpretation specialist, the GC/MS identification cannot be considered a qualitatively confident mass spectral identification (regardless of the concentration).

11.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Following are guidelines for making tentative identification:

11.2.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree to within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30%and 70%.)

11.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.2.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or the presence of co-eluting compounds.

11.2.5 Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.2.6 Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

11.3 Isomers with identical mass spectra and close elution times pose problems for definitive identification. The following compounds fall into this category:

Aniline and bis(2-chloroethyl) ether
Dichlorobenzenes
Methylnaphthalenes
Methylphenols
Trichlorophenols
Tetrachlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b), (k), and (j)fluoranthene
Chrysene, benzo(a)anthracene

Identification of these compounds requires both experience and extra precautions on the part of the analyst. To begin, the isomers in a standard mix must be completely resolved (i.e., the baseline to valley height between the isomers is less than 50% of the sum of the two peak heights). Otherwise, the isomers must be identified as isomeric pairs. Next, the analyst must carefully compare the retention times between the unknown and the calibration standard.

11.4 A second category of problem compounds consist of the poor responders or compounds that chromatograph poorly. The integrations for these types of compounds should be checked manually. The following compounds are included in this category:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol

3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol
Benzidine

11.5 Calculating the Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{RF} \times 100\%$$

Where:

RF = Mean of RFs from the initial calibration for a compound

SD = Standard deviation for the mean RF from the initial calibration for a compound

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}}$$

RF_i = RF for each of the calibration levels

n = Number of RF values

11.6 Calculating the Continuing Calibration Percent Drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

Where:

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

11.7 Calculating the Concentration in the Extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

11.7.1 Average Response Factor Calibration

If the average of all the RSDs of the response factors in the initial calibration is ≤15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

Where:

C_{ex} = Concentration in the extract, µg/mL

R_x = Response for the analyte

R_{is} = Response for the internal standard

C_{is} = Concentration of the internal standard

$\overline{RF}$ = Average response factor

11.7.2 Linear Fit Calibration

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

Where:

C_{ex}	=	Concentration in the extract, µg/mL
R_x	=	Response for the analyte
R_{is}	=	Response for the internal standard
C_{is}	=	Concentration of the internal standard
A	=	Intercept of linear calibration line
B	=	Slope of linear calibration line

11.7.3 Quadratic Fit Calibration

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

Where:

C_{ex}	=	Concentration in the extract, µg/mL
R_x	=	Response for the analyte
R_{is}	=	Response for the internal standard
C_{is}	=	Concentration of the internal standard
A	=	Intercept
B	=	Factor for the linear term of the quadratic calibration function
C	=	Factor for the curvature term of the quadratic calibration function

11.8 Calculating the Concentration in the Sample

11.8.1 Calculation for Aqueous Samples

$$\text{Concentration, } \mu\text{g / L} = \frac{C_{ex} V_t}{V_o}$$

Where:

C_{ex}	=	Concentration in the extract
V_t	=	Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then V_t = 2,000.)
V_o	=	Volume of the sample that was extracted (mL)

11.8.2 Calculation for Sediment, Soil, Sludge, and Waste Samples

Results for sediments, sludges, and soils are usually calculated on a dry-weight basis, and for waste, on a wet-weight basis.

$$\text{Concentration, } \mu\text{g / kg} = \frac{C_{ex} V_t}{W_s D}$$

Where:

C_{ex}	=	Concentration in the extract

V_t = Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then V_t = 2,000.)

W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry-weight basis or 1 for a wet-weight basis

11.9 MS/MSD Percent Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where:

S_{SR} = Spike sample result

S_R = Sample result

S_A = Spike added

11.10 Calculating the Relative Percent Difference (RPD) MS/MSD Pair

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

Where:

RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

11.11 Relative Response Factor Calculation

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound being measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_x = Concentration of the compound being measured (µg/L)

C_{is} = Concentration of the specific internal standard (µg/L)

11.12 Calculation of TICs

The calculation of TICs (tentatively identified compounds) is identical to the above calculation (11.11) with the following exceptions:

A_x = Area of the total ion chromatogram for the compound being measured

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

11.13 Calculating Percent DDT Breakdown

$$\%\,\text{DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDDarea}}$$

The areas for the 235 ion are used for this calculation.

11.14 Calculating the Peak Tailing Factor

$$TailingFactor = \frac{BC}{AB}$$

Where:

Peak width (AC) is measured at 10% peak height, and divided into two line segments at the peak centroid, so that .

AC = AB + BC, with
AB = left-hand segment
BC = right-hand segment

11.15 Upon completion of the analytical sequence:

11.15.1 Create a worklist on Chrom that reflects the machine run sequence. The Chrom worklist will serve as the instrument sequence logbook. For the Rinse Blank in the sequence, add the solvent to the sample reagent tab. This will serve as the record of the solvent lot used to dilute the samples.

11.15.2 Review chromatograms online and determine whether manual data manipulations are necessary.

11.15.3 All manual integrations must be justified and documented. See Corporate SOP CA-Q-S-002 for requirements for manual integration.

11.15.4 Manual integrations are processed using Chrom which saves the before and after chromatograms, the reason for the change, and attaches the analyst's electronic signature.

11.16 Compile the raw data for all the samples and QC samples in an analytical batch.

11.16.1 Perform a level 1 data review, acknowledge any Data Review Checker (DRC) findings, and document the review on the data review checklist.

11.16.2 Submit the review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.1.1 Instrumentation software must have each target limit set to the lowest MDL. CHROM (LOD)

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

12.4 Non-standard Analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration should include the analysis of an extracted standard at the reporting limit and a single point calibration.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Acidic extracted sample and QC wastewater. After the extraction has been completed the spent water is neutralized and then collected into the organics extraction water conical reservoir. The collected wastewater is then purged with air to remove any remaining methylene chloride. The wastewater can then be discarded down the drain.

14.1.2 Methylene chloride waste. Solvent/Methylene Chloride waste. Any waste solvents are collected in beakers and then poured into a 4-liter amber bottle labeled "Hazardous Waste" located in the hood. After the extraction has been completed the MeCl2 collected in the 4 L bottles is emptied into the MeCl2 satellite waste barrel located next to the neutralization tank in lab hood #17. The funnel lid on the drum must be closed after each use At or before the satellite waste reaches 55 gallons the barrel is transferred to the waste disposal room from where it is sent out for recycling or fuel blending.

14.1.3 Vialed extract waste. Sample extracts that have been placed in vials for analysis are discarded into plastic satellite waste buckets labeled "Hazardous Waste" located underneath the bench top. Once the buckets are full the GC vials are bulked into the non-PCB GC vial waste barrel located in the waste room and sent out for incineration.

14.1.4 Extract waste. Unused sample extracts are held for at least 40 days, in case further testing is deemed necessary. After at least 40 days has passed these extracts are transported to the waste room in racks of 100 were they are bulked into a flammable loose pack waste stream and sent out for incineration.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Update IV, February 2007, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Method 8270D.

15.2 *U.S. Department of Defense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.1, 2017*

16.0 Method Modifications:

Item	Method	Modification
1	Include method references	A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method
2	8270D	The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification
3	8000B/8270D	This procedure includes the option for weighted linear regression curves using 1/concentration^2 weighting factors. Section 7.5.2 of Method 8000B discusses the use of weighted least square regression based on 1/standard deviation^2 weighting factors, which would require multiple analyses of each standard to determine the standard deviation. IAETL has presented information to the EPA Office of Solid Waste demonstrating that the variance (standard deviation^2) is proportional to the standard concentration. EPA accepted this argument and issued a letter in July 1998, which authorizes the use of 1/concentration^2 weighting factors

17.0 Tables, Attachments, and Appendices

Table 1: Current Compounds Applicable to Method
Table 2: Suggested Instrument Conditions
Table 3: DFTPP Key Ions and Ion Abundance Criteria
Table 4: 8270D Surrogate Compounds
Table 5: Table of Poorly Performing Compounds
Table 6: Summary of QC Requirements
Table 7: Characteristic Ions – SIM

Attachment 1: Example Internal Standard Evaluation Custom Report
Attachment 2: Example Breakdown Evaluation Custom Report
Attachment 3: Example Tailing Evaluation Custom Report

APPENDIX A: Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph

18.0 Revision History

- Revision 4, dated 23 April 2018
  - Removed reference of neutral extraction, section 1.2

  - Added allowance for extended calibration range from range in table, section 7.2.3.1.
  - Clarified control limit exceeded must be the upper limit, section 9.6.1
  - Removed PAH from SIM section title, 10.3
  - Corrected area Internal Area responce, section 10.7.3
  - Updated QSM reference, section 15.2
- Revision 3, dated 20 April 2017
  - Removed mention of low-level analysis and updated RL ranges, section 1.3
  - Added additional extraction methods, sections 2.0 and 10.1
  - Removed PIBLK, sections 3.7 and 9.7
  - Updated column, section 6.2
  - Updated standards, section 7.0
  - Updated sections 8.2 and 10.3
  - Removed requirement for DoD IS to link to ICIS, section 10.7.3
  - Removed hardcopy requirement for manual integrations, sections 10.7.6 and 11.15.4.
  - Added matrix affecting retention times, section 11.1
  - Updated section 11.1.2
  - Added Data Review Checker (DRC), section 11.16.1
  - Updated Tables

- Revision 2 dated 26 July 2016
  - Added criteria to replace ICAL reagents opened frequently, section 7.7
  - Added criteria for checking ICAL older than 3 months, section 10.5.18
  - Updated example sequence, section 10.15
  - Added Chrom worklist instructions, section 11.15.1

- Revision 1 dated 16 January 2015
  - Added calibration points to example calibration in section 7.2.3.1.
  - Changed benzidine and PCP tailing factors to < 2. Section 10.4.5.
  - Changed resolution requirement to 50% in section 10.5.7.
  - Poor performers in ICV changed to 50-150% in section 10.5.15.
  - Changed CCV criteria for DOD to 20% for all reported analytes in section 10.6.3.
  - Changed table 9 to reflect 50% resolution requirement.
  - Changed table 9 to reflect proper tailing requirement.

- Revision 0, dated 07 February 2014 (initial revision using existing 8270C SOP (TA-MS-0313) updated to include 8270D requirements and remove non-applicable 8270C requirements)

Table 1: Current Compounds Applicable to Method

8270D Full Scan			
1,1'-Biphenyl	2-Fluorophenol	Atrazine	Di-n-octyl phthalate
1,2,4,5-Tetrachlorobenzene	2-Methylnaphthalene	Azobenzene	Fluoranthene
1,2,4-Trichlorobenzene	2-Methylphenol	Benzidine	Fluorene
1,2-Dichlorobenzene	2-Nitroaniline	Benzo[a]anthracene	Hexachlorobenzene
1,3-Dichlorobenzene	2-Nitrophenol	Benzo[a]pyrene	Hexachlorobutadiene
1,3-Dinitrobenzene	3 & 4 Methylphenol	Benzo[b]fluoranthene	Hexachlorocyclopentadiene
1,4-Dichlorobenzene	3,3'-Dichlorobenzidine	Benzo[g,h,i]perylene	Hexachloroethane
1,4-Dioxane	3-Nitroaniline	Benzo[k]fluoranthene	Hexadecane
1-Methylnaphthalene	4,4'-DDD	Benzofluoranthene	Indene
2,2'-oxybis[1-chloropropane]	4,4'-DDE	Benzoic acid	Indeno[1,2,3-cd]pyrene
2,3,4,6-Tetrachlorophenol	4,4'-DDT	Benzyl alcohol	Isophorone
2,4,5-Trichlorophenol	4,6-Dinitro-2-methylphenol	Bis(2-chloroethoxy)methane	Naphthalene
2,4,6-Trichlorophenol	4-Bromophenyl phenyl ether	Bis(2-chloroethyl)ether	n-Decane
2,4'-DDE	4-Chloro-3-methylphenol	Bis(2-ethylhexyl) phthalate	Nitrobenzene
2,4-Dichlorophenol	4-Chloroaniline	Butyl benzyl phthalate	N-Nitrosodimethylamine
2,4-Dimethylphenol	4-Chlorophenyl phenyl ether	Caprolactam	N-Nitrosodi-n-propylamine
2,4-Dinitrophenol	4-Nitroaniline	Carbazole	N-Nitrosodiphenylamine
2,4-Dinitrotoluene	4-Nitrophenol	Chrysene	n-Octadecane
2,6-Dichlorophenol	Acenaphthene	Dibenz(a,h)anthracene	Pentachlorophenol
2,6-Dinitrotoluene	Acenaphthylene	Dibenzofuran	Phenanthrene
2-Chloronaphthalene	Acetophenone	Diethyl phthalate	Phenol
2-Chlorophenol	Aniline	Dimethyl phthalate	Pyrene
2-Fluorobiphenyl	Anthracene	Di-n-butyl phthalate	Pyridine

8270D SIM		
1,3-Dinitrobenzene	Acenaphthylene	Hexachlorobenzene
1,4-Dioxane	Anthracene	Hexachlorobutadiene
1-Methylnaphthalene	Benzo[a]anthracene	Hexachlorocyclopentadiene
2,4,6-Trichlorophenol	Benzo[a]pyrene	Hexachloroethane
2,4-Dinitrophenol	Benzo[b]fluoranthene	Indeno[1,2,3-cd]pyrene
2,4-Dinitrotoluene	Benzo[g,h,i]perylene	Naphthalene
2,6-Dinitrotoluene	Benzo[k]fluoranthene	Nitrobenzene
2-Fluorobiphenyl	Benzofluoranthene	Nitrobenzene-d5
2-Fluorophenol	Bis(2-chloroethyl)ether	N-Nitrosodimethylamine
2-Methylnaphthalene	Chrysene	N-Nitrosodi-n-propylamine
3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene	Pentachlorophenol
4-Chloroaniline	Fluoranthene	Phenanthrene
Acenaphthene	Fluorene	Pyrene

Table 2: Suggested Instrument Conditions

Mass Range:	35 - 550 amu for SCAN, select ions for SIM
Scan Time:	About 3 scan/sec
Initial Column Temperature/Hold Time:	45 °C hold 3 min
Column Temperature Program:	30 °C/min to 280 °C 9 °C/min to 325 °C
Final Column Temperature/Hold Time:	325 °C hold for 2 min
Injector Temperature:	260 °C
Transfer Line Temperature:	280 °C
Source Temperature:	According to manufacturer's specifications
Injector:	Pulsed splitless
Sample Volume:	1.0 µl or 2.0 µl
Carrier Gas:	Helium at 3.3 mL/min.

Current instrument conditions can be found noted in the maintenance logbook for each instrument.

Table 3: DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	10 - 80% of base peak
68	<2% of mass 69
69	Present
70	<2% of mass 69
127	10 - 80% of base peak
197	<2% of mass 198
198	Base peak or >50% of mass 442
199	5 - 9% of mass 198
275	10 - 60% of base Peak
365	>1% of base Peak
441	Present and < mass 443
442	Base peak or >50% of mass 198
443	15 - 24% of mass 442

Table 4: Surrogate Compounds

8270C Full Scan

Surrogate Compounds	Spiking Level, µg/mL in standard
Nitrobenzene-d5	100
2-Fluorobiphenyl	100
Terphenyl-d14	100
Phenol-d5	100
2-Fluorophenol	100
2,4,6-Tribromophenol	100

Recovery limits for surrogates are generated from historical data and are maintained in the LIMS.

8270C SIM PAH

Surrogate Compounds	Spiking Level, µg/mL in standard
Terphenyl-d14	100
2,4,6-Tribromophenol[2]	100
2-methylnaphthalene-d10[1]	100
Fluoroanthene-d10[1]	100

Recovery limits for surrogates are generated from historical data and are maintained in the LIMS.

1. Included in standard mix, but not routinely evaluated for method 8270C SIM PAH list, non-DoD projects.

2. Included in standard mix, but not routinely evaluated for method 8270C, unless Pentachlorophenol or other associated compound is a target analyte.

8270C SIM Alternative Analyte List

Surrogate Compounds	Spiking Level, µg/mL in standard
Nitrobenzene-d5	100
2-Fluorobiphenyl	100
Terphenyl-d14	100
2-Fluorophenol	100
2,4,6-Tribromophenol	100
2-methylnaphthalene-d10[1]	100
Fluoroanthene-d10[1]	100

Recovery limits for surrogates are generated from historical data and are maintained in the LIMS.

1. Included in standard mix, but not routinely evaluated for method 8270C SIM PAH list, non-DoD projects.

Table 5: Table of Poor Performing Compounds*

2,3,4,6-Tetrachlorophenol	4-Nitrophenol
2,3,5,6-Tetrachlorophenol	Aniline
2,4-Dinitrophenol	Benzidine
3-Nitroaniline	Benzoic Acid
3,3' Dichlorobenzidine	Carbazole
4-Chloroaniline	N-Nitrosodimethylamine
4-Nitroaniline	

* - This is not a comprehensive list and is subject to change. Each project's target list should be evaluated for poor performers.

Table 6: Summary of QC Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
DFTPP Tune	Prior to ICAL and at the beginning of each 12-hour period	See Section 10.5	Retune instrument and verify. Rerun affected samples.
Breakdown Check	At the beginning of each 12-hour period and prior to analyzing samples.	Degradation ≤ 20% for DDT. Benzidine tailing < 2.0 and PCP tailing < 2.0. **For DoD:** Benzidine and PCP should be present at their normal responses, and should not exceed a tailing factor of 2.	Correct problem then repeat breakdown check. No samples can be run until degradation is acceptable.
Minimum 5-point Initial Calibration	Initial calibration prior to sample analysis	Option 1: RSD for each analyte ≤ 20% (<15% for DOD) Option 2: Linear regression r ≥ 0.990 **Option 2 for DOD:** Linear regression r ≥ 0.995. Option 3: Non linear regression r^2 ≥ 0.990 and 6 points must be used.	Terminate analysis; correct the problem; recalibrate. Problem must be corrected. No samples may be run until ICAL has passed.
ICV	Following initial calibration.	70-130% for non-DoD projects (e.g., 8270D HSL components); and 50-150% for poor performers **For DoD:** 80 - 120% recovery	Terminate analysis; correct the problem; recalibrate.
Relative Retention Times (RRT)	With each sample	RRT of each target analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL. Laboratory may update RTs based on the CCV to account for minor performance fluctuations or after routine system maintenance (e.g. column clipping).

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
CCV	Daily before sample analysis and every 12 hours of analysis time.	**For non-DoD projects:** 80-120% recovery for all 8270 standard compounds in Table 1 and surrogates; 50-150% recovery for 8270 poor performing compounds in Table 5. **For DoD/BP LaMP projects:** ; 1. %D/Drift for all standard target compounds in Table 1 and surrogates ≤ 20%D; 2. Closing CCV requires 50-150%D for all compounds.	Correct problem, then rerun CCV. If that fails, then repeat ICAL. Reanalyze all samples since the last successful CCV.
Internal Standards (IS) verification	Every field sample, standard, and QC sample	Retention time ± 30 seconds from RT of the midpoint standard in ICAL; EICP area within -50% to +100% of ICAL midpoint standard. **For DOD:** Retention time must be + or – 10 seconds from the RT of the midpoint standard in the ICAL.	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples while system was malfunctioning is mandatory.
Method Blank	One per batch of 20 field samples or fewer.	The result must be < RL or < 1/10 the amount measured in any sample or 1/10 the regulatory limit. **For DoD:** No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit. For common laboratory contaminants no analytes detected > RL.	Re-extract and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.
LCS	One per batch of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must contain	See Section 9.4 for additional requirements.

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
		all analytes to be reported. Must be within acceptance criteria specified by DOD, if available. Otherwise, use in-house control limits.	
Surrogate	All field and QC samples.	Must be within laboratory control limits, **For DoD:** Must be within acceptance criteria specified by DOD, if available. Otherwise, use in-house control limits.	See Section 9.6 for additional requirements.
Matrix Spike/Laboratory Fortified Matrix	One per lot of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must contain all analytes to be reported. Must be within acceptance criteria specified by DOD, if available. Otherwise, use in-house control limits.	See Section 9.5 for additional requirements.

Table 7A: Characteristic Ions – SIM PAHs

SIM Group	Quantitation Ion	Qualifier Ions	Compound
1	136	108	Naphthalene-d8 (istd)
1	128	102, 127	Naphthalene
2	152	122	2-methylnaphthalene-d10 (surr)
2	142	141, 115	2-methylnaphthalene
2	142	141, 115	1-methylnaphthalene
3	152	151, 153	Acenaphthylene
3	164	162	Acenapthene-d10 (istd)
3	153	154, 152	Acenaphthene
4	166	165, 167	Fluorene
4	330	141	2,4,6-Tribromophenol (surr)
5	266	264, 268	Pentachlorophenol
5	188		Phenanthrene-d10 (istd)
5	178	179, 176	Phenanthrene
5	178	179, 176	Anthracene
6	212	106	Fluoranthene-d10
6	202	101, 203	Fluoranthene
6	202	101, 203	Pyrene
6	244	122	Terphenyl-d14 (surr)
7	228	229, 226	Benzo(a)anthracene
7	240	236	Chrysene-d12 (istd)
7	228	226, 229	Chrysene
8	252	253, 126	Benzo(b)fluoranthene
8	252	253, 126	Benzo(k)fluoranthene
8	252	253, 126	Benzo(a)pyrene
8	264	260	Perylene-d12 (istd)
9	276	138, 277	Indeno(1,2,3-cd)pyrene
9	278	276, 138	Dibenz(a,h)anthracene
9	276	138, 277	Benzo(g,h,i)perylene

Table 7B: Characteristic Ions – Alternative SIM Method

SIM Group	Quantitation Ion	Qualifier Ions	Compound
1	88	58, 43	1,4-Dioxane
1	74	42, 43	N-Nitrosodimethylamine
1	112	64	2-Fluorophenol (surr)
2	99	71	Phenol-d5 (surr)
2	93	63, 95	Bis(2-chloroethyl)ether
2	152	150	1,4-Dichlorobenzene-d4 (istd)
3	70	42, 130	N-Nitrosodi-n-propylamine
3	117	201, 199	Hexachloroethane
3	82	128	Nitrobenzene-d5 (surr)
3	77	123, 65	Nitrobenzene
4	136	108	Napthalene-d8 (istd)
4	127	129, 65	4-Chloroaniline
4	225	190, 118	Hexachlorobutadiene
5	152	122	2-methylnaphthalene-d10 (surr)
5	237	235, 272	Hexachlorocyclopentadiene
5	196	198, 200	2,4,6-Trichlorophenol
5	172	171	2-Fluorobiphenyl (surr)
6	168	122, 76	1,3-Dintrobenzene
6	165	89, 63	2,6-Dinitrotoluene
6	164	162	Acenaphthene-d10 (istd)
6	184	63, 154	2,4-Dinitrophenol
6	165	89, 63	2,4-Dinitrotoluene
7	330	332	2,4,6-Tribromophenol (surr)
7	284	142, 249	Hexachlorobenzene
7	266	264, 268	Pentachlorophenol
7	188	94	Phenanthrene-d10 (istd)
8	212	106	Fluoranthene-d10 (surr)
8	244	122	Terphenyl-d14 (surr)
9	252	254, 154	3,3'-Dichlorobenzidine
9	240	236	Chrysene-d12 (istd)
10	252	253, 126	Benzo(a)pyrene
10	264	260	Perylene-d12 (istd)
11	278	276, 138	Dibenz(a,h)anthracene

Table 8: 8270D Minimum RF criteria

Analyte	Minimum RF for initial and continuing calibration
1,2,4-Trichlorobenzene	0.01
Acenaphthene	0.9
2,4-Dinitrotoluene	0.2
Pyrene	0.6
N-Nitroso-di-n-propylamine	0.5
1,4-Dichlorobenzene	0.01
Pentachlorophenol	0.05
Phenol	0.8
2-Chlorophenol	0.8
4-Chloro-3-methylphenol	0.2
N-Nitrosodimethylamine	0.01
Bis(2-chloroethyl)ether	0.7
n-Decane	0.01
1,3-Dichlorobenzene	0.01
Benzyl alcohol	0.01
1,2-Dichlorobenzene	0.01
2-Methylphenol	0.7
2,2'-oxybis[1-chloropropane]	0.01
3 & 4-Methylphenol	0.6
Hexachloroethane	0.3
Nitrobenzene	0.2
Isophorone	0.4
2-Nitrophenol	0.1
2,4-Dimethylphenol	0.2
Benzoic Acid	0.01
Bis(2-chloroethoxy)methane	0.3
2,4-Dichlorophenol	0.2
Naphthalene	0.7
4-Chloroaniline	0.01
Acetophenone	0.01
Hexachlorobutadiene	0.01
4-Nitrophenol	0.01
2-Methylnaphthalene	0.4
1-Methylnaphthalene	0.4
Hexachlorocyclopentadiene	0.05
2,4,6-Trichlorophenol	0.2

2,4,5-Trichlorophenol	0.2
2-Chloronaphthalene	0.8
2-Nitroaniline	0.01
Dimethyl phthalate	0.01
2,6-Dinitrotoluene	0.2
Acenaphthylene	0.9
3-Nitroaniline	0.01
2,4-Dinitrophenol	0.01
Dibenzofuran	0.8
2,3,4,6-Tetrachlorophenol	0.01
Diethyl phthalate	0.01
4-Chlorophenyl phenyl ether	0.4
4-Nitroaniline	0.01
Fluorene	0.9
4,6-Dinitro-2-methylphenol	0.01
N-Nitrososdiphenylamine	0.01
Azobenzene	0.01
4-Bromophenyl phenyl ether	0.1
Hexachlorobenzene	0.1
n-Octadecane	0.01
Phenanthrene	0.7
Anthracene	0.7
Di-n-butyl phthalate	0.01
Fluoranthene	0.6
Butyl benzyl phthalate	0.01
3,3'-Dichlorobenzidine	0.01
Bis(2-ethylhexyl) phthalate	0.01
Benzo(a)anthracene	0.8
Chrysene	0.7
Di-n-octyl phthalate	0.01
Benzo(b)fluoranthene	0.7
Benzo(k)fluranthene	0.7
Benzo(a)pyrene	0.7
Indeno(1,2,3-cd)pyrene	0.5
Dibenz(a,h)anthracene	0.4
Benzo(g,h,i)perylene	0.5
Carbazole	0.01

Attachment 1: Example Internal Standard Evaluation Custom Report

FORM VIII
GC/MS SEMI VOA INTERNAL STANDARD AREA AND RETENTION TIME SUMMARY

Lab Name: TestAmerica Tacoma Job No.: 580-12197-1

SDG No.:

Sample No.: CCVIS 580-39026/2 Date Analyzed: 12/10/2008 13:19

Instrument ID: TAC040 GC Column: ZB-5MS ID: 0.25(mm)

Lab File ID (Standard): ak018739.D Heated Purge: (Y/N) N

		DCB		NPT		ACN	
		AREA #	RT #	AREA #	RT #	AREA #	RT #
12 HOUR STD		11172	3.20	17716	4.18	11176	5.59
UPPER LIMIT							
LOWER LIMIT							
LAB SAMPLE ID	CLIENT SAMPLE ID						
MB 580-38946/1-A		7654	3.20	18328	4.18	11486	5.59
LCS 580-38946/2-A		8484	3.20	19108	4.18	11938	5.59
580-12197-3	08FTW336B-32	7980	3.20	19016	4.18	11411	5.59
580-12197-3 MS	08FTW336B-32 MS	7765	3.20	17983	4.18	11310	5.59
580-12197-3 MSD	08FTW336B-32 MSD	7232	3.20	18301	4.18	11655	5.59

DCB = 1,4-Dichlorobenzene-d4
NPT = Naphthalene-d8
ACN = Acenaphthene-d10

Area Upper Limit = 200% of Internal Standard Area
Area Lower Limit = 50% of Internal Standard Area

Column used to flag values outside QC limits

FORM VIII 8270C

Attachment 2: Example Breakdown Evaluation Custom Reports

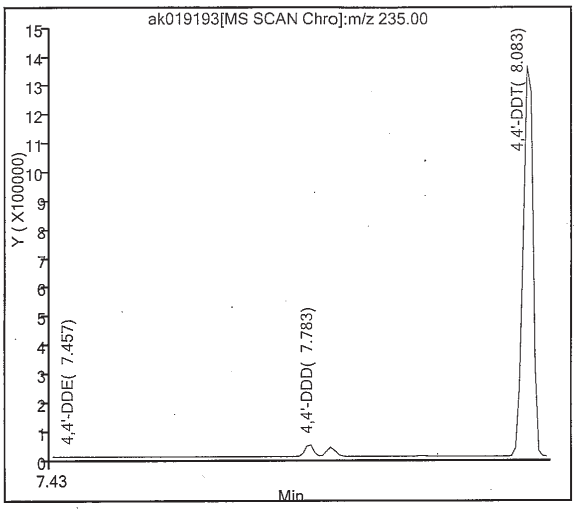
Report Date: 01-Apr-2009 15:08:23 Chrom Revision: 1.0.2009.312

Preliminary Report

Breakdown Report

Data File:	\\TACSVR5\Chromdata\TAC040\20090401-1.b\ak019193.D		
Inj Date:	01-Apr-2009 07:56:30	Limit Group:	8270C Standard
Lims Batch ID:	42046	Lims Sample ID:	1
Client ID:		Instrument:	TAC040
Sample Info:	dftpp		
Sample Amount:	1.00 uL	Operator:	RBF

93 4,4'-DDT, Detector: MS SCAN



SW-846 Method

%Breakdown =
(Area Breakdown Cpnds/
Total Area Breakdown Cpnds) * 100

93 4,4'-DDT Area = 1276732
89 4,4'-DDE Area = 2208
91 4,4'-DDD Area = 33705

%Breakdown: 2.74%, Max Limit: 20.00%
Passed

Attachment 3: Example Tailing Evaluation Custom Reports

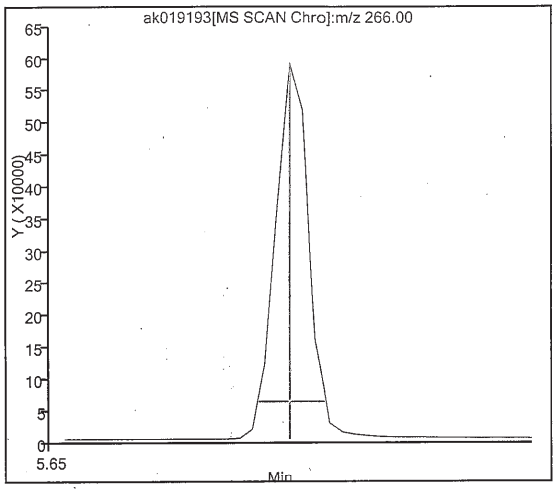
Report Date: 01-Apr-2009 15:09:32 Chrom Revision: 1.0.2009.312

Preliminary Report

Peak Tailing Report

Data File: \\TACSVR5\Chromdata\TAC040\20090401-1.b\ak019193.D
Inj Date: 01-Apr-2009 07:56:30 Limit Group: 8270C Standard
Lims Batch ID: 42046 Lims Sample ID: 1
Client ID: Instrument: TAC040
Sample Info: dftpp
Sample Amount: 1.00 uL Operator: RBF

60 Pentachlorophenol_T, Detector: MS SCAN

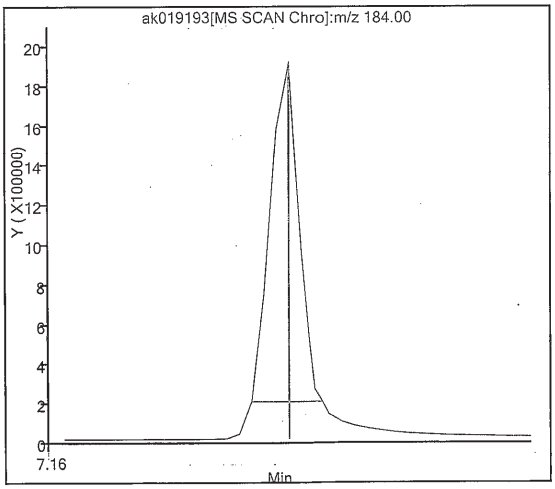


Peak Tailing Factor =
BackWidth/FrontWidth @ 10% Peak Height

Back Width = 0.015 (min.)
Front Width = 0.014 (min.)

Tailing Factor = 1.1, Max. Tailing < 5.00
Passed

85 Benzidine_T, Detector: MS SCAN



Peak Tailing Factor =
BackWidth/FrontWidth @ 10% Peak Height

Back Width = 0.013 (min.)
Front Width = 0.016 (min.)

Tailing Factor = 0.8, Max. Tailing < 3.00
Passed

APPENDIX A
Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph

MASS SPECTROMETER Instrument Maintenance Schedule				
Daily	Weekly	As Needed	Quarterly	Annually
Check for sufficient gas supply. Check for correct column flow and/or inlet pressure	**Check mass calibration (PFTBA or FC-43).**	**Check level of oil in mechanical pumps and diffusion pump if vacuum is insufficient. Add oil if needed between service contract maintenance.**	**Check vacuum, relays, gas pressures, and flows.**	**Replace the exhaust filters on the mechanical rough pump every 1 to 2 years.**
Check temperatures of injector, detector. Verify temperature programs.		**Replace electron multiplier when the tuning voltage approaches the maximum and/or when sensitivity falls below required levels.**		**Change the oil in the mechanical rough pump.**
Check inlets, septa.		**Clean source, including all ceramics and lenses. Source cleaning is indicated by a variety of symptoms, including inability of the analyst to tune the instrument to specifications, poor response, and high background contamination.**		**Relubricate the turbomolecular pump-bearing wick.**
Check baseline level.		**Repair/replace jet separator.**		
Check values of lens voltages, electron multiplier, and relative abundance and mass assignments of the calibration compounds.		**Replace filaments when both filaments burn out or performance indicates the need for replacement.**		

APPENDIX A (continued)
Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph

GAS CHROMATOGRAPH Instrument Maintenance Schedule (For GC/MS only.)	
Daily	As Needed
Check for sufficient supply of carrier and detector gases. Check for correct column flow and/or inlet pressures.	**Replace front portion of column packing or guard column or break off front portion of capillary columns. Replace column if this fails to restore column performance or when column performance indicates it is required (e.g., peak tailing, poor resolution, high backgrounds, etc.).**
Check temperatures of injectors and detectors. Verify temperature programs.	**Change glass wool plug in injection port and/or replace injection port liner when front portion of column packing is changed or front portion of capillary column is removed.**
Check inlets, septa. **Clean injector port.**	**Replace septa.**
Check baseline level.	**Perform gas purity check (if high baseline indicates that impure carrier gas may be in use).**
Inspect chromatogram to verify symmetrical peak shape and adequate resolution between closely eluting peaks.	**Repair or replace flow controller if constant gas flow cannot be maintained.**
	Reactivate flow controller filter dryers when the presence of moisture is suspected.
	Autosampler: Replace syringe, fill wash bottle, dispose of waste bottle contents.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Trace Metals Analysis by ICP [Methods 6010B, 6010C, *6010D*, and 200.7]

Approvals

Signatures on File

Stan Palmquist — Date
Inorganic Department Manager

Manjit Nijjar — Date
Health & Safety Manager / Coordinator

Manjit Nijjar — Date
Quality Assurance Assistant
For Terri Torres
Quality Assurance Manager

Dennis Bean — Date
Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP). This procedure references Method 6010 for hazardous waste (RCRA) testing and 200.7 Revision 4.4 for water and wastes compliance testing.

1.1.2 The elements that can be determined by this procedure are listed in Table I, together with the routine reporting limits. Additional elements may be analyzed under Methods 6010 and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.1.3 Method 6010 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, and TCLP.

1.1.4 The laboratory digests water samples according to SOP TA-IP-0205. The methods require digestion of waters, with one exception, i.e., Method 200.7 states that dissolved metals can be analyzed undigested if the sample meets all of the following criteria:

- The sample is visibly transparent with a turbidity measurement of 1 NTU or less.
- The sample consists of one liquid phase and is free of particulate or suspended matter following acidification.

1.1.5 Silver concentrations must be below 2.0 mg/L in aqueous sample digestates and 100 mg/kg in solid matrix sample digestates. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data. For aqueous samples analyzed by Method 200.7, the silver concentration in the digestate must be below 0.1 mg/L. Samples with silver concentrations exceeding these levels must be re-prepared and reanalyzed using a smaller sample amount.

1.1.6 The digestion procedure for soil samples is described in SOP TA-IP-0220.

1.1.7 State-specific requirements may take precedence over this SOP for drinking water sample analyses. Review special instructions for each project before starting work.

1.1.8 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 The laboratory uses simultaneous ICP instruments, with both axial and radial viewing configurations. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs.

2.2 Characteristic atomic-line emission spectra are produced by a radio frequency ICP. The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photo-multiplier tubes or a charge injection device (CID). The photo-

currents from the photo-multiplier tubes or a CID are processed and controlled by a computer system.

2.3 A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.4 Refer to the appropriate SOPs for details on sample preparation methods: TA-IP-0205 for aqueous samples and TA-IP-0220 for soil samples.

3.0 Definitions

3.1 Radial ICP – an ICP with the viewing angle across the radius of the torch.

3.2 Axial ICP – an ICP with the viewing angle along the long axis of the torch.

3.3 Dual View ICP – an ICP equipped with both radial and axial viewing capabilities.

3.4 Dissolved Metals - Those elements that pass through a 0.45-μm membrane. (The sample is acidified after filtration).

3.5 Suspended Metals - Those elements that are retained by a 0.45-μm membrane.

3.6 Total Metals - The concentration determined on an unfiltered sample following vigorous digestion.

3.7 Total Recoverable Metals - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.8 Reporting Limit (RL) - The lowest concentration to which results are reported without qualification. Details concerning RLs are presented in SOP TA-QA-0620.

4.0 Interferences

4.1 Spectral, physical, and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by the following:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.2 A background correction technique is used to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.3 Spectral Interferences

Spectral interference results from an overlap of spectral lines, molecular band spectra and background contribution from continuous, recombination phenomena or stray light. Inter-

element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte signal. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections must be applied to the analyte to compensate for the effects of these unwanted emissions.

Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference.

To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference.

Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions.

When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. The interference effects must be evaluated for each individual instrument since the intensities will vary.

When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when there is a significant change in the instrument such as a change of nebulizers or any other plasma conditions. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

When interelement corrections are not used, verification of absence of interferences is required.

4.4 Physical Interferences

An internal standard (IS), yttrium, indium, or other suitable element, is added to all solutions to correct and monitor physical interferences. Use of a peristaltic pump and the mass flow controller also help to overcome physical interferences. Physical interferences are generally considered to be effects associated with sample transport, nebulization, and conversion within the plasma. These interferences may result in differences between

instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If IS recoveries are not acceptable (see Section 10.4.12), then dilution of the sample may be necessary to overcome the interferences. Where the use of an IS might actually degrade the accuracy of the analytical result, sample results may be reported without IS correction.

Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, better control of the argon flow rate, especially to the nebulizer, can improve instrument performance: this may be accomplished with the use of mass flow controllers

4.5 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not significant with the ICP technique, but if observed, can be minimized by buffering the sample, matrix matching, or standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The **RF Generator** produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Simultaneous ICP with background correction, various makes and models
- Computer controlled data system for ICP
- Recirculating Chiller

6.2 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- Data acquisition/processing system: Thermo iTEVA Analyst version 2.5.0.84 or equivalent
- LIMS system: TALS version 1.0 or higher

6.3 Supplies

- Specimen cups with poly lids
- Disposable Metals Digestion cups
- Disposable culture tubes, HDPE

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619. Reagents are good for 6 months from time of preparation.

7.2 Laboratory de-ionized (DI) water

7.3 Calibrating standards from CPI (or equivalent) as follows (see Table III):

7.3.1 Solution A: Al, Fe, P at 5000 µg/mL and Ca, K, and Mg, at 10,000 µg/mL and Na at 7500 µg/mL

7.3.2 Solution B: Bi, Co, Mo, Ni, Ti, V at 250 µg/mL, Cd, Cu, Cr, Mn, Sb, Zn at 500 µg/mL, and Sn, Tl at 1250 µg/mL.

7.3.3 Solution C: Be at 50 µg/mL, Ag at 250 µg/mL, and As, Ba, Se, Pb, and Sr at 2500 µg/mL.

7.3.4 Solution D: B at 1250 µg/mL

7.3.5 Solution E: Si at 10000 µg/mL

Preparation of calibration standards and CCV (see Table IV): Dilution of standards are prepared with Reagent Blank (Section 7.10). The final concentrations of each analyte in the standards and the CCV standard are provided in tabular form in Table V.

NOTE: the CCV standard concentration may vary within the calibration range.

7.4 Laboratory control and matrix spiking standard for PDS. CPI or comparable. Concentrations provided in tabular form in Table II.

7.5 Standards ICSA and ICSAB (interference check standard). Concentrations provided in tabular form in Table VI. See Table IV for ICSA/AB preparation. CPI or comparable.

7.6 ICV Outside check standard. The ICV is at a concentration of approximately 10 times the Seattle reporting limits. Specific analyte concentrations provided in tabular form in Table V. Preparation of ICV provided in Table IV.

7.7 Reporting limit (RL) check standard (also LLICV, LLCCV, CCVL, STD-1). Made up from a blend of two Elements custom blend standards, and several single element CPI standards at concentrations at or below TestAmerica Seattle's reporting limits. Specific analyte concentrations are provided in tabular form in Table V. Preparation of RL provided in Table IV.

7.8 Linear range verification standards are prepared from the same stock as the calibration standards. The semi-annual linear range studies are conducted at the specific analyte concentrations are provided in tabular form in Table VII.

7.9 Argon gas, liquid.

7.10 Concentrated HCl, trace metals grade or better.

7.11 Concentrated HNO_3, trace metals grade or better.

7.12 Reagent Blank.

Preparation: add 1 L of concentrated HCl and 0.5 L of concentrated HNO_3 to 20 L DI water.

7.13 Internal Standard (IS) Solution for Thermo ICP. Add 2.00 mL of 10,000 ppm Yttrium and *4.00 mL* of 10,000 ppm Indium to a 1 liter polyethylene bottle. Dilute to volume with Reagent Blank

7.14 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standardsreagents and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Aqueous samples and digestates are stored at room temperature.

8.2 Sample holding times for metals are six months from the time of collection to the time of analysis. The exception is the analysis of dissolved silica by Method 200.7, which must be analyzed within 28 days from the date of collection.

8.3 Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis. For samples that will be analyzed by Method 200.7 for compliance with Safe Drinking Water regulations, the samples must be held for a minimum of 24 hours prior to verifying the pH.

8.4 Soil samples do not require preservation but must be stored at 0-6°C until the time of preparation.

8.5 Dissolved samples should be filtered immediately after sampling, however sometimes filtration is not available in the field. If a sample is received for dissolved metals and is not filtered it should be filtered and preserved immediately upon receipt. (Please see SOP TA-QA-0035.)

NOTE: The newly preserved sample must be held for 24 hours before beginning the digestion process.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	HDPE	50 mL	HNO_3, pH < 2;	180 Days	40 CFR Part 136.3
Soils with Hg Analysis	Glass	1 gram	≤ 6 C	180 Days	SW-846, Chapter 3 Table 3.1
Soils	Glass	1 gram	None	180 days	SW-846, Chapter 3 Table 3.1

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. Initial and periodic performance studies (IDOCs, detection limits, linear range studies, IECs, background correction points, and rinse time determinations) are described in Section 12. The process of establishing control limits, and the use of control charts are described more completely in TA-QA-0620, Quality Control Program. Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.2 QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). Failing QC that is automatically flagged by TALS does not need a NCM as long as it is a routine failure. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same

procedures and reagents within the same time period. See SOP TA-QA-0620 for further details.

9.4 Method Blank (MB)

In Method 200.7, this is referred to as a Laboratory Reagent Blank (LRB). The method blank is DI water taken through the procedure as if it were a sample. A method blank is required with every batch of 20 or less samples.

Note: All projects that are under the DoD QSM will evaluate the calibration blanks to ensure the criteria of no analytes being detected above the LOD. Any analyte above the LOD will be qualified B on all associated samples. Some programs (LaMP) and method 6010C require no detections in the method blank more than 10% of the low limit calibration check solution. This can not be obtained in most cases. TestAmeria Seattle will only evaluate the method blank to 1/2 the RL or Project DQOs and when specific DQOs are not provided by the client the RL will be defined as the DQO.

Acceptance Criteria: The method blank must not contain any analytes of interest above the reporting limit or above one-tenth of the concentration found in the associated samples (for samples with concentrations above the RL). BP LaMP requires that the blank be less than one half of the RL.

Corrective Action: If the method blank exceeds allowable levels, all associated samples must be redigested and reanalyzed. A possible exception is the situation, in which the analyte is not detected in the associated samples, but this can only be done with client approval and it must be addressed in the final report case narrative.

9.5 Laboratory Control Sample (LCS)

In Method 200.7, this is called a Laboratory Fortified Blank (LFB). The LCS is prepared as described in Section 7.4. One LCS is required with each analytical batch. If there is not sufficient sample volume for a matrix spike duplicate or sample duplicate, then precision information for the batch will need to be derived by processing a LCSD.

Acceptance Criteria: The recovery of the LCS must be within historical control limits. Historical control limits are based on three standard deviations of past results, and must be 80-120% for method 6010, DoD QSM 5 limits for DoD 6010 projects and 85-115% for Method 200.7. In the instance where the LCS recovery is greater than the upper limit and the sample results are < RL for non-DoD projects, the data may be reported with qualifiers. For DoD projects this may be reported with qualifiers only if variance from the QSM has been received from the client. **Such action must be taken in consultation with the client and must be addressed in the report narrative.** The process of establishing control limits is described in more detail in the SOP TA-QA-0620. The control limits are stored in the lab's LIMS system.

Corrective Action: If the LCS recovery falls outside of the established limits, all associated samples must be redigested and reanalyzed.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

In Method 200.7, this is referred to as a Laboratory Fortified Matrix (LFM). MS/MSD are prepared as described in Section 7.4. One MS/MSD pair is required with each analytical batch for methods 6010, and one pair per 10 client samples for method 200.7. Some client specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSD. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing on only the specific sample spiked. If there is not sufficient sample volume for a matrix spike duplicate or sample duplicate, then precision information for the batch will need to be derived by processing a LCSD.

Samples identified as field blanks cannot be used for MS/MSD analysis. Note that if client instructions on the chain of custody form tell the lab to use a field blank for the MS/MSD, this should be double-checked with the laboratory PM.

Acceptance Criteria: The **recoveries** for the MS and MSD must be within 80-120% for Methods 6010 and 200.7 or the QSM 5.0 limits for DoD 6010 projects. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated).

Corrective Action: If MSD/MSD recoveries fall outside of the established limits and the LCS is in control, the data will be flagged as outside of control limits. Document the results, which are then used by the lab PM to prepare the case narrative to warn the client that the sample result is suspect.

Acceptance Criteria: The **relative percent difference** (RPD) between the MS and MSD must be less than or equal to the historical RPD control limit. Historical control limits are based on three standard deviations of past results, and must be no greater than 20%. The same criteria would apply to sample duplicates, if analyzed.

Corrective Action: If the RPD fails to meet precision limit and the recoveries pass, the control limits should be checked as this would be a very rare occurrence if the limits are set properly. If the LCS is in control, it indicates long-term precision, and precision failures within the batch may be due to sample non-homogeneity. MS/MSD results which fall established control limits must be addressed in the narrative. Document the result, which is then used by the lab PM to prepare the case narrative.

9.7 Serial Dilution Test (SD)

A dilution test is performed for each batch of samples. The purpose of this test is to ensure that neither positive nor negative interferences are biasing the analytical results. The serial dilution test should be performed on the same sample used to perform the MS/MSD.

Acceptance Criteria: If the analyte concentration is sufficiently high (minimally, a factor of 20 times the RL), an analysis of a 1:5 dilution (e.g., 1 mL of sample diluted to 5 mL final volume with reagent blank solution) must agree within ± 10% of the original determination.

Corrective Action: If the two results do not agree within ± 10%, then a chemical or physical interference is suspected. A qualifier flag is assigned to the data, which is then used by the lab PM to prepare the case narrative to warn the client the sample result is suspect.

9.8 Post Digestion Spike (PDS)

Whenever a new or unusual sample matrix is encountered, a PDS spike must be performed. This is called an "analyte addition test" in Method 200.7. Some programs, e.g., DoD QSM, require a PDS to be included whenever the dilution test fails. Check project requirements. For these programs, the same sample that was used for the serial dilution test should be used for the PDS. PDS spike levels should be at the same concentration as the LCS and MS/MSD.

Acceptance Criteria: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75-125% of the known value for Method 6010B, 80-120% for Method 6010C, or 85-115% for Method 200.7. The spike addition should produce a minimum level of 10 times to a maximum of 100 times the instrumental detection limit. Some analytes with unusually low IDLs or that are routinely found at elevated concentrations are spiked at levels greater than the suggested limit.

Corrective Action: If the spike is not recovered within the specified limits, a matrix effect is confirmed. The series of tests (MS/MSD, serial dilution, and PDS) can be described in NCMs so that they can be included in the report case narrative.

9.9 Interference Check Analysis (ICSA/ICSAB)

This is referred to as the Spectral Interference Check (SIC) in Method 200.7. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Section 7.5 for the preparation of the ICSA and ICSAB solutions. Table IV lists the final concentrations. All analytes are spiked into the ICSAB solution. The ICSA and ICSAB solutions are analyzed at the beginning of the run. **For analytical sequences that include BNSF and/or BP LAMP samples** the ICSA and ICSAB solutions must be analyzed at the beginning of the ICP analytical sequence, every 8 hours and/or at the end of the ICP analytical sequence.

Acceptance Criteria: The ICSAB results for the all analytes must fall within 80-120% of the true value. If any ICSAB analyte result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the samples rerun.

The absolute value of ICSA results for the all non-spiked analyte must be < RL (or < LOD for DoD) unless they are a verified trace impurity from one of the spiked analytes).

Corrective action: If the ICSA results for the non-interfering elements do not meet these limits, the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required, then the sample data can be accepted.

- If the interfering elements are not present in the field sample at a concentration above the RL, then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal > 2 x RL, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions, then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually, the calculations must be clearly documented on the raw data.

9.10 Monitoring Internal Standard Results

Yttrium and indium are automatically added as internal standards (IS) to every solution tested through use of a third pump channel and mixing coil. The analyst must monitor the response of the IS throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

Acceptance Criteria: If the IS counts fall within ±50% (±40% for BP LaMP) of the counts observed in the ICAL blank, then the data are acceptable.

Corrective Action: If the IS counts in the field samples are outside of the control limits, the following apply:

- The field samples must be diluted and reanalyzed; or
- The IS concentrations must be raised; or
- A different IS must be used: or
- IS use is discontinued for the entire run of the samples with matrix issues causing the IS failure.

9.11 Quality Control Sample (QCS) – The Method 200.7 requirement for a quarterly QCS is satisfied by the analysis of the second-source ICV, which is analyzed with each initial calibration (see discussion in Section 10).

9.12 **Instrument QC**

9.13 Initial Calibration (ICAL)

9.13.1 The calibration curve is established on each day of operation using a blank and four standards. The preparation of the ICAL standards is described in Section 7. The final concentrations of the ICAL standards are presented in Table III. An r-value of 0.995 *(0.998 for 6010C)* or better is required for analysis to continue for any element. If an element does not meet the requirement, it must be recalibrated. If an element does not meet this requirement it may not be reported during that days runs.

9.13.2 The validity of the calibration curve is confirmed by analysis of the ICV, ICB, and RL Check standards, which are run immediately after the ICAL. Some programs require a high-level verification check as well.

9.14 Initial Calibration Verification (ICV)

Calibration accuracy is verified using a second-source standard (ICV) that is at or below a concentration near the mid-point of the working range. The ICV is analyzed immediately after the ICAL. The preparation of this standard is described in Section 7.6. The concentrations of the ICV standard are presented in Table III.

Acceptance Criteria: For Method 6010, the ICV result must be within 10% of the true value. For Method 200.7, the ICV result must fall within 5% of the true value. The standard deviation must be <5% (the laboratory is using at least two exposures for all ICP analyses).

Corrective Action: If the ICV fails to meet acceptance limits, the standard may be reanalyzed without modification to the instrument operating conditions. Two consecutive, acceptable analyses are required before the analytical run may continue. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.15 Continuing Calibration Verification (CCV)

In Method 200.7, this is the Instrument Performance Check (IPC). The preparation of the CCV solution is described in Section 7. 3. The final concentration of the CCV is presented in Table III. Note that the CCV is made at a different concentration than the ICV to meet NELAC requirements. CCVs are analyzed after the ICV, after every ten samples, and at the end of the analytical run.

Acceptance Criteria: The CCV must be within 10% of the expected value to meet 6010 and Method 200.7. The relative standard deviation must be <5% (<3% for Method 200.7).

Corrective Action: If the CCV fails to meet any of these criteria, the standard may be reanalyzed without modification to the instrument operating conditions. Two consecutive, acceptable analyses are required before the analytical run may continue. Otherwise, the instrument must be recalibrated and the samples reanalyzed since the last successful CCV must be reanalyzed.

9.16 Initial Calibration Blank (ICB)

System cleanliness is verified by analyzing an ICB after the first ICV. The preparation of the ICB is described in Section 7.12.

Acceptance Criteria: The absolute value of the ICB result must be < RL. Note that some programs (e.g., BP LaMP) require the blank to be ≤ 1/2 x RL. For DoD, the blank must be ≤ LOD (see 10.3.4.1).

Corrective Action: If the ICB fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.17 RL Calibration Check Standard (LLICV, LLCCV, CCVL, CRI)

Calibration accuracy at the RL is verified by analyzing a standard prepared at a concentration at or below the laboratory's standard reporting limit. The preparation of this standard is described in Section 7.7. For analytical sequences that include BNSF and/or

BP LAMP samples the Calibration Check Standard must be analyzed at the beginning of the ICP analytical sequence, every 8 hours and/or at the end of the ICP analytical sequence. For 6010C, a *CCVL* must run at the end of each batch.

Acceptance Criteria: For 6010B, the acceptance limits are ± 50% of the expected value. For 6010C and BP LAMP, the acceptance limit is ± 30% for LLICV and LLCCV. For *6010D and* DoD QSM 5.0, the acceptance limit is ± 20% for LLICV.

Corrective Action: If the RL Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.18 Continuing Calibration Blank (CCB)

CCB, prepared as in Section 7.12, are analyzed after each CCV.

Acceptance Criteria: The absolute value of the CCB must be less than the RL or less than $^{1}/_{10}$ the concentration found in associated samples. Note that some programs (e.g., BP LaMP) require the CCB to be ≤ ½ RL . For DoD, the CCB must be ≤ LOD (see 10.3.4.1).

Corrective Action: If the CCB is greater than these limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, instrument maintenance should be considered, the calibration re-verified, and all samples analyzed since the last successful CCB must be reanalyzed.

9.19 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

10.1 Sample Preparation

Refer to the appropriate SOP (see section 1) for sample preparation.

10.2 Instrument Operating Conditions

10.2.1 The current operating conditions of each instrument must be either written, or printed out and attached to the corresponding instrument maintenance logbook.

10.3 Calibration

10.3.1 Initial Calibration Procedures. One instrument blank and four standards containing all analytes of interest are analyzed for initial calibration (analyte-specific concentrations). Standards are analyzed in triplicate, three readings for each analysis, and the results are averaged. A calibration curve is generated using the blank and the average values for the four standards. For details regarding calibration models and algorithms, refer to corporate SOP CA-Q-S-005. An initial calibration is performed daily. An initial calibration verification (ICV) and initial calibration blank (ICB) standard are analyzed daily.

10.3.2 Continuing Calibration Procedures. A continuing calibration verification standard containing a mid-range concentration of each analyte is analyzed immediately after the ICV and ICB, after 10 samples, and at the end of the analytical sequence. The calculated concentration is compared to the actual concentration of the

standard analytes. If QC criteria are not met, a new initial calibration is performed and the affected samples are re-analyzed.

10.3.2.1 All projects that are under the DoD QSM will evaluate the calibration blanks to ensure the criteria of no analytes being detected above the LOD. Any analyte above the LOD will be qualified B on all associated samples.

10.3.3 All project(s) that are under the DoD QSM will also have the following calibration standards analyzed.

10.3.3.1 A second source calibration verification will be analyzed this is referred to as the ICV in section 7.6.

10.3.3.2 A low level calibration check standard that has the analytes at a concentration less than or equal to the report limit (RL). This is referred to as the reporting limit check standard in section 7.7.

10.4 Sample Analysis

10.4.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP #TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

10.4.2 Any unauthorized deviations from this procedure must also be documents as a nonconformance, with a cause and corrective action described.

10.4.3 Samples, sample leachates, and sample digests are provided to the analyst in specimen cups labeled with laboratory number.

10.4.4 Samples are poured into disposable culture tubes and placed in a rack for analysis.

10.4.5 Samples are nebulized and injected into the plasma torch. The solution concentrations are determined and reported as raw instrument data.

10.4.6 Replicate Readings. The laboratory averages the results from three exposures or burns.

10.4.6.1 For analytical sequences that include BNSF and/or BP LAMP samples the RPD between multiple instrument integrations must be <20% if the analyte is greater than the reporting limit. If the RSD is above 20% then the laboratory must reanalyze the sample.

10.4.7 Rinse Time between Samples

Prior to calibration and between each sample/standard, the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds.

10.4.8 If smart rinse or IRINSE is used the rinse time may be reduced to less than 60 seconds.

10.4.9 An example of a typical sequence run log is as follows:

Instrument Calibration
ICV
ICB
RL / LLICV Verification Standard
ICSA
ICSAB
CCV
CCVL (6010C only)
CCB
10 samples
CCV
CCVL (6010C only)
CCB

10.4.10 Full method-required QC must be available for each wavelength used in determining reported analyte results. Guidelines are provided in the appendices for minimizing contamination of samples and standards (Appendix B), performing preventive maintenance (Section 10.4), and troubleshooting (Appendix A).

10.4.11 Dilutions for High Levels of Elements of Interest

For Method 200.7, measurements for all target elements must fall within 90% of the defined linear range where spectral interference correction factors are valid. For 6010, results must fall within the linear range with the exception of *6010D and* DoD projects where results must fall within the calibration range. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. Dilutions must be prepared using the reagent blank solution to maintain the correct acid strength.

10.4.12 Dilutions for High Levels of Interfering Elements

Dilutions are also required for an element that is included in an IEC calculation if it exceeds the linear range. If a dilution is not performed, the IEC may be inaccurately applied. Therefore, even if an over-range analyte may not be required to be reported for a sample, if that analyte is an interferent for any requested analyte in that sample, the sample must be diluted to a level at or below the working range

Data Reduction and Review

10.4.13 Upon completion of the analytical sequence, perform a level 1 data review and document the review on the data review checklist.

10.4.14 Submit the data package and review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

10.4.15 Update instrument sequence logbook.

10.5 Instrument Maintenance

10.5.1 All instrument maintenance must be documented in the instrument maintenance logbook.

- The logbook must include the instrument name, serial number for each major component (e.g., AA, autosampler) and the date of start-up.
- When an instrument is not capable of analyzing samples, it needs to be tagged “Out of Service”.
- Routine Maintenance (which includes, but is not limited to daily, weekly, and semiannual maintenance) is completed periodically and does not necessary indicate the instrument is out of control is noted in the logbook with the notation “RM”.
- For non-routine maintenance or repairs, logbook entries must include a description of the problem and what actions were taken to address the problem.
- When non-routine maintenance or repairs are complete, the instruments return to control is noted in the logbook with the notation “RTC”.

10.5.2 Daily Use and Maintenance.

These procedures are performed daily prior to instrument calibration.

- Instrument should not be turned off.
- Place fresh rinse solution in the rinse bottle.
- Ignite plasma.
- Verify smooth and continuous uptake and flow.
- Verify that there is consistent drainage.
- Allow the instrument to warm up for approximately 30 minutes.
- Check the argon pressure and gas connections.
- For the Thermo, IS (Y 3774) intensities of the first calibration blank analyzed each day will be monitored and a printout retained in the instrument sequence logbook.

10.5.3 Weekly Maintenance (or more frequently if needed)

- Change the pump tubing as needed.
- Check pump and pump rollers.

10.5.4 Monthly Maintenance (or more frequently if needed)

- Clean the nebulizer as needed when instrument reading are inconsistent.
- Clean the torch as needed. Soak nebulizer in mild soap for 10 minutes to clean.
- Clean the spray chamber if dirty.
- Check the air filters on the power supply and spectrometer, and clean if dirty.

10.5.5 Semiannual Maintenance (or more frequently if needed)

- Clean the chiller.
- Drain completely; disconnect water lines and pump water into a 5 gallon bucket.

- Rinse with tap water pumping for a few minutes.
- Refill with fresh distilled water and 0.5 g Chloramine-T.

10.5.6 Spare Parts

10.5.6.1 Instrument.

- Purge windows.
- Injector tip.

10.5.6.2 Plasma Torch Assembly.

- Quartz torch.
- Spray chamber.
- Nebulizer.

10.5.6.3 Tubing

- Sample tubing. (White – orange 0.64 mm)
- Drain tubing. (White – white 1.02 mm)
- Internal standard tubing. (Blue – orange 0.25 mm)
- Sample capillary tubing.

10.6 Troubleshooting

10.6.1 Refer to Appendix A, Troubleshooting Guide.

11.0 Calculations / Data Reduction

For details regarding calibration models and algorithms, refer to corporate SOP CA-Q-S-005.

11.1 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Concentration

11.3.1 Liquid samples, report as mg/L.

mg/L = (instrument reading) * (final dilution)

11.3.2 Solid samples (except filters), report as mg/kg:

$$\text{mg/kg} = \frac{\text{(instrument reading) * (final dilution)}}{\text{(sample weight) (percent solids)}}$$

11.3.3 Filters, report as µg (or as µg/cm^3)

$$\mu g = (\text{instrument reading}) * (\text{final dilution})$$

$$\mu g/cm^3 = \frac{(\text{instrument reading}) * (\text{final dilution}) * (1000)}{(\text{air volume in L})}$$

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

12.0 Method Performance

12.1 Instrument and Method Detection Limit Studies

12.1.1 Instrument Detection Limit (IDL) - IDLs are determined by analyzing seven replicates of low concentration undigested standards on each of three nonconsecutive days, calculating the standard deviation for each day's results, and calculating the average of the three standard deviations. The IDL must be performed annually.

12.1.2 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TC-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.2 Linear Dynamic Range (LDR)

12.2.1 Linear range standards (see Section 7.8 for preparation) must be analyzed semi-annually.

Acceptance Criteria: The highest standard must produce a recovery within 90-110% of the expected value. Then the highest LDR is 90% of the highest successful standard.

Correction Action: Samples producing results above the LDR must be diluted reanalyzed.

12.3 Linear Range Verification

12.3.1 The LDRs should be verified whenever, in the judgment of the analyst, a change in the analytical performance caused by either a change in instrument hardware or operating conditions would dictate the necessity to re-establish them.

Acceptance Criteria: The LDR verification standard must produce a result within 90-110% of the expected value.

Corrective Action: If this limit is not met, then a new LDR study is required.

12.4 Interelement Correction Factors (IECs)

12.4.1 IECs need to be updated every 6 months, or after major instrument maintenance.

12.4.2 Follow the procedures outlined by the instrument manufacturer.

12.4.3 IECs may be adjusted as needed based on instrument performance on an ongoing basis.

12.4.4 After any adjustments or updates are made to the IECs, an IEC summary with an effective date will be generated for that instrument and kept on-file within the department.

12.5 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.6 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Acidic waste containing nitric acid and hydrochloric acid generated by the extraction, standards and rinse solutions. The remaining sample extraction fluid is held in the extraction vessels, which are stored in the waste disposal area next to the waste disposal hood in case further testing is deemed necessary. After 30-45 days, the extraction fluid is poured into the Acid Waste Drum which is sent out for waste water treatment. Remaining standard and rinse fluid is also added to the Acid Waste Drum.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996, Method 6010B.

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Update IV, Revision 3, February 2007, Method 6010C.

15.3 Approved method for SDWA compliance testing: "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry," US EPA / EMSL, Method 200.7, Revision 4.4, May 1994.

15.4 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 5.1, January 2017.

16.0 Method Modifications:

Item	Method	Modification
1	200.7 and 6010B/C	This procedure uses mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods

2	200.7 and 6010B/C/*D*	Methods 200.7 and 6010 state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific "concentration range around the calibration blank." Because of the lack of definition for "concentration range around the calibration blank," the laboratory has adopted the procedure in EPA CLP ILMO4.0 for determining IECs
3	200.7 and 6010B	Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because the laboratory sometimes does not receive prior information from clients regarding new or unusual matrices, the analyst may select to perform a dilution test on one sample in each preparation batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. In this procedure, matrix interference is determined by evaluating data for the LCS, MS/MSD, and serial dilutions. The laboratory must request documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample
4	200.7	Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but greater than the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica has adopted an absolute control limit of ±RL from zero for calibration blank criteria (For DoD, the CCB must be ≤ LOD). Section 9.16 provides the detailed corrective action criteria that must be followed
5	6010B/C/*D*	Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit (For DoD and BP LaMP, the blank must be ≤ ½ the RL)
6	6010B	Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3 times the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica has adopted an absolute control limit of ± RL from zero for calibration blank criteria. See SOP Sections SOP Section 9 for a detailed description of the required corrective action procedures.
8	6010C	Method Blank criteria of no detections in the method blank more than 10% of the low limit calibration check solution. TestAmeria Seattle will only evaluate the method blank to 1/2 the RL or Project DQOs and when specific DQOs are not provided by the client the RL will be defined as the DQO.
9	200.7	9.3.4 states that four or greater replicates will be run for the initial IPC (ICV). Instrument software limitations do not allow for increasing replicates on individual samples. TestAmerica Seattle will only run three replicates for the initial IPC.

10	6010B/C	Method 6010C section 4.2.7 (6010B, 3.1.7) requires a 0.5 nm scan across analyte wavelengths to verify the absence of spectral Interference. Hardware restrictions do not allow for scans this wide so spectral interferences are checked at the same nm width as the analytical run, approximately 0.1 nm.
11	6010	IDL Studies are being performed annually not every 3 months..

17.0 Tables and Appendices

TABLE I - Metals Analyzed by ICP and Reporting Limits
TABLE II - Matrix Spike and Aqueous Laboratory Control Sample Levels
TABLE III - Custom Standard Mixes
TABLE IV - Calibration, Verification and Interference Standards Recipes
TABLE V - Initial Calibration and Continuing Calibration Verification Standards
TABLE VI - Interference Check Sample Concentrations
TABLE VII – Linear Dynamic Range Concentrations
TABLE VIII - Summary of Quality Control Requirements

Appendix A - TROUBLESHOOTING GUIDE
Appendix B - CONTAMINATION CONTROL GUIDELINES

18.0 Revision History

- Revision 28, dated 23 March 2018
  - Added reference requirements for 6010D
  - Table I: updated limits
  - Table VIII: updated 6010D requirements
  - Changed MSDS to SDS

- Revision 27, dated 13 February 2017
  - Changed Standard E concentration in section 7.3.5
  - Updated Table III and IV to new Standard E concentrations
  - Updated R value in section 9.13.1
  - Updated LLCCV information in section 9.17
  - Removed High-Level Calibration Check Standard section
  - Updated DoD QSM to version 5.1, section 15.4

- Revision 26, dated 17 December 2015 2015
  - Incorporated ROMD00062
  - Updated Table V and VI to new standard concentrations
- Revision 25, dated 20 July 2015
  - Incorporated ROMD 00056 in section 9.13.1
  - Removed references to 200.7 R3.3
  - Updated limits, Table I
  - STD-1 is now made from the RL solution.
  - Added 6010C requirement for r>0.998 (section 9.13.1 and Table VIII)
  - Removed unused definition, Potentially Dissolved Metals
  - Removed duplicate calibration standard prep table in section 7.3.6
  - Added 16.9 and 16.10 method modifications
  - Added PDS levels in section 9.8
- Revision 24, dated 11 August 2014
  - Changed water from ASTM type II to DI, multiple sections.

  - Updated standard concentrations, sections 7.3.2, 7.3.3, 7.3.4 and 7.3.6
  - Reduced acid matrix for Blank Water by half, section 7.12
  - Added ICAL criteria, section 9.13.1
  - Updated concentrations in Table III, IV, and V
- Revision 23, dated 4 Feb 2014
  - Added computer hardware and software, section 6.2
  - Updated NCM criteria, section 9.2
  - Updated method blank criteria, section 9.4
  - Updated section 9.17 to include LLICV and LLCCV
- Revision 22, dated 25 July 2013
  - Removed reference to Perkin Elmer instrument requirements
  - Added reagent shelf life to section 7.0
  - Updated table references in body of SOP to match changes made to tables in last revision.
  - Updated reporting limits and standard concentrations in body and tables
- Revision 21, dated 6 August 2012
  - Updated table, section 7.3.6
  - Updated waste stream, section 14.1
  - Added Tables II (Custom Standard Mixes) an III (Standard Recipes).
  - Re-order Tables IV through VIII
  - Corrected NA ICV concentration, Table V
- Revision 20, dated 25 April 2011
  - Added DoD blank acceptance criteria to sections 9.4, 9.16, 9.19 and 16.0 Preservation temps aligned with SW-846 Chapter 3 were added in section 8.5
  - Added Thermo IS solution section 7.14
  - Incorporated ROMD 00018 in section 9.6.
  - Incorporated ROMD 00025 in sections 9.5 and 9.6
  - Addressed acceptance criteria for sample duplicate RPD in section 9.6
  - Section 9.2.2 was added for the Thermo ICP
  - Incorporated ROMD 00020 in section 10.2.1
  - Incorporated ROMD 00022 in sections 10.3.3 and 11.0.
  - Added new section (10.5) on data reduction and review
  - Incorporated ROMD 00033 in section 10.6.2
  - Added new section 12.4 outlining IEC requirements.
- Revision 19, dated 16 April 2010
  - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
  - Added removal of expired standards Section 7.8.
  - Added BP/BNSF requirements for ACSA/ACSB solutions, Section 9.9
  - Added BP LaMP QC criteria Section 9
  - Added DoD blank acceptance criteria to sections 9.4, 9.16, 9.19 and 16.0
  - Added requirement to evaluate extra QC Section 9.20
  - Added maintenance documentation and return to service requirements, Section 10.4.1
- Revision 18, dated 25 April 2009
  - Updated Calibration Standard Information in Section 7.2 and Table III to include a fourth standard.
  - Updated RLs in Table I.
  - Updated Table VI Summary of Quality Control Requirements to include new DoD QSM version 4.1 requirements.
- Revision 17, dated 13 April 2008

- Integration for TestAmerica and STL operations.
- This revision is a complete rewrite and an expansion of scope.
- This SOP is the combination of SOPs 0200.16 and 0230.5.

TABLE I - Metals Analyzed by ICP and Reporting Limits

ELEMENT	Symbol	CAS #	6010 Analyte	200.7 Analyte	Reporting Limit (mg/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	X	1.5	75
Antimony	Sb	7440-36-0	X	X	0.06	3
Arsenic	As	7440-38-2	X	X	0.06	3
Barium	Ba	7440-39-3	X	X	*0.02*	0.5
Beryllium	Be	7440-41-7	X	X	0.02	*1.0*
Bismuth	Bi	7440-69-9	X		0.28	14
Boron	B	7440-42-8	X	X	2.5	125
Cadmium	Cd	7440-43-9	X	X	0.02	1
Calcium	Ca	7440-70-2	X	X	1.1	55
Chromium	Cr	7440-47-3	X	X	0.025	1.3
Cobalt	Co	7440-48-4	X	X	0.02	1
Copper	Cu	7440-50-8	X	X	*0.06*	2.5
Iron	Fe	7439-89-6	X	X	0.5	*65*
Lead	Pb	7439-92-1	X	X	0.03	1.5
Magnesium	Mg	7439-95-4	X	X	1.1	55
Manganese	Mn	7439-96-5	X	X	0.02	*2*
Molybdenum	Mo	7439-98-7	X	X	*0.04*	*2*
Nickel	Ni	7440-02-0	X	X	0.02	1
Phosphorus	P	7723-14-0	X	X	6	300
Potassium	K	7440-09-7	X	X	3.3	165
Selenium	Se	7782-49-2	X	X	0.1	5
Silicon	Si	7631-86-9	X	X	1.05	52.25
Silver	Ag	7440-22-4	X	X	0.05	2.5
Sodium	Na	7440-23-5	X	X	2	100
Strontium	Sr	7440-24-6	X		0.1	5
Thallium	Tl	7440-28-0	X	X	0.1	5
Tin	Sn	7440-31-5	X		0.1	5
Titanium	Ti	7440-32-6	X		0.03	*2.0*
Vanadium	V	7440-62-2	X	X	*0.03*	*2.0*
Zinc	Zn	7440-66-6	X	X	0.04	*4*

TABLE II - Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS, MS, and PDS Levels (mg/L)
Aluminum	4.0
Antimony	3.0
Arsenic	4.0
Barium	4.0
Beryllium	0.1
Boron	5.0
Cadmium	0.1
Calcium	20
Chromium	0.4
Cobalt	1.0
Copper	0.5
Iron	22
Lead	1.0
Magnesium	20
Manganese	1.0
Molybdenum	5.0
Nickel	1.0
Phosphorous	20
Potassium	20
Selenium	4.0
Silicon	20
Silver	0.5
Sodium	20
Strontium	4.0
Thallium	4.0
Tin	5.0
Titanium	5.0
Vanadium	1.0
Zinc	1.0

TABLE III - Custom Standard Mixes

CPI or ESI Custom Standards

Solution A

Al	5000 ppm
Ca	10000 ppm
Fe	5000 ppm
K	10000 ppm
Mg	10000 ppm
Na	7500 ppm
P	5000 ppm

Solution B

Bi	250 ppm
Cd	500 ppm
Co	250 ppm
Cu	500 ppm
Cr	500 ppm
Mo	250 ppm
Mn	500 ppm
Ni	250 ppm
Sb	500 ppm
Sn	1250 ppm
Ti	250 ppm
Tl	1250 ppm
V	250 ppm
Zn	500 ppm

Solution C

As	2500 ppm
Ag	250 ppm
Ba	2500 ppm
Be	50 ppm
Pb	2500 ppm
Se	2500 ppm
Sr	2500 ppm

Solution D

B	1250 ppm

Solution E

Si	*10000 ppm*

(Order 500 ml bottle of each solution)

TABLE IV – Calibration, Verification and Interference Standards Recipes

ICP Calibration Standards

All standards are made to 1.00 L with 5% (%v/v) HCl and 2.5% HNO_3

STD#1 1.0 mL of RL Stock Solution A and B

STD#2 1.60 mL of stock Standard A
0.80 mL of stock Standard B, C, and D
0.4 mL of stock Standard E

STD#3 8.0 mL of stock Standard A
4.0 mL of stock Standard B, C, and D
2.0 mL of stock Standard E

STD#4 16.0 mL of stock Standard A
8.0 mL of stock Standard B, C, and D
4.0 mL of stock Standard E

CCV 4.0 mL of stock Standard A
2.0 mL of stock Standard B, C, and D
1.0 mL of stock Standard E

ICP ICV Standard

ICV 5.0 mL of each ICV Stock Standards: 3-172YP and 3-173YP

ICP RL Standard/CCVL

RL 1.0 mL of RL Stock Solution A and B
Note: This is the same as STD-1

Interference Check Standards

ICSA 100 mL of ICSA Stock Solution,

ICSAB 100 mL of ICSA Stock Solution
10 mL each of Interference Check Standard 18 solution A and B,
Interference Check Standard 1 and 3

TABLE V - Initial Calibration & Continuing Calibration Verification Standards

Element	Wave length	Calibration Levels (mg/L)				ICV (mg/L)	CCV (mg/L)	RL (mg/L)
		Std 1	Std 2	Std 3	Std 4			
Al	308.215	1.5	8.0	40.0	80.0	5.0	20.0	1.5
Sb	206.833	0.05	0.4	2.0	4.0	2.5	0.50	0.06
As	189.042	0.06	2.0	10.0	20.0	2.5	5.0	0.06
Ba	455.403	0.01	2.0	10.0	20.0	1.0	5.0	0.01
Be	313.042	0.01	0.04	0.20	0.40	0.25	0.10	0.02
B	208.959	2.5	1.0	5.0	10.0	10.0	2.5	2.5
Cd	226.502	0.01	0.40	2.0	4.0	0.50	1.0	0.02
Ca	315.887	1.1	16.0	80.0	160.0	5.0	40.0	1.1
Cr	267.716	0.025	0.40	2.0	4.0	1.0	1.0	0.025
Co	228.616	0.01	0.20	1.0	2.0	0.50	0.50	0.02
Cu	327.396	0.02	0.40	2.0	4.0	1.0	1.0	0.05
Fe	271.441	0.50	8.0	40.0	80.0	10.0	20.0	0.50
Pb	220.353	0.03	2.0	10.0	20.0	1.0	5.0	0.03
P	178.284	3.3	8.0	40.0	80.0	15.0	20.0	6.0
Mg	279.076	1.1	16.0	80.0	160.0	5.0	40.0	1.1
Mn	257.610	0.02	0.40	2.0	4.0	1.0	1.0	0.02
Mo	202.030	0.01	0.20	1.0	2.0	0.50	0.50	0.02
Ni	231.604	0.02	0.20	1.0	2.0	1.0	0.50	0.02
K	766.490	3.3	16.0	80.0	160.0	15.0	40.0	3.3
Se	196.090	0.10	2.0	10.0	20.0	5.0	5.0	0.10
Si	251.611	1.0	4.0	20.0	40.0	2.5	10.0	1.0
Ag	328.068	0.05	0.20	1.0	2.0	0.50	0.50	0.05
Na	589.592	2.0	12.0	60.0	120.0	10.0	30.0	2.0
Sr	407.771	0.10	2.0	10.0	20.0	5.0	5.0	0.10
Tl	190.856	0.10	1.0	5.0	10.0	5.0	2.5	0.10
Sn	189.989	0.10	1.0	5.0	10.0	2.5	2.5	0.10
Ti	334.941	0.01	0.20	1.0	2.0	0.50	0.50	0.03
V	292.402	0.02	0.20	1.0	2.0	0.50	0.50	0.02
Zn	206.200	0.04	0.40	2.0	4.0	1.0	1.0	0.04

*Note: Wavelengths listed are suggestions only and others may be used

TABLE VI - Interference Check Sample Concentrations

Element	ICSA (mg/L)	ICSAB (mg/L)
Aluminum	500	500
Antimony	-	1.0
Arsenic	-	1.0
Barium	-	1.0
Beryllium	-	0.1
Boron	-	10
Cadmium	-	1.0
Calcium	500	500
Chromium	-	1.0
Cobalt	-	1.0
Copper	-	1.0
Iron	500	500
Lead	-	1.0
Magnesium	500	500
Manganese	-	1.0
Molybdenum	-	1.0
Nickel	-	1.0
Potassium	-	10
Selenium	-	1.0
Silicon	-	10
Silver	-	1.0
Sodium	-	10
Strontium	-	1.0
Thallium	-	1.0
Tin	-	1.0
Titanium	-	1.0
Vanadium	-	1.0
Zinc	-	1.0

TABLE VII – Linear Dynamic Range Concentrations

Element	LDR (mg/L)
Aluminum	5000
Antimony	125
Arsenic	125
Barium	125
Beryllium	5
Bismuth	50
Boron	120
Cadmium	12.5
Calcium	1000
Chromium	25
Cobalt	25
Copper	25
Iron	250
Lead	250
Magnesium	2000
Manganese	25
Molybdenum	25
Nickel	25
Phosphorus	250
Potassium	2000
Selenium	250
Silicon	500
Silver	10
Sodium	1500
Strontium	25
Thallium	125
Tin	62.5
Titanium	50
Vanadium	25
Zinc	25

TABLE VIII - Summary Of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Four-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV fails.	r ≥ 0.995 and RSD between multiple exposures ≤5%. r≥ 0.998 for 6010C	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. Method 6010: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
ICB	Beginning of every analytical run, immediately following the initial CCV.	The result must be within ± RL from zero. **For DoD**: < LOD.	Terminate analysis; Correct the problem; Recalibrate.
CRI/LLICV/RL	Daily, after calibration	6010B: 50 – 150% 6010C: 70-130% *6010D: 80-120%* **For DoD:** 80 – 120%	Correct problem; then reanalyze.
CCV	After the ICV, after every 10 samples and at the end of the run.	90 - 110 % recovery	Re-run one time, if problem still exists, terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	The result must be within ± RL from zero. **For DoD**: < LOD	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run	Absolute value of concentration for all non-spiked analytes < *RL. DoD < LOD* (unless they are a verified impurity).	See Section 9.9
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.9
Serial Dilution Test	One per prep batch.	For samples > 20x RL, dilutions must agree within 10%. **For DoD:** Dilution must within ± 10%.	Narrate the possibility of physical or chemical interference per client request.

TABLE VIII - Summary of Quality Control Requirements (Continued)

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. **For DoD** ≤ ½ RL. Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.4).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.10 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	LCS must be within 80 - 120% recovery, in-house control limits or DoD QSM 5.0 limits.. (85-115% for 200.7) Samples for which the contaminant is < RL and the LCS results are > 120% (115% for 200.7) may not require redigestion or reanalysis (see Section 9.5)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike (MS)	One per sample preparation batch of up to 20 samples. 10% frequency for some programs (see 9.6)	80 – 120% recovery, in-house control limits or DoD QSM 5.0 limits. For TCLP See Section 9.6.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section9.6.
Matrix Spike Duplicate (MSD)	One per sample preparation batch of up to 20 samples. 10% frequency for some programs (see 9.6)	80 – 120 % recovery; RPD ≤ 20%, in-house control limits or DoD QSM 5.0 limits.	See Corrective Action for Matrix Spike.
Post Digestion Spike	For DoD, when Dilution Test fails.	80 – 120 % recovery	Narrate the possibility of physical or chemical interference per client request.

APPENDIX A

TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber
Instrument Drift	RF not cooling properly Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves should not be used in the metals laboratory because the powder contains silica and zinc as well as other metallic analytes.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipette tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

Title: Mercury Analysis by CVAA [Methods 245.1, 7470A, 7471A]

Approvals

Signatures on File	
Stan Palmquist Date	Manjit Nijjar Date
Metals Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, and domestic and industrial wastes. SW-846 Method 7471A is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials.

Standard Aqueous RL	0.2 µg/L
Brine RL	60 µg/L
TCLP RL	2.0 µg/L
Soil RL	20 µg/kg

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

This method describes the determination of mercury in solution by CVAA. Prepared samples are treated so that mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer at 253.7 nm. Intensity of absorption (attenuation of light signal) is directly related to the concentration of mercury by comparison with standards.

3.0 Definitions

3.1 Dissolved metals = those metals that will pass through a 0.45 µm membrane filter.

3.2 Suspended metals = those elements which are retained by a 0.45 µm membrane filter.

3.3 Total metals = the concentration determined of an unfiltered sample after digestion or; the sum of the dissolved plus suspended concentrations.

3.4 Total recoverable metals = the concentration determined of an unfiltered sample after treatment with hot, dilute mineral acid.

4.0 Interferences

4.1 Potassium permanganate, which is used to breakdown organic mercury compounds, is added as a reagent to eliminate interference from sulfide.

4.2 Copper also has been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3 High chloride concentration requires additional permanganate (free chlorine must be absent during oxidation steps). Excess of hydroxylamine sulfate reagent eliminates chlorine interference.

4.4 Interference from certain volatile organic materials that absorb at the wavelength used for the method may also occur. If suspected, a preliminary run without stannous chloride can

determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5 Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.1.2 Potassium permanganate is a strong oxidizing agent. It is incompatible and must be stored separately from hydroxylamine hydrochloride and stannous chloride, the reducing agents used in this procedure, and from acids.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating.

Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.

A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (100 µg/ml in Reagent)	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m^3 - TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Digestion Tubes (CPI) , certified for cleanliness and volume

If the digestion tubes come with certifications of cleanliness and certifications of volume, the following procedures do not have to be done for each lot of tubes received:

6.1.1 Ten tubes are used to process ten Method Blanks and the digestates are analyzed by ICP-MS. The lot number of the digestion tubes is recorded on the batch sheet and the results of the analyses are place in a three ring binder with the batch sheets. The lot of digestion tubes is considered acceptable if all analytes are less than ½ the ICP-MS RLs.

6.1.2 Volumetric verification is performed on same ten digestion tubes. Each digestion tube is tared on a balance and DI water is filled to the 50 ml mark. The weight of the water is recorded and should equal 50 g ±0.5 g to be considered acceptable. This procedure is repeated for 10 replicates on each tube. Verification is documented in the same digestion batch as the Method Blanks in Section 6.

6.2 Instrumentation

- Leeman Labs Hydra AA Automated Mercury Analyzer
- Computer controlled data system for Hydra AA
- Analytical balance, 0.1 mg accuracy
- Hot Bloc digestion block, capable of maintaining constant temperature at 90 - 95℃

6.3 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- Data acquisition/processing system: Envoy 1.8 or higher
- LIMS system: TALS version 1.0 or higher

6.4 Supplies

- Graduated cylinder, 100 mL.
- Volumetric flasks, 100 mL and 1000 mL.
- Disposable polyethylene tubes, 16 x 125 mm.
- Poly dispensing bottles
- Wooden tongue depressors

7.0 Reagents and Standards

7.1 Document reagents/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 DI water.

7.3 Argon gas, high purity grade

7.4 Sulfuric acid, concentrated, trace reagent grade.

7.5 Nitric acid, concentrated, trace reagent grade of low mercury content.

7.6 Nitric acid, 50%

7.6.1 Preparation: Dilute concentrated nitric by adding to equal volume of DI water.

7.7 Hydrochloric acid, concentrated, trace reagent grade.

7.8 Stannous chloride, Certified ACS.

7.9 Sodium chloride, Certified ACS.

7.10 Hydroxylamine hydrochloride, Certified ACS.

7.11 Potassium permanganate, Certified ACS.

7.12 Potassium persulfate, Certified ACS.

7.13 Aqua Regia

7.13.1 Preparation: 0.6 mL of Nitric acid, 1.8 mL of hydrochloric acid, and 2.5 mL of DI water are added directly to each standard and sample before digestion (solid samples only).

7.14 2:1 Sulfuric:Nitric (mixed acid).

7.14.1 Preparation: 700 mL trace grade nitric acid mixed into 1400 mL trace grade sulfuric acid.

7.15 Stannous chloride ($SnCl_2$) reagent.

7.15.1 Preparation: Add 100 mL of trace grade Hydrochloric acid, 100 g stannous chloride to 1000 mL of warm DI water.

7.16 Sodium chloride-hydroxylamine hydrochloride solution.

7.16.1 Preparation: Dissolve 500 g of sodium chloride and 500 g of hydroxylamine hydrochloride DI water and dilute to 3600 mL.

7.17 Potassium permanganate, mercury-free, 5% solution (w/v).

7.17.1 Preparation: Dissolve 180 g of potassium permanganate DI water and dilute to 3600 mL.

7.17.2 5% Potassium Permanganate solution may also be purchased.

7.18 Potassium persulfate, 5% solution (w/v).

7.18.1 Preparation: Dissolve 180 g of potassium persulfate DI water and dilute to 3600 mL.

7.19 Calibration and laboratory control sample/matrix spiking mercury stock standard, 100 µg/mL (AccuStandard or equivalent).

7.20 Working standard preparation: 50 mL DI water mixed with 0.15 mL nitric acid, 0.1 mL mercury stock standard; dilute to 100 mL.

7.20.1 Preparation of calibration standards (0.2, 0.5, 2.0, 5.0, and 10.0 µg/L) - All mercury calibration standards are prepped each day and included in the first LIMS prep (digestion) batch of the day.

7.20.1.1 Liquid matrix calibration standards for methods 245.1 and 7470A:

7.20.1.1.1 Perform dilutions of mercury working standard with DI water into the digestion vessels. The final concentration for each calibration level is listed in the following table:

Calibration Level	Volume of Calibration Working Solution (100 µg/L)	Final Volume (mL)	Final Hg Concentration (µg/L)
Blank	**0.0**	**50.0**	**0.0**
1	**0.1**	**50.0**	**0.2**
2	**0.25**	**50.0**	**0.5**
3	**1.0**	**50.0**	**2.0**
4	**2.5**	**50.0**	**5.0**
5	**5.0**	**50.0**	**10.0**

7.20.1.1.2 Add 2.5 mL of Sulfuric Acid and 1.25 mL of Nitric acid to each digestion vessel.

7.20.1.1.3 Add 7.5 mL of potassium permanganate solution to each digestion vessel, and allow to stand for at least 15 minutes.

7.20.1.1.4 Add 4 mL of potassium persulfate to each digestion vessel and heat for 2 hours in the Digestion Bloc maintained at 90 - 95℃.

7.20.1.1.5 Cool and add 3 mL of sodium chloride-hydroxylamine Hydrochloride to reduce the excess permanganate.

7.20.1.1.6 Bring the cooled solution to a final volume of 50 mL with DI water.

7.20.1.2 Solid matrix calibration standards for method 7471A:

7.20.2 Perform dilutions of mercury working standard with DI water into the digestion vessels. The final concentration for each calibration level is listed in the following table: All mercury calibration standards are prepped each day and included in the first LIMS prep (digestion) batch of the day.

Calibration Level	Volume of Calibration Working Solution (100 µg/L)	Final Volume (mL)	Final Hg Concentration (µg/L)
Blank	**0.0**	**50.0**	**0.0**
1	**0.1**	**50.0**	**0.2**
2	**0.25**	**50.0**	**0.5**
3	**1.0**	**50.0**	**2.0**
4	**2.5**	**50.0**	**5.0**
5	**5.0**	**50.0**	**10.0**

7.20.2.1 Add enough DI water to each vessel to make a total volume of 10 mL. Add 0.6 mL of nitric acid, and 1.8 mL of hydrochloric acid to each standard. Heat for 2 minutes in the Digestion Bloc maintained at 90 - 95℃.

7.20.2.2 Cool and add 25 mL of DI water and 7.5 mL of potassium permanganate solution to each bottle.

7.20.2.3 Mix thoroughly and place in the Digestion Bloc maintained at 90 - 95℃ for 30 minutes.

7.20.2.4 Cool and add 3 mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate.

7.20.2.5 Bring the cooled solution to a final volume of 50 ml with DI water.

7.21 Second Source Check Standard (stock), 100 µg/mL (ELEMENTS or equivalent).

7.22 Second Source Check Standard (working), 100 µg/L, 50 mL DI water mixed with 0.15 mL nitric acid, 0.1 mL mercury stock standard; dilute to 100 mL.

7.23 ICV Solution

7.23.1 Preparation:

- ICV (4 µg/L): 2.0 mL of 100 µg/L Second Source Check standard diluted to 50 mL with DI water.

7.24 LCS and MS/MSD Solution / CCV Solution

7.24.1 Preparation:

- LCS and MS/MSD (2 µg/L): 1.0 mL of 100 µg/L Calibration Solution diluted to 50 mL with DI water.
- CCV (5 µg/L): 2.5 mL of 100 µg/L Calibration Solution diluted to 50 mL with DI water.

7.25 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards/reagents and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.2 Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis. The samples are pH checked when they are received in Sample Control. If the pH is not <2, the pH is adjusted in Sample Control. The pH adjustment must be noted by generation of an NCM within the LIMS and placement of a preservation label on the sample container indicating date and time of preservation. If a sample requires preservation the sample must be allowed to rest for at least 24 hours following preservation to dissolve any metals that adsorb to the container walls. This 24 hr requirement was published in the Federal Register, Volume 72, Number 57, Monday, March 26, 2007, Rules and Regulations, page 14233. After this time, the pH must be verified as < 2.0.

8.3 Soil samples do not require preservation, but are to be stored at ≤ 6°C until the time of analysis.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	HDPE	50 mL	HNO_3, pH < 2;	28 Days	40 CFR Part 136.3
Soils	Glass	3 g	≤ 6 ℃	28 Days	N/A

[1] Inclusive of digestion and analysis.

9.0 Quality Control

This section describes routine quality control practices, which are also summarized in Attachment 1. Preparation of QC materials is described in Section 7. Initial calibrations and calibration verifications are discussed in Section 10. Initial performance studies are described in Section 12. Current control limits are stored in the laboratory LIMS system.

9.1 The process of establishing control limits, and the use of control charts are described more completely in TA-QA-0620, Quality Control Program.

9.2 QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). Failing QC that is automatically flagged by TALS does not need a NCM as long as it is a routine failure. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP # TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.4 Preparation Batch

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS, and a matrix spike/matrix spike duplicate pair (MS/MSD). As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.5 Method Blank (MB)

The MB consists of an empty vessel or <1-mm glass beads (for DoD projects) containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. At least one method blank (MB) must be processed with each preparation batch.

Acceptance Criteria: Some programs (e.g., DoD) require control of method blanks to have a concentration less than or equal to one-half of the RL. Some programs (LaMP) and method 7470A require no detections in the method blank more than 10% of the low limit calibration check solution. Method 245.1 requires no detection in the method blank greater than 2.2X the MDL. This can not be obtained in most cases. TestAmerica Seattle will only evaluate the method blank to 1/2 the RL or Project DQOs and when specific DQOs are not provided by the client the RL will be defined as the DQO.

Corrective Action: All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If mercury was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.6 Laboratory Control Sample (LCS)

The preparation of the LCS is described in Section 7.22. At least one aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire

analytical procedure. If there is not sufficient sample volume for a matrix spike duplicate or sample duplicate, then precision information for the batch will need to be derived by processing a LCSD.

Acceptance Criteria: For Methods 7470/7471, the maximum control limits for LCS recoveries are 80-120%. In-house control limits based on three standard deviations of the mean of historical results are used as long as they are at least as tight as 80-120% (see SOP TA-QA-0620 for further details on establishing control limits).

For Method 245.1, the maximum control limits for LCS recoveries are 85-115%.

Corrective Action: If LCS recoveries are outside established control limits, the system is out of control and corrective action must occur. If recoveries are above control limits and mercury is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed - BP LaMP makes no allowance for out high/ND scenarios) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair must be processed for each preparation batch. Some programs may require the use of sample duplicates in place of or in addition to MS/MSDs. In addition, some programs will allow spikes to be reported only for project-related samples. Samples identified as field blanks cannot be used for MS/MSD analysis. If there is not sufficient sample volume for a matrix spike duplicate or sample duplicate, then precision information for the batch will need to be derived by processing a LCSD.

Acceptance Criteria: Control limits are statistically determined based on three standard deviations of the mean of the laboratory's historical data. The MS/MSD recoveries must fall within 80-120%; the relative percent difference (RPD) between the MS and MSD cannot exceed 20%.

Corrective Action: If analyte recovery or RPD fails acceptance criteria, the LCS recovery must be in control for the data to be reported. If there is no evidence of analytical problems and all other QC criteria are met, then qualified results may be reported and the situation must be described in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC, then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

9.8 Instrument QC

9.8.1 Initial Calibration (ICAL)

9.8.1.1 Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

9.8.1.2 Calibrate using five standards and a blank (see Section 7.20.)

NOTE: It is generally not acceptable to reject calibration points for this method.

9.8.1.3 The calibration curve must have a correlation coefficient of ≥ 0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

9.8.2 Initial and Continuing Calibration Blanks

9.8.2.1 An initial calibration blank (ICB) is tested immediately after the daily ICAL standards.

Acceptance Criteria: The absolute value of the blank result must be less than the reporting limit (< Limit of Detection (LOD) for DoD). As noted with the method blank, some programs require that results for blanks must be less than two times the method detection limit (refer to special project requirements). Samples analyzed for BP LaMP must be less than ½ the RL.

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.8.2.2 Continuing calibration blanks (CCBs) are run after every 10 samples and at the end of the run.

Acceptance Criteria: The absolute value of the blank result must be less than the reporting limit (< LOD for DoD). As just noted, some programs require that results for blanks must be less than two times the method detection limit (refer to special project requirements). Samples analysed for BP LaMP must be less than ½ the RL.

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.8.3 RL Calibration Check Standard (for BP and BNSF)

Calibration accuracy at the RL is verified by analyzing a standard prepared within two times the laboratory's standard reporting limit. The preparation of this standard is described in Section 7. For analytical sequences that include BNSF and/or BP LAMP

samples, the Calibration Check Standard must be analyzed at the beginning of the analytical sequence, every 8 hours and/or at the end of the analytical sequence.

Acceptance Criteria: The acceptance limits are ± 50% of the expected value.

Corrective Action: If the RL Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.8.4 Initial Calibration Verification (ICV)

The accuracy of the calibration standards is verified by testing a second source standard (ICV).

Acceptance Criteria: For Methods 7470/7471, the ICV recovery must be within 90-110%.

For Method 245.1, the ICV recovery must be 95-105%.

Corrective Action: If the ICV acceptance limit is exceeded, the analysis should be terminated, the accuracy of the calibration standards checked, and the instrument recalibrated.

9.8.5 Continuing Calibration Verification (CCV)

Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the run.

Acceptance Criteria: For Methods 7470/7471, the CCV recovery must be within 80-120%.

For Method 245.1, the CCV recovery must be 90-110%.

Correction Action: Sample results may be reported only when bracketed by valid CCV pairs. If a CCV fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and the affected samples reanalyzed. If the cause of the CCV failure was not directly related to the instrument, the associated samples must be reanalyzed.

9.9 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

10.1 Sample Preparation

10.1.1 Liquid sample preparation methods 245.1 and 7470A.

All TCLP leachates MUST be prepared for digest immediately after the sample has been filtered.

10.1.1.1 Transfer 50 mL, or an aliquot diluted to 50 mL, to a digestion vessel. TCLP leachates are diluted 1:10 prior to digestion.

10.1.1.2 Add 2.5 mL of concentrated sulfuric acid and 1.25 mL of concentrated Nitric acid.

10.1.1.3 Add 7.5 mL of potassium permanganate solution to each sample bottle

10.1.1.4 Add 4 mL of potassium persulfate to each bottle and heat for 2 hours in the Digestion Bloc maintained at 90 - 95℃. Record the corrected and uncorrected temperatures of the digestion within the appropriate field of the batch prep sheet within the LIMS. Monitor the Digestion Bloc temperature during digestion.

10.1.1.4.1 If necessary, add more potassium permanganate until purple color persists for at least 15 minutes

10.1.1.5 Cool and add 3 mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate.

10.1.1.6 Bring the cooled solution to a final volume of 50 mL with DI water.

10.1.2 Solid sample preparation method 7471A.

10.1.2.1 Check the Balance Logbook to determine if the daily calibration check was completed. If the balance requires a check, verify the calibration as detailed in SOP TA-QA-0014.

10.1.2.2 Using wooden tongue depressor, mix the sample thoroughly to achieve homogeneity (refer to SOP TA-QA-0028 for subsampling procedures).

Soil samples submitted under the BP LaMP must be transferred from their field container to a plastic or Teflon pan and then mixed thoroughly with wooden tongue depressor while reducing it to BB-sized clumps. After subsampling for this preparation, return unused portion to the original field container. Document on the container and in the digestion log that sample was “BP LaMP Homogenized.

10.1.2.3 Using a wooden tongue depressor, weigh triplicate 0.2 g portions of sample into a digestion tube.

10.1.2.4 Add 2.5 mL of DI water, 0.6 mL of nitric acid, and 1.8 mL of hydrochloric acid to each sample, blank, and QC sample. Heat for 2 minutes in the Digestion Bloc maintained at 90 - 95℃. Record the corrected and uncorrected temperatures of the digestion within the appropriate field of the batch prep sheet within the LIMS.

10.1.2.5 Cool and add 25 mL DI water and 7.5 mL potassium permanganate solution to each sample vessel. Add more if necessary, until the purple color persists for at least 15 minutes.

10.1.2.6 Mix thoroughly and place in the Digestion Bloc for 30 minutes at 90 - 95℃. Record the corrected and uncorrected temperatures of the digestion within the appropriate field of the batch prep sheet within the LIMS.

10.1.2.6.1 If necessary, add more potassium permanganate until purple color persists for at least 15 minutes

10.1.2.7 Cool and add 3 mL of sodium chloride-hydroxylamine hydrochloride to reduce excess permanganate.

10.1.2.8 Bring the cooled solution to a final volume of 50 mL with DI water.

10.1.3 ISM Solid sample preparation method 7471A.

10.1.3.1 Check the Balance Logbook to determine if the daily calibration check was completed. If the balance requires a check, verify the calibration as detailed in SOP TA-QA-0014.

10.1.3.2 Using wooden tongue depressor, mix the sample thoroughly to achieve homogeneity (refer to SOP TA-QA-0028 for subsampling procedures).

10.1.3.3 Using a wooden tongue depressor, weigh triplicate 1.7 g portions of sample into a 300 mL glass digestion tube.

10.1.3.4 Add 12.5 mL of DI water, 3.0 mL of nitric acid, and 9 mL of hydrochloric acid to each sample, blank, and QC sample. Heat for 2 minutes in the Digestion Bloc maintained at 90 - 95℃. Record the corrected and uncorrected temperatures of the digestion within the appropriate field of the batch prep sheet within the LIMS.

10.1.3.5 Cool and add 125 mL DI water and 37.5 mL potassium permanganate solution to each sample vessel. Add more if necessary, until the purple color persists for at least 15 minutes.

10.1.3.6 Mix thoroughly and place in the Digestion Bloc for 30 minutes at 90 - 95℃. Record the corrected and uncorrected temperatures of the digestion within the appropriate field of the batch prep sheet within the LIMS.

10.1.3.6.1 If necessary, add more potassium permanganate until purple color persists for at least 15 minutes

10.1.3.7 Cool and add 15 mL of sodium chloride-hydroxylamine hydrochloride to reduce excess permanganate.

10.1.3.8 Bring the cooled solution to a final volume of 250 mL with DI water.

10.2 Instrument Operating Conditions

10.2.1 The current operating conditions of each instrument must be either written, or printed out and attached to the corresponding instrument maintenance logbook.

10.3 Calibration

10.3.1 Initial Calibration Procedures. An instrument blank and five standards (0.2, 0.5, 2.0, 5.0, and 10.0 µg/L) are injected in triplicate by the autosampler. The injection order is blank, 0.2 µg/L, 0.5 µg/L, 2.0 µg/L, 5 µg/L, and finally the 10 µg/L standard. The instrument calculates an average value for each standard and the instrument blank; the average instrument response is used to generate the calibration curve. The %RSD for the triplicate measurements should be less than 20%. For details regarding calibration models and algorithms, refer to corporate SOP CA-Q-S-005.

10.3.2 Continuing Calibration Verification Procedures. After every 10 samples and at the end of the run, a continuing calibration verification (CCV) standard at 5.0 µg/L, or other mid-range concentration is injected singly by an auto sampler. The analysis of the CCV is immediately following by the analysis of a continuing calibration blank (CCB).

10.4 Sample Analysis

10.4.1 Samples are poured into disposable culture tubes and placed in an autosampler rack for analysis.

10.4.2 Samples are analyzed using the Leeman system, following manufacturer's instructions. The solution concentrations are determined by the instrument data handling system and reported as raw instrument data.

10.4.3 When a sample concentration *is within 90%* of the upper calibration range the sample must be diluted and reanalyzed in order to bring the concentration *within 90% of the* calibration range.

10.5 Following is a typical analytical sequence:

ICAL
ICV
ICB
CRDL (for BP and BNSF)
Method Blank
LCS and LCSD (in included)
7 injections or 8 if only LCS in included
CCV and CCB
10 injections
CCV and CCB
10 injections
CCV and CCB

10.6 The instrument ID and the analyst initials must be documented on the raw data.

10.7 Data Reduction and Review

10.7.1 Upon completion of the analytical sequence, perform a level 1 data review and document the review on the data review checklist.

10.7.2 Submit the data package and review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

10.7.3 Update instrument sequence logbook.

10.8 Instrument Maintenance

10.8.1 All instrument maintenance must be documented in the instrument maintenance logbook.

- The logbook must include the instrument name, serial number for each major component (e.g., AA, autosampler) and the date of start-up.
- When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service".
- Routine Maintenance (which includes, but is not limited to daily, weekly, and semiannual maintenance) is completed periodically and does not necessary indicate the instrument is out of control is noted in the logbook with the notation "RM".

- For non-routine maintenance or repairs, logbook entries must include a description of the problem and what actions were taken to address the problem.
    - When non-routine maintenance or repairs are complete, the instruments return to control is noted in the logbook with the notation “RTC”.

10.8.2 Daily Use and Maintenance.

10.8.2.1 These procedures are performed daily prior to instrument calibration.

10.8.2.2 Turn off the “overnight macro”.

10.8.2.3 Check the stability of the diagnostics-aperture (should be ± 200 or better), zero detector, and acquisition 5-volt reference.

10.8.2.4 Check the rinse and $SnCl_2$ levels. The reservoirs should be full.

10.8.2.5 Start the “warmstrt” macro.

10.8.2.6 Run calibration macro (“cal245”).

10.8.2.7 The Hg lamp intensities will be monitored each day and the value recorded in the instrument maintenance logbook.

10.8.3 Bi-monthly Maintenance

10.8.3.1 Change tubing as needed if pumping is not consistent.

10.8.3.2 Clean the pump clamps whenever tubing is changed.

10.8.3.3 Oil the autosampler bars.

10.8.4 Quarterly Maintenance

10.8.4.1 If the instrument counts drop below 250,000, clean the optic cell.

10.8.4.2 Clean out the interior of the instrument.

10.8.4.3 Change exhaust lines as needed.

10.8.5 Instrument QC Check

10.8.5.1 Whenever the optic cell is replaced, the “coldstrt” macro is run. This allows the optic cell to warm to a constant temperature, and will also condition new tubing. If the flow is consistent, the instrument is ready for calibration.

10.8.6 Spare Parts

10.8.6.1 Tubing

- Sample tubing.
- Reductant tubing.
- Drain tubing.
- Sample tips.
- Mixing Coil

10.8.6.2 Optics Cell

- Lenses
- Gaskets
- Complete spare optics cell

10.8.6.3 Other Parts

- Liquid gas separator
- Drying tube apparatus.

10.9 Trouble Shooting

See Attachment 2

11.0 Calculations / Data Reduction

For details regarding calibration models and algorithms, refer to corporate SOP CA-Q-S-005.

11.1 Accuracy

$$\textbf{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{Known concentration}} \times 100$$

$$\textbf{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{Spiked concentration}} \times 100$$

11.2 Precision (RPD)

$$\textbf{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.3 Concentration

11.3.1 Liquid samples, report as mg/L.

$$\text{mg/L} = \frac{\text{(instrument reading) * (final dilution)}}{\text{(Initial volume)}}$$

11.3.2 Solid samples (except filters), report as mg/Kg:

$$\text{mg/Kg} = \frac{\left[\frac{\text{(instrument reading) * (final dilution)}}{\text{(sample weight)}}\right]}{\text{(percent solids)}}$$

11.3.3 Filters, report as µg (or as µg/cm^3)

$$\mu g = \text{(instrument reading) * (final dilution)}$$

$$\mu g/cm^3 = \frac{\text{(instrument reading) * (final dilution) * (1000)}}{\text{(air volume in L)}}$$

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a

calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036. The following waste streams are produced when this method is carried out.

14.1 Waste Streams Produced by the Method

14.1.1 Aqueous Acidic (Metals) - Corrosive. Acidic waste generated by the digestion with a mercury concentration less than 0.2ppm and rinse solutions are poured into the acid neutralization tank, neutralized and then discarded down the drain.

14.1.2 Remaining standard and any sample digestion fluid with a mercury concentration greater than 0.2ppm are disposed of in the high mercury concentration satellite disposal container located in the analysis lab. At or before the satellite waste containers reaches 55 gallons, it is taken to the waste warehouse where it is sent out for retort.

14.1.3 Expired standard and reagents: i.e. Potassium Permanganate or Potassium Persulfate will be lab packed and sent out for incineration.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.1, April 2009.

15.3 U.S. Department of Defense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.0, July 2013.

15.4 EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983, Methods 245.1 and 245.2.

16.0 Method Modifications:

Item	Method	Modification
1	245.1 and 7470A	This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is (sic) not considered a significant change in the methodology."
2	7470A and 7471A	Methods 7470A and 7471A state that working mercury standards "should be prepared fresh daily." The laboratory frequently prepares up to three batches of mercury samples, including digested calibration standards, each day. The third batch is typically prepared and digested late in the day, and then is analyzed the morning of the next day. The laboratory has developed the following information demonstrating that analysis within 24 hours, but on the second calendar day from preparation produces reliable results and is acceptable to the EPA: • Successful proficiency testing PT results for samples that were prepared and analyzed within 24 hours, but on successive days (e.g., ERA WP-66); • Successful analysis of true NIST mercury standards within every analytical batch; and • A written comment from the EPA MICE Hotline stating that, with the supporting lab data, their opinion was that the laboratory's practice is "within the letter of the method as written
3	7471A	80 mL polyethylene digestion vessels and a Bloc Digester are used during the procedure in lieu of the 300 mL BOD bottles and water bath.
4	SW-846	Chapter 1 of SW846 specifies the use of DI water with a purity equivalent to ASTM Type II water. This SOP specifies the use of DI water. This SOP requires that DI water must be free of the analytes of interest as demonstrated through the analysis of method blanks
5	7470A	Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.
6	7471A	Method 7471A does not state control criteria within the text of the method. The QC section of 7471A refers the analyst to Section 8.0 of Method 7000A, the generic atomic absorption method, which discusses flame and furnace methods. The ICV criteria stated in Method 7000A is ± 10%. This SOP requires ICV control limits of ± 20% based on the fact that the mercury ICV, unlike the ICV for the flame and furnace analytes, is digested and therefore is equivalent to an LCS. The CLP protocol 245.5 CLP-M recognizes this factor and requires control limits of ± 20%.
7	245.1	Method 245.1 Section 12.8 states that concentrations should be reported as follows: Between 0.1 and 1 µg/g, to the nearest 0.01 µg; between 1 and 10 µg/g, to the nearest 0.1µg; and above 10 µg/g, to the nearest µg. TestAmerica Seattle reports all mercury results under this SOP to two significant figures.
8	7470A and	Method Blank criteria of no detections in the method blank more than

Item	Method	Modification
	7471A	10% of the low limit calibration check solution. TestAmerica Seattle will only evaluate the method blank to 1/2 the RL or Project DQOs and when specific DQOs are not provided by the client the RL will be defined as the DQO.
9	245.1	Method Blank criteria of no detections in the method blank more than 2.2 times method detection limit. TestAmerica Seattle will only evaluate the method blank to 1/2 the RL for DoD and LaMP projects and to the RL for all other projects.

17.0 Attachments

Attachment 1: Summary of Quality Control Requirements
Attachment 2: Troubleshooting

18.0 Revision History

- Revision 26, dated 13 April, 2018
  - Incorporated ROMD 00068, dilutions required within 90% of upper calibration, section 10.4.3.
-
- Revision 25.1, dated 23 March, 2018
  - Updated approvers
- Revision 25, dated 7 March, 2017
  - Updated approvers
- Revision 24, dated 2 March, 2016
  - Moved Troubleshooting to attachment 2
  - Added DoD QSM version 5.0 to References
- Revision 23, dated 30 October, 2014
  - Changed all instances of “inert utensils” to “wooden tongue depressors”.
  - Changed all instances of water references to “DI water”
  - Added that Sample Receiving checks and corrects pH, section 8.2
  - Added TCLP Leachate prep information, section 10.1.1
  - Defined the DI water used, section 16
  - Added information on the acceptance of the blank sections 9.5 and 16.0
- Revision 22, dated 9 April, 2014
  - Added Computer hardware and software, section 6.3
  - Updated NCM criteria, section 9.2
  - Added the prep procedure for ISM samples section 10.1.3
  - Added information on the acceptance of the blank sections 9.5 and 16.0
- Revision 21, dated 29 July 26, 2013
  - Added option of purchasing potassium permanganate solution to section 7.17
- Revision 20, dated 6 August 2012
  - Updated safety intro, section 5.0
  - Updated waste streams, section 14.1

- Revision 19, dated 25 April 2011
  - Updated soil RL in section 1.1
  - Incorporated ROMD 00025 in sections 9.6 and 9.7
  - Incorporated ROMD 00021 in sections 10.1.1.4, 10.1.2.4 and 10.1.2.6.
  - Incorporated ROMD00005 into section 10.1.2.3.
  - Incorporated ROMD 00020 in section 10.2.1
  - Incorporated ROMD 00022 in sections 10.2.1 and 11.0
  - Added new section (10.7) on data reduction and review
  - Incorporated ROMD 00033 in section 10.8.2
  - In section 8.3 added that the required temp is $\leq$ 6 C
  - In the table under section 8.3 added the preservation temp of $\leq$ 6 C for mercury soils
  - In section 7.15 change sulfuric acid to hydrochloric acid when making up the stannous chloride reagent
  -
- Revision 18, dated 16 April 2010
  - Added documentation of reagents and reagent preparation (Section 7.1).
  - Added documentation of standards and standard preparation (Section 7.18).
  - Added removal of expired standards Section (7.25).
  - Added Method 245.1 QC acceptance criteria for LCSs in section 9.6 and Attachment 1.
  - Added CRDL standard, section 9.8.3
  - Added Method 245.1 QC acceptance criteria for ICVs and CCVs in sections 9.8.3 and 9.8.4.
  - Added instructions to evaluate extra QC (Section 9.9)
  - Added section 10.1.1.6
  - Added verification of balance calibration check (Section 10.1.2.1)
  - Added BP sample homogenization requirements (Section 10.1.2.2)
  - Updated standard concentrations in section 10.2.1.
  - Added requirement to apply correction factor to temperature readings throughout section 10.1
  - Added maintenance documentation and return to service requirements, Section 10.6.1.
  - Clarified the order of analysis for CCVs and CCBs (Section 10.2.2)
  - Added documentation of analyst and instrument ID (Section 10.5)
  - Updated use of 1:1sulfuric:Nitric acid to concentrated sulfuric acid only(Sections 7.21.1.1.2 and 10.1.1.2)

- Revision 17, dated 5 May 2009
  - Updated Summary of Quality Control Requirements table to include requirements from the DoD QSM v. 4.1

- Revision 16, dated 27 March 2008
  - Integration for TestAmerica and STL operations.
  - This revision is a complete rewrite and an expansion of scope.

Attachment 1. - Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Minimum five-point Initial Calibration	Beginning of every analytical run, every 24 hours, when instrument is modified, or CCV fails.	r ≥ 0.995	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Immediately following ICAL	95 -105% for 245.1 90 - 110 % for 7470A/7471A including DoD	Terminate analysis; correct the problem; recalibrate or re-prepare and reanalyze batch.
ICB	Following ICB	Absolute value < RL **For DoD**: < LOD	Terminate analysis; correct the problem; recalibrate or re-prepare and reanalyze batch.
CCV	Every 10 samples and at the end of the run	90 -110% for 245.1 80 - 120 % for 7470A and 7471A including DoD	Terminate analysis; correct the problem; recalibrate and rerun all samples not bracketed by acceptable CCVs or re-prepare and reanalyze batch.
CCB	Immediately following each CCV	Absolute value < RL **For DoD**: < LOD	Terminate analysis; correct the problem; recalibrate and rerun all samples not bracketed by acceptable CCVs or re-prepare and reanalyze batch.
Method Blank	One per sample preparation batch of up to 20 samples.	≤RL; **For DoD**: ½ RL Sample results greater than 10% the blank concentration are acceptable. Samples for which the contaminant is < RL do not require re-digestion.	Re-digest and reanalyze samples. Note exceptions under criteria section.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	85 - 115% for 245.1. Recovery must be within statistical control limits, not to exceed 80 - 120% for 7470A/7471A.	Terminate analysis; correct the problem; redigest and reanalyze all samples associated with the failed LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Recovery must be within statistical control limits, not to exceed 75-125% (80-120% for DoD). 50-150% for TCLP Leachates	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added.
Matrix Spike Duplicate	See Matrix Spike	Recovery within statistical control limits, not to exceed 75-125 % recovery; RPD ≤ 20% (80-120% for DoD)	See Corrective Action for Matrix Spike.

Attachment 1. - Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Duplicate		≤20% RPD for water ≤35% RPD for solid ≤50% RPD for leachates **For DoD:** ≤20% RPD for all	See Corrective Action for Matrix Spike.

* An RL check standard is analyzed for BP LaMP and BNSF. The acceptance criteria is ±50% of the true value.

Attachment 2. –
Troubleshooting

13 Troubleshooting

13.1 Troubleshooting Tools

13.1.1 Module LED indicators

The LED lamps on the instrument modules are useful for indicating general health of the instrument. The LEDs can be seen on the front of the AA module and the Pump module.

13.1.1.1 AA Module LEDs

As seen from left to right:

Data Acquisition - Pulses for each data acquisition.
Program Mode - On when programming new firmware.
Timer Interrupt (CPU alive) - Pulses indicating the internal CPU is alive.
(Send/Receive) - Communication with PC.
(Send/Receive) - Communication with PC.
Power - On when power is operational.

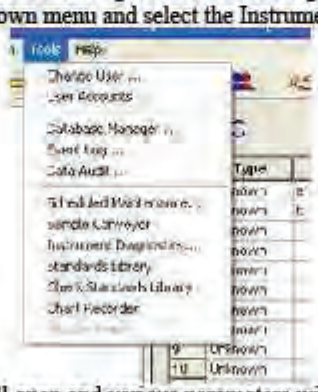
13.1.1.2 Pump Module LEDs

As seen from left to right:

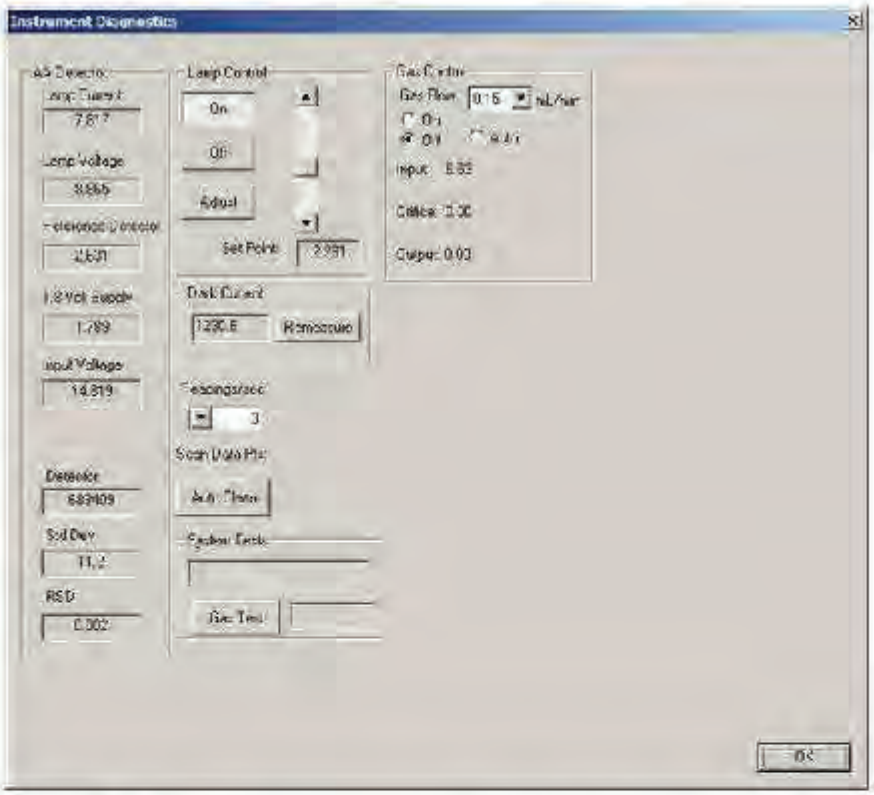
(Send/Receive) - Communication with PC.
(Send/Receive) - Communication with PC.
Power - On when power is operational.

13.1.2 Instrument Diagnostics

Various diagnostic readouts can be viewed using the instrument diagnostic page. To view the instrument diagnostic page use the Tools pulldown menu and select the Instrument Diagnostics.



The Instrument Diagnostic page will open and various parameters will be displayed and updated in real time.



Typical parameter values:

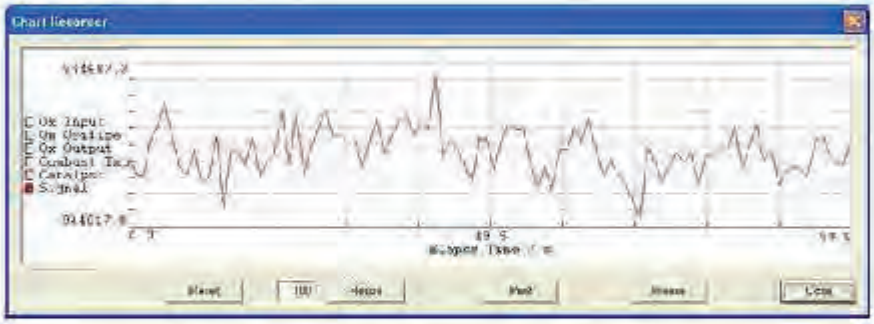
Parameter	Minimum	Maximum
Lamp Voltage	5	12.2
1.8Volt Supply	1.6	2.0
Input Voltage	12	18
Detector (Lamp on)	250000	8000000
Dark Current	10	2500
Orifice pressure (@0.50LPM)	0.59	0.63

13.1.2.1 Future Subject

13.1.3 Real-Time Chart Recording

The Real-Time Chart Recorder is a screen that can be opened and viewed while running the instrument. The Chart Recorder can monitor various parameters by plotting values versus time. The chart recording automatically wraps around when it reaches the right most edge. To launch the chart recorder use Tools pulldown and select Chart Recorder.

Select the parameter by clicking it on the left side of the chart recorder. To increase or decrease the time window, enter a new value to the left of the Resize button. Then click the Resize button to accept. Reset will restart the recording on the left side.



13.2 No or Low Signal for Standards

Possible Cause	Corrective Action
Hg Lamp is not turned on	Turn the mercury lamp on.
Stannous Chloride is not being pumped	Check that the pump tubing is not fatigued and that the lever is fully rotated to apply adequate pressure. Verify that the stannous chloride is flowing by temporary removal of the tubing from the reductant bottle and observing air pumping into the tubing.
Stannous Chloride is not potent	Replace the stannous chloride solution if it is old. The solution slowly oxidizes over time. Stannous chloride granules ($SnCl_2 \cdot 2H_2O$)

	should go into solution in 10% HCl very rapidly. If it does not reorder.
Standards are not being pumped	Check that the pump tubing is not fatigued and that the lever is fully rotated to apply adequate pressure.
Standards are old	Standard properly acidified and in glass or Teflon containers should be stable for several days, even at low concentrations. However, if not properly acidified or stored in other types of plastic container, mercury can be lost quickly. Remake standard dilutions from a stock standard of known accuracy. This is especially true in nitric acid. The best stability is in HCl acid.
Carrier gas is not flowing	Check the liquid/gas separator to ensure proper gas flow. Check the exhaust of the CVAAS module by placing tubing into beaker of water and observe bubbling.
A leak in the sample vapor path	Check all tubing connections are tight and that the absorption cell windows are in place.
A blockage in the sample vapor path	Submerge the CVAAS exhaust line in a small beaker of water to confirm that the carrier gas is flowing throughout the system.

13.3 No or Low Signal for Samples (Standards are good)

Possible Cause	Corrective Action
Digestion is incomplete	Stannous chloride reduces Hg^{+2} to Hg^{0}. The oxidation steps in the digestion procedures are designed bring mercury to the +2 state. Samples high in organic content may require additional oxidant or heating during the digestion to complete oxidation
Samples are high in known interferents	If samples are high in interferents such as iodide, the signal response will be low. Diluting the sample will decrease the concentration of the interference and limit its impact.

13.4 Poor Precision for Repeats

Possible Cause	Corrective Action
The Signal has not reached plateau	Increase the uptake time or gas flow.
Integration time is too long	Once the signal has reached plateau it will continue to rise slowly. If repeats are taken

	without returning to rinse, the slight rise is signal over time can result in poorer precision. Drop the integration time to 2 seconds.
Integration time is too short	If repeats are taken with a return to rinse between readings, a longer integration time should result in better precision. Increase the integration time to 5 seconds or more.
More care is required with timing in manual mode	If the sampler is not controlling solution uptake it is critical that the times for rinse and uptake be consistent. Move the probe to the appropriate solution and click OK promptly when directed.
Low light intensity	Check the signal value displayed on the Method/ Instrument Control display. The value should be 250000 or greater. If low make sure the cells are properly held in clamps and clean optics if necessary.

13.5 Lamp Does Not Light

Possible Cause	Corrective Action
Hydra II is not plugged in and powered up.	Check electrical connections and ensure right-most LED is lit on CVAAS module.
Envoy software reports instrument status as IDLE	Make sure all communication Indicators at the bottom right of the screen are green. If not, power down the instrument and exit Envoy software, power up the instrument and restart Envoy program. If problem persists call Customer Support.
Lamp status is Off	View Menu bar/Tools/Instrument Diagnostics. Confirm lamp is on. Click Adjust button and view lamp current & voltage values.
Lamp assembly is not fully inserted in control board	**CAUTION**- Power off instrument before touching Hg lamp. Pull up on the lamp to release contacts, then re-insert lamp noting the increased resistance as the contacts are made.
If all above is correct	Replace lamp assembly PN 122-00189-1. See Hg Lamp Replacement **CAUTION**- Power off instrument before touching Hg lamp. Call Customer Support at 1-800-LEEMANS

Quality Assurance Manual

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Approval Signatures

Signatures on File

Laboratory Director – Dennis Bean — Date

Quality Manager – Terri Torres — Date

Technical Manager, Project Management – Kris Allen — Date

Technical Manager, Volatiles – Justin McKell — Date

Technical Manager, Semivolatiles – Ryan Zboralski — Date

Technical Manager, Inorganics – Stan Palmquist — Date

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REFERENCED CORPORATE SOPs AND POLICIES

SOP / Policy Reference	Title
CA-I-P-002	Electronic Reporting and Signature Policy
CA-L-P-002	Contract Compliance Policy
CW-L-S-004	Subcontracting
CA-Q-M-002	Corporate Quality Management Plan
CA-Q-S-001	*Acid and* Solvent Lot Testing and Approval *Program*
CA-Q-S-002	Manual Integrations
CA-Q-S-006	Detection *and Quantitation Limits*
CA-T-P-001	Qualified Products List
CW-E-M-001	Corporate Environmental Health & Safety Manual
CW-F-P-002	Company-Wide Authorization Matrix
CW-F-P-004	Procurement and Contracts Policy
CW-F-S-007	*Fixed Asset Acquisition, Retention and Safeguarding*
CW-L-P-004	Ethics Policy
CW-L-S-002	Internal Investigation of Potential Data Discrepancies and Determination for Data Recall
CW-Q-S-001	Corporate Document Control and Archiving
CW-Q-S-002	Writing a Standard Operating Procedure (SOPs)
CW-Q-S-003	Internal Auditing
CW-Q-S-004	Management Systems Review

REFERENCED LABORATORY SOPs

SOP Reference	Title
TA-QA-0528	Document Control
TA-QA-0529	Complaint Resolution
TA-QA-0530	Management of Change
TA-QA-0506	Archiving Reports and Report File Maintenance
TA-QA-0608	Employee Training Procedures
TA-QA-0500	Standard Operating Procedures
TA-QA-0617	Analyst Demonstration of Capability
TA-IP-0226	Multi Incremental Subsampling of Soils and Sediments
TA-QA-0028	Subsampling of Solid Samples
TA-QA-0001	Sample Receipt & Login
TA-QA-0610	Laboratory Corrective Action Procedures
TA-QA-0635	Data Review
TA-QA-0014	Selection and Use of Laboratory Balances
TA-QA-0024	Use, Calibration and Maintenance of Laboratory Thermometers
TA-QA-0016	Volumetric Verification

TA-QA-0610	Laboratory Corrective Action Procedures
TA-QA-0619	Receipt, Storage and Verification of Standards
TA-QA-0600	Quality Control Charting and Establishing

SECTION 3. INTRODUCTION, SCOPE AND APPLICABILITY

3.1 Introduction and Compliance References

TestAmerica Seattle's Quality Assurance Manual (QAM) is a document prepared to define the overall policies, organization objectives and functional responsibilities for achieving TestAmerica's data quality goals. The laboratory maintains a local perspective in its scope of services and client relations and maintains a national perspective in terms of quality.

The QAM has been prepared to assure compliance with The NELAC Institute (TNI) Standard, dated 2009, Volume 1 Modules 2 and 4, and ISO/IEC Guide 17025:2005(E). In addition, the policies and procedures outlined in this manual are compliant with TestAmerica's Corporate Quality Management Plan (CQMP) and the various accreditation and certification programs listed in Appendix 3. The CQMP provides a summary of TestAmerica's quality and data integrity system. It contains requirements and general guidelines under which all TestAmerica facilities shall conduct their operations.

The QAM has been prepared to be consistent with the requirements of the following documents:

- ANSI/ASQC, E4-1994, "Specifications and Guidelines for Quality Management Systems for Environmental Data Collection and Environmental Technology Programs" (American National Standard, January 5, 1995, or most recent version)
- "EPA Requirements for Quality Management Programs" (QA/R-2) (EPA/240/B-01/002, May 31, 2006).
- EPA 600/4-88/039, Methods for the Determination of Organic Compounds in Drinking Water, EPA, Revised July 1991.
- EPA 600/R-95/131, Methods for the Determination of Organic Compounds in Drinking Water, Supplement III, EPA, August 1995.
- EPA 600/4-79-019, Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA, March 1979.
- Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996; Final Update IV, January 2008.
- U.S. Department of Defense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version *5.1, 2017*.
- Federal Register, 40 CFR Parts 136, 141, 172, 173, 178, 179 and 261.
- APHA, Standard Methods for the Examination of Water and Wastewater, 18th Edition, 19th, 20th, 21st, and on-line Editions.
- Marine Protection, Research, and Sanctuaries Act (MPRSA).
- Toxic Substances Control Act (TSCA).

3.2 Terms and Definitions

A Quality Assurance Program is a company-wide system designed to ensure that data produced by the laboratory conforms to the standards set by state and/or federal regulations. The program functions at the management level through company goals and management policies, and at the analytical level through Standard Operating Procedures (SOPs) and quality control. The TestAmerica program is designed to minimize systematic error, encourage constructive, documented problem solving, and provide a framework for continuous improvement within the organization.

Refer to Appendix 2 for the Glossary/Acronyms.

3.3 Scope / Fields of Testing

The laboratory analyzes a broad range of environmental and industrial samples every month. Sample matrices vary among effluent water, groundwater, hazardous waste, sludge, sediments and soils. The Quality Assurance Program contains specific procedures and methods to test samples of differing matrices for chemical and physical parameters. The Program also contains guidelines on maintaining documentation of analytical processes, reviewing results, servicing clients and tracking samples through the laboratory. The technical and service requirements of all analytical requests are thoroughly evaluated before commitments are made to accept the work. Measurements are made using published reference methods or methods developed and validated by the laboratory.

The methods covered by this manual include the most frequently requested methodologies needed to provide analytical services in the United States and its territories. The specific list of test methods used by the laboratory can be found in the Laboratory Information Management System (LIMS). The approach of this manual is to define the minimum level of quality assurance and quality control necessary to meet these requirements. All methods performed by the laboratory shall meet these criteria as appropriate. In some instances, quality assurance project plans (QAPPs), project specific data quality objectives (DQOs) or local regulations may require criteria other than those contained in this manual. In these cases, the laboratory will abide by the requested criteria following review and acceptance of the requirements by the Laboratory Director and the Quality Assurance (QA) Manager. In some cases, QAPPs and DQOs may specify less stringent requirements. The Laboratory Director and the QA Manager must determine if it is in the lab's best interest to follow the less stringent requirements.

3.4 Management of the Manual

3.4.1 Review Process

The template on which this manual is based is reviewed annually by Corporate Quality Management Personnel to assure that it remains in compliance with Section 3.1. This manual itself is reviewed annually by senior laboratory management to assure that it reflects current practices and meets the requirements of the laboratory's clients and regulators as well as the CQMP. Occasionally, the manual may need changes in order to meet new or changing regulations and operations. The QA Manager will review the changes in the normal course of business and incorporate changes into revised sections of the document. All updates will be reviewed by the senior laboratory management staff. The laboratory updates and approves such changes according to our Document Control procedures (refer to SOP No. TA-QA-0528).

SECTION 4. MANAGEMENT REQUIREMENTS

4.1 Overview

TestAmerica Seattle is a local operating unit of TestAmerica Laboratories, Inc.. The organizational structure, responsibilities and authorities of the corporate staff of TestAmerica Laboratories, Inc. are presented in the CQMP. The laboratory has day-to-day independent operational authority overseen by corporate officers (e.g., President, Chief Executive Officer, Corporate Quality, etc.). The laboratory operational and support staff work under the direction of the Laboratory Director. The organizational structure for both Corporate & TestAmerica Seattle is presented in Figure 4-1.

4.2 Roles and Responsibilities

In order for the Quality Assurance Program to function properly, all members of the staff must clearly understand and meet their individual responsibilities as they relate to the quality program. The following descriptions briefly define each role in its relationship to the Quality Assurance Program.

4.2.1 Additional Requirements for Laboratories

The responsibility for quality resides with every employee of the laboratory. All employees have access to the QAM, are trained to this manual, and are responsible for upholding the standards therein. Each person carries out his/her daily tasks in a manner consistent with the goals and in accordance with the procedures in this manual and the laboratory's SOPs. Role descriptions for Corporate personnel are defined in the CQMP. This manual is specific to the operations of TestAmerica's Seattle laboratory.

4.2.2 President and Chief Executive Officer (CEO)

The President and CEO is a member of the Board of Directors and is ultimately responsible for the quality and performance of all TestAmerica facilities. The President and CEO establishes the overall quality standard and data integrity program for the Analytical Business, providing the necessary leadership and resources to assure that the standard and integrity program are met.

4.2.3 Chief Operation Officer (COO)

The COO reports directly to the President and CEO of TestAmerica. The COO oversees the operations of all TestAmerica laboratories and the EMLab P&K business unit. The VP's of Operations report directly to COO

4.2.4 Vice President of Operations

Each VP of Operations reports directly to the Chief Operation Officer and is a part of the Executive Committee. Each VP of Operations is responsible for the overall administrative and operational management of their respective laboratories. The VP's responsibilities include allocation of personnel and resources, long-term planning, goal setting, and achieving the financial, business, and quality objectives of TestAmerica. The VP's ensure timely compliance with Corporate Management directives, policies, and management systems reviews. The VP's are also responsible for restricting any laboratory from performing analyses that cannot be consistently and successfully performed to meet the standards set forth in this manual.

4.2.5 Vice President of Quality and Environmental Health and Safety (VP-QA/EHS)

The Vice President (VP) of QA/EHS reports directly to the President and CEO. With the aid of the Executive Committee, Laboratory Directors, Quality Directors, Safety Manager, EH&S Coordinators and QA Managers, the VP-QA/EHS has the responsibility for the establishment, general overview and Corporate maintenance of the Quality Assurance and EH&S Programs within TestAmerica. Additional responsibilities include:

- Review of QA/QC and EHS aspects of Corporate SOPs & Policies, national projects and expansions or changes in services.
- Work with various organizations outside of TestAmerica to further the development of quality standards and represent TestAmerica at various trade meetings.
- Preparation of a monthly report that includes quality metrics across the analytical laboratories and a summary of any quality related initiatives and issues.
- Preparation of a monthly report that includes EH&S metrics across the analytical laboratories and a summary of any EH&S related initiatives and issues.
- Work with various organizations outside of TestAmerica to further the development of quality standards and represent TestAmerica at various trade meetings.
- With the assistance of the Corporate Senior Management Teams and the EHS Directors, development and implementation of the TestAmerica Environmental, Health and Safety Program.

4.2.6 Vice President of Client Service

The VP of Client Services leads the Client Service Organization (CSO) and is responsible for client satisfaction, driving operational excellence and improving client responsiveness. The VP provides direction to the Client Service Directors, Programs Managers and Project Managers.

4.2.7 Quality Assessment Director

The Quality Assessment Director reports to the VP-QA/EHS. The Quality Assessment Director has QA oversight of laboratories; responsible for the internal audit system, schedule and procedure; monitors laboratory internal audit findings; identifies common laboratory weaknesses; and monitors corrective action closures. Together with the Quality Compliance Director, the Quality Systems Director, and the VP-QA/EHS, the Quality Assessment Director has the responsibility for the establishment, general overview and maintenance of the Analytical Quality Assurance Program within TestAmerica.

4.2.8 Quality Compliance Director

The Quality Systems Director reports to the VP-QA/EHS. The Quality Systems Director has QA oversight of laboratories; develops quality policies, procedures and management tools; monitors and communicates regulatory and certification requirements; identifies common laboratory weaknesses; and monitors corrective action closures. Together with the Quality Assessment Director, Quality Compliance Director and the VP-QA/EHS, the Quality Systems Director has the responsibility for the establishment, general overview and maintenance of the Analytical Quality Assurance Program within TestAmerica.

4.2.9 Quality Information Manager

The Quality Information Manager is responsible for managing all company official documents (e.g., Policies, Procedures, Work Instructions), the company's accreditation database, intranet websites, external laboratory subcontracting, regulatory limits for clients on the company's TotalAccess website; internal and external client support for various company groups (e.g., Client Services, EH&S, Legal, IT, Sales) for both quality and operational functions. The Quality Information Manager reports to the VP-QA/EHS; and works alongside the Quality Assessment, Quality Compliance and Quality System Directors and EHS Managers to support both the Analytical Quality Assurance and EHS Programs within TestAmerica.

4.2.10 Technical Services Director

The Technical Services Director is responsible for establishing, implementing and communicating TestAmerica's Analytical Business's Technical Policies, SOPs, and Manuals. Other responsibilities include conducting technical assessments as required, acting as a technical resource in national contracts review, coordinating new technologies, establishing best practices, advising staff on technology advances, innovations, and applications.

4.2.11 Ethics and Compliance Officers (ECOs)

TestAmerica has designated two senior members of the Corporate staff to fulfill the role of Ethics and Compliance Officer (ECO) – Corporate Counsel & VP of Human Resources and the VP-QA/EHS. Each ECO acts as a back-up to the other ECO and both are involved when data investigations occur. Each ECO has a direct line of communication to the entire senior Corporate and lab management staff.

The ECOs ensure that the organization distributes the data integrity and ethical practices policies to all employees and ensures annual trainings and orientation of new hires to the ethics program and its policies. The ECO is responsible for establishing a mechanism to foster employee reporting of incidents of illegal, unethical, or improper practices in a safe and confidential environment.

The ECOs monitor and audit procedures to determine compliance with policies and to make recommendations for policy enhancements to the President and CEO, VPOs, Laboratory Director or other appropriate individuals within the laboratory. The ECO will assist the laboratory QA Manager in the coordination of internal auditing of ethical policy related activities and processes within the laboratory, in conjunction with the laboratories regular internal auditing function.

The ECOs will also participate in investigations of alleged violations of policies and work with the appropriate internal departments to investigate misconduct, remedy the situation, and prevent recurrence of any such activity.

4.2.12 Chief Information Officer (CIO)

The CIO is responsible for establishing, implementing and communicating TestAmerica's Information Technology (IT) Policies, SOPs and Manuals. Other responsibilities include coordinating new technologies, development of electronic communication tools such as TestAmerica's intranet and internet sites, ensuring data security and documentation of software, ensuring compliance with the NELAC standard, and assistance in establishing, updating, and maintaining Laboratory Information Management Systems (LIMS) at the various TestAmerica facilities.

4.2.13 Environmental Health and Safety Managers (Corporate)

The EHS Managers report directly to the VP-QA/EHS. The EHS Managers are responsible for the development and implementation of the TestAmerica Environmental, Health and Safety program. Responsibilities include:

- Consolidation and tracking all safety and health-related information and reports for the company, and managing compliance activities for TestAmerica locations.
- Coordination/preparation of the corporate Environmental, Health and Safety Manual Template that is used by each laboratory to prepare its own laboratory-specific Safety Manual/ CHP.
- Preparation of information and training materials for laboratory EHS Coordinators.
- Assistance in the internal and external coordination of employee exposure and medical monitoring programs to insure compliance with applicable safety and health regulations.
- Serving as Department of Transportation (D.O.T.) focal point and providing technical assistance to location management.
- Serving as Hazardous Waste Management main contact and providing technical assistance to location management.

4.2.14 Laboratory Director

TestAmerica Seattle's Laboratory Director is responsible for the overall quality, safety, financial, technical, human resource and service performance of the whole laboratory and reports to their respective GM. The Laboratory Director provides the resources necessary to implement and maintain an effective and comprehensive Quality Assurance and Data Integrity Program.

Specific responsibilities include, but are not limited to:

- Provides one or more technical managers for the appropriate fields of testing. If the Technical Manager is absent for a period of time exceeding 15 consecutive calendar days, the Laboratory Director must designate another full time staff member meeting the qualifications of the Technical Manager to temporarily perform this function. If the absence exceeds 65 consecutive calendar days, the primary accrediting authority must be notified in writing.
- Ensures that all analysts and supervisors have the appropriate education and training to properly carry out the duties assigned to them and ensures that this training has been documented.
- Ensures that personnel are free from any commercial, financial and other undue pressures that might adversely affect the quality of their work.
- Ensures TestAmerica's human resource policies are adhered to and maintained.
- Ensures that sufficient numbers of qualified personnel are employed to supervise and perform the work of the laboratory.
- Ensures that appropriate corrective actions are taken to address analyses identified as requiring such actions by internal and external performance or procedural audits. Procedures that do not meet the standards set forth in the QAM or laboratory SOPs may be temporarily suspended by the Laboratory Director.
- Reviews and approves the laboratory specific QAM, policies, SOPs prior to their implementation and ensures all approved procedures are implemented and adhered to.

- Pursues and maintains appropriate laboratory certification and contract approvals. Supports ISO 17025 requirements. Organizes bid activities for prospective new projects and clients.
- Ensures client specific reporting and quality control requirements are met.
- Captains the management team, consisting of the QA Manager, the Technical Manager(s), and the Operations Manager as direct reports.
- Annually assesses the effectiveness of the QMP and QAM within the laboratory.

4.2.15 Quality Assurance (QA) Manager or Designee

The QA Manager has responsibility and authority to ensure the continuous implementation of the quality system.

The QA Manager reports directly to the Laboratory Director and their Corporate Quality Director. This position is able to evaluate data objectively and perform assessments without outside (e.g., managerial) influence. Corporate QA may be used as a resource in dealing with regulatory requirements, certifications and other quality assurance related items. The QA Manager directs the activities of the QA officers to accomplish specific responsibilities, which include, but are not limited to:

- Compliance with ISO 17025.
- Compliance with DoD/DOE QSM.
- Serves as the focal point for QA/QC in the laboratory.
- Having functions independent from laboratory operations for which he/she has quality assurance oversight.
- Maintaining and updating the QAM.
- Monitoring and evaluating laboratory certifications; scheduling proficiency testing samples.
- Monitoring and communicating regulatory changes that may affect the laboratory to management.
- Training and advising the laboratory staff on quality assurance/quality control procedures that are pertinent to their daily activities.
- Have documented training and/or experience in QA/QC procedures and the laboratory's Quality System.
- Having a general knowledge of the analytical test methods for which data audit/review is performed (and/or having the means of getting this information when needed).
- Arranging for or conducting internal audits on quality systems and the technical operation.
- The laboratory QA Manager will maintain records of all ethics-related training, including the type and proof of attendance.
- Maintain, improve, and evaluate the corrective action database and the corrective and preventive action systems.
- Notifying laboratory management of deficiencies in the quality system and ensuring corrective action is taken. Procedures that do not meet the standards set forth in the QAM or laboratory SOPs shall be investigated following procedures outlined in Section 12.

- Objectively monitors standards of performance in quality control and quality assurance without outside (e.g., managerial) influence.
- Coordinating of document control of SOPs, MDLs, control limits, and miscellaneous forms and information.
- Review a percentage of all final data reports for internal consistency. Review of Chain of Custody (COC), correspondence with the analytical request, batch QC status, completeness of any corrective action statements, 5% of calculations, format, holding time, sensibility and completeness of the project file contents.
- Review of external audit reports and data validation requests.
- Follow-up with audits to ensure client QAPP requirements are met.
- Establishment of reporting schedule and preparation of various quality reports for the Laboratory Director, clients and/or Corporate QA.
- Development of suggestions and recommendations to improve quality systems.
- Research of current state and federal requirements and guidelines.
- Captains the QA team to enable communication and to distribute duties and responsibilities.
- Ensuring Communication & monitoring standards of performance to ensure that systems are in place to produce the level of quality as defined in this document.
- Evaluation of the thoroughness and effectiveness of training.
- Compliance with ISO 17025.
- Compliance with the DoD/DOE QSM.

4.2.16 Quality Assurance Assistant

The Quality Assurance Assistant performs several roles. The QA Assistant reports to the facility QA Manager. The QA Assistant is responsible for QA documentation and involvement in the following activities:

- Assisting the QA Manager in performing the annual internal laboratory audits, compiling the evaluation, and coordinating the development of an action plan to address any deficiency identified.
- Assisting the QA Manager in maintaining the laboratory's reference data to keep it current and accurate.
- Preparing certification applications for states as directed by QA Manager.
- Reviewing and maintaining personnel training records.
- Performing document control maintenance.
- Assisting departments in generating MDL spreadsheets and calculations, reviewing MDL studies submitted to QA.
- Assisting in control limit generation.
- Ensuring maintenance of records archives.
- Maintaining historical indices for all technical records including SOPs, QC records, laboratory data, etc.

- Assisting the QA Manager in meeting the responsibilities of the QA Department as described in laboratory policies and SOPs.
- Compliance with ISO 17025.
- Compliance with the DoD/DOE QSM.

4.2.17 Technical Managers or Designees

The Technical Managers report directly to the Laboratory Director. He/she is accountable for all analyses and analysts under their experienced supervision and for compliance with the ISO 17025 Standard. The scope of responsibility ranges from the new-hire process and existing technology through the ongoing training and development programs for existing analysts and new instrumentation. Specific responsibilities include, but are not limited to:

- Exercises day-to-day supervision of laboratory operations for the appropriate field of accreditation and reporting of results. Coordinating, writing, and reviewing preparation of all test methods, i.e., SOPs, with regard to quality, integrity, regulatory and optimum and efficient production techniques, and subsequent analyst training and interpretation of the SOPs for implementation and unusual project samples. He/she insures that the SOPs are properly managed and adhered to at the bench. He/she develops standard costing of SOPs to include supplies, labor, overhead, and capacity (design vs. demonstrated versus first-run yield) utilization.
- Reviewing and approving, with input from the QA Manager, proposals from marketing, in accordance with an established procedure for the review of requests and contracts. This procedure addresses the adequate definition of methods to be used for analysis and any limitations, the laboratory's capability and resources, the client's expectations. Differences are resolved before the contract is signed and work begins. A system documenting any significant changes is maintained, as well as pertinent discussions with the client regarding their requirements or the results of the analyses during the performance of the contract. All work subcontracted by the laboratory must be approved by the client. Any deviations from the contract must be disclosed to the client. Once the work has begun, any amendments to the contract must be discussed with the client and so documented.
- Monitoring the validity of the analyses performed and data generated in the laboratory. This activity begins with reviewing and supporting all new business contracts, insuring data quality, analyzing internal and external non-conformances to identify root cause issues and implementing the resulting corrective and preventive actions, facilitating the data review process (training, development, and accountability at the bench), and providing technical and troubleshooting expertise on routine and unusual or complex problems.
- Providing training and development programs to applicable laboratory staff as new hires and, subsequently, on a scheduled basis. Training includes instruction on calculations, instrumentation management to include troubleshooting and preventive maintenance.
- Enhancing efficiency and improving quality through technical advances and improved LIMS utilization. Capital forecasting and instrument life cycle planning for second generation methods and instruments as well as asset inventory management.
- Coordinating sample management from "cradle to grave," insuring that no time is lost in locating samples.

- Scheduling all QA/QC-related requirements for compliance, e.g., MDLs, etc..
- Captains department personnel to communicate quality, technical, personnel, and instrumental issues for a consistent team approach.
- Coordinates audit responses with the QA Manager.
- Compliance with ISO 17025.
- Compliance with the DoD/DOE QSM.

4.2.18 Hazardous Waste Coordinator

The Hazardous Waste Coordinator reports directly to the Laboratory Director. The duties consist of:

- Managing laboratory generated hazardous waste in accordance with appropriate regulations.
- Staying current with the hazardous waste regulations.
- Continuing training on hazardous waste issues.
- Reviewing and updating annually the Hazardous Waste Contingency Plan in the Environmental Health & Safety Manual.
- Auditing the staff with regard to compliance with the Hazardous Waste Contingency Plan.
- Contacting the hazardous waste subcontractors for review of procedures and opportunities

4.2.19 Laboratory Analysts

Laboratory analysts are responsible for conducting analysis and performing all tasks assigned to them by the department manager, group leader or supervisor. The responsibilities of the analysts are listed below:

- Perform analyses by adhering to analytical and quality control protocols prescribed by current SOPs, this QA Manual, and project-specific plans honestly, accurately, timely, safely, and in the most cost-effective manner.
- Document standard and sample preparation, instrument calibration and maintenance, data calculations, sample matrix effects, and any observed non-conformance on worklists, benchsheets, lab notebooks and/or the Non-Conformance Database.
- Report all non-conformance situations, instrument problems, matrix problems and QC failures, which might affect the reliability of the data, to their supervisor, the Technical Manager, and/or the QA Manager or member of QA staff.
- Ensures sample and data integrity by adhering to internal chain-of-custody procedures.
- Perform 100% review of the data generated prior to entering and submitting for secondary level review.
- Suggest method improvements to their supervisor, the Technical Manager, and the QA Manager. These improvements, if approved, will be incorporated. Ideas for the optimum performance of their assigned area, for example, through the proper cleaning and maintenance of the assigned instruments and equipment, are encouraged.
- Work cohesively as a team in their department to achieve the goals of accurate results, optimum turnaround time, cost effectiveness, cleanliness, complete documentation, and personal knowledge of environmental analysis.

- Work Cell: A "work cell" is considered to be all those individuals who see a sample through the complete process of preparation, extraction, and analysis. To ensure that the entire preparation, extraction, and analysis process is completed by a group of capable individuals, the laboratory shall ensure that each member of the work cell (including a new member entering an already existing work cell) demonstrates capability in his/her area of responsibility in the sequence. Even though the work cell operates as a "team," the demonstration of capability at each individual step in the sequence, as performed by each individual analyst/team member, remains of utmost importance. A work cell may NOT be defined as a group of analysts who perform the same step in the same process (for example, extractions for Method 8270), represented by one analyst who has demonstrated capability for that step.

4.2.20 Safety Officer

The Safety Officer reports to the Laboratory Director and ensures that systems are maintained for the safe operation of the laboratory. The Safety Officer is responsible to:

- Conduct ongoing, necessary safety training and conduct new employee safety orientation.
- Assist in developing and maintaining the Chemical Hygiene/Safety Manual.
- Administer dispersal of all Material Safety Data Sheet (MSDS) information.
- Perform regular chemical hygiene and housekeeping instruction.
- Give instruction on proper labeling and practice.
- Serve as chairman of the laboratory safety committee.
- Provide and train personnel on protective equipment.
- Oversee the inspection and maintenance of general safety equipment – fire extinguishers, safety showers, eyewash fountains, etc. and ensure prompt repairs as needed.
- Supervise and schedule fire drills and emergency evacuation drills.
- Determine what initial and subsequent exposure monitoring, if necessary to determine potential employee exposure to chemicals used in the laboratory.
- When determined necessary, conduct exposure monitoring assessments.
- Determine when a complaint of possible over-exposure is "reasonable" and should be referred for medical consultation.
- Assist in the internal and external coordination of the medical consultation/monitoring program conducted by TestAmerica's medical consultants.
- Manages facility maintenance.

4.2.21 Sample Receiving Staff

The Sample Receiving Technicians report to the Sample Receiving Supervisor; the Supervisor reports to the Operations Manager. The responsibilities are outlined below:

- Ensures implementation of proper sample receipt procedures, including maintenance of chain-of-custody.
- Reports nonconformances associated with condition-upon-receipt of samples.
- Logs incoming samples into the LIMS.

- Ensures that all samples are stored in the proper environment.
- Ensure the verification of data entry from login.
- Responsible for meeting quality requirements including documenting preservation.
- Responsible for ensuring the timely and correct shipment of sample containers, including proper preservatives and instructions, to clients
- Assists Environmental Health and Safety staff with sample disposal.

4.2.22 Manager of Project Management

The Project Manager Supervisor reports to the Client Services Director and serves as the interface between the laboratory's technical departments and the laboratory's clients. The staff consists of the Project Management team. With the overall goal of total client satisfaction, the functions of this position are outlined below:

- Technical training and growth of the Project Management team.
- Technical liaison for the Project Management team.
- Human resource management of the Project Management team.
- Has signature authority for laboratory reports.
- Assesses and assures customer satisfaction.
- Provides feedback to management on changing customer needs.
- Works with the Department Managers and/or Analysts/Technicians to ensure the requirements of projects are met in a timely manner.
- Organizes bid activities for prospective new projects and clients.

4.2.23 Project Managers

The Project Managers report to the Manager of Project Management and serve as the interface between the laboratory and the clients. With the overall goal of total client satisfaction, the functions of this position are outlined below:

- Responsible to ensure that clients receive the proper sampling supplies.
- Accountable for response to client inquiries concerning sample status.
- Responsible for assistance to clients regarding the resolution of problems concerning COC.
- Ensuring that client specifications, when known, are met by communicating project and quality assurance requirements to the laboratory. Prepares a Quality Assurance Summary (QAS) or equivalent summary form as needed.
- Notifying the supervisors of incoming projects and sample delivery schedules.
- Accountable to clients for communicating sample progress in daily status meeting with agreed-upon due dates.
- Approves customer requested variances to methods and to standard laboratory protocols.
- Responsible for discussing with client any project-related problems, resolving service issues, and coordinating technical details with the laboratory staff.

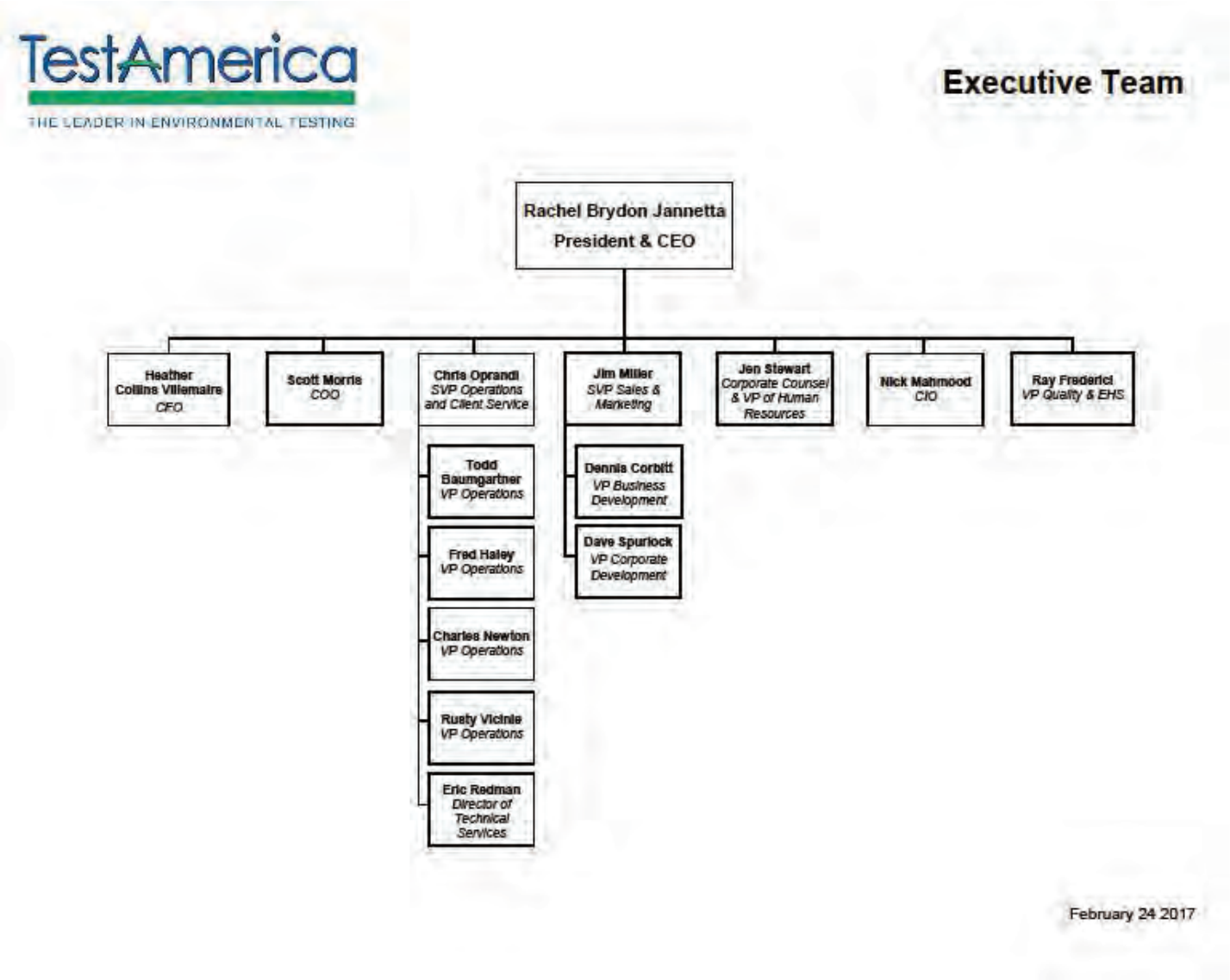
- Reports client inquiries involving data quality issues or data acceptability to the facility, CSM, Laboratory Director, QA Manager, and to the appropriate staff.
- Responsible for staff familiarization with specific quotes, sample log-in review, and final report completeness.
- Monitor the status of all data package projects in-house to ensure timely and accurate delivery of reports. Reviews project data packages for completeness and compliance to client needs and have signature authority for final reports.
- Inform clients of data package-related problems and resolve service issues.
- Coordinate requests for sample containers and other services (data packages).
- Prepares re-issue requests for project data.
- Organizes bid activities for prospective new projects and clients.
- Has signature authority for laboratory reports.

4.3 Deputies

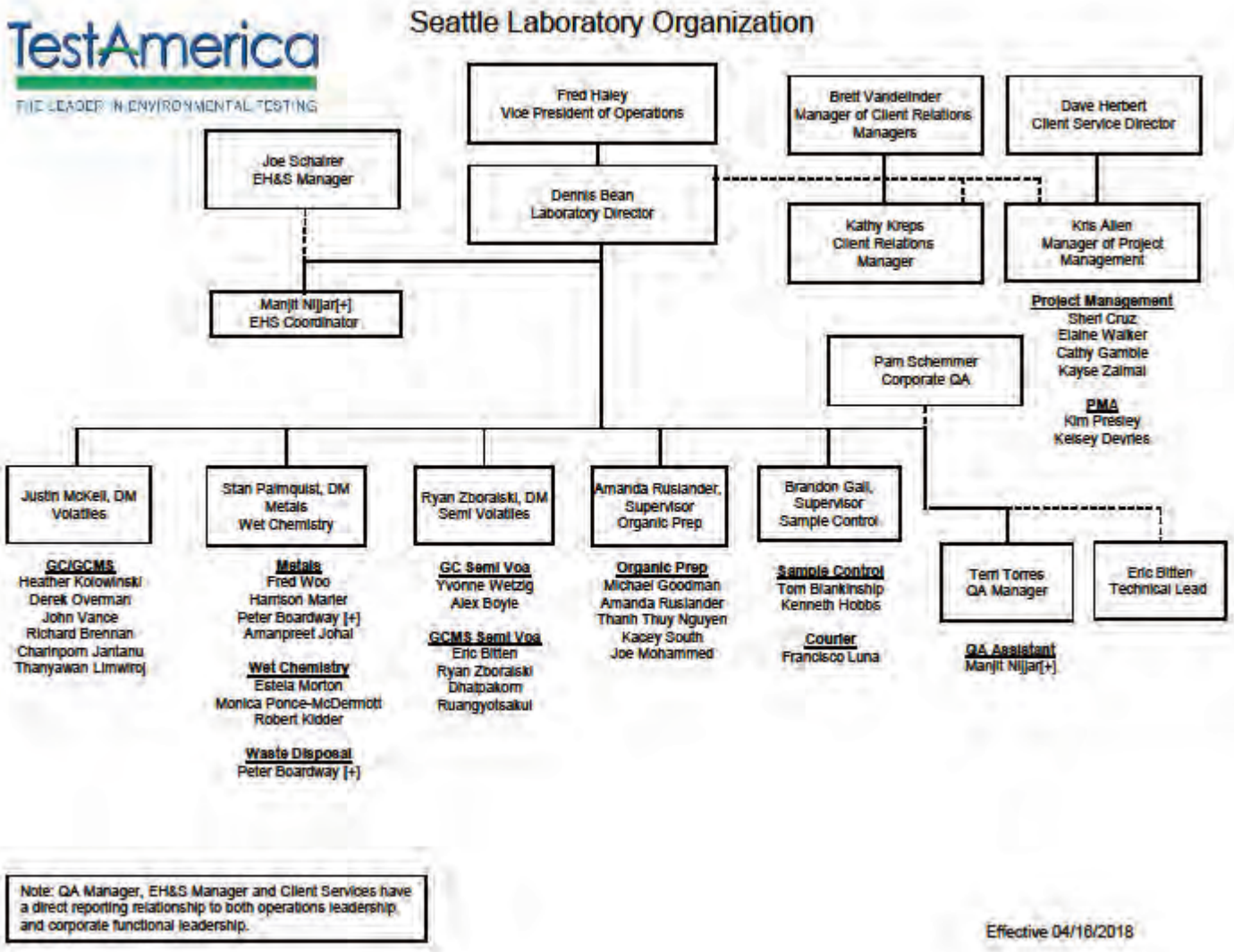
The following table defines who assumes the responsibilities of key personnel in their absence:

Key Personnel	Deputy
Laboratory Director	QA Manager
QA Manager	Laboratory Director
Inorganic Technical Manager	Laboratory Director
Semivolatile Technical Manager	Laboratory Director
Volatile Technical Manager	Laboratory Director
EHS Coordinator	Laboratory Director
Project Manager Supervisor	Laboratory Director

Figure 4-1. Corporate and Laboratory Organization Charts



TestAmerica Seattle
Organization Chart



SECTION 5. QUALITY SYSTEM

5.1 Quality Policy Statement

It is TestAmerica's Policy to:

- Provide data of known quality to its clients by adhering to approved methodologies, regulatory requirements and the QA/QC protocols.
- Effectively manage all aspects of the laboratory and business operations by the highest ethical standards.
- Continually improve systems and provide support to quality improvement efforts in laboratory, administrative and managerial activities. TestAmerica recognizes that the implementation of a quality assurance program requires management's commitment and support as well as the involvement of the entire staff.
- Provide clients with the highest level of professionalism and the best service practices in the industry.
- To comply with the ISO/IEC 17025:2005(E) International Standard, the 2009 TNI Standard and to continually improve the effectiveness of the management system.

Every staff member at the laboratory plays an integral part in quality assurance and is held responsible and accountable for the quality of their work. It is, therefore, required that all laboratory personnel are trained and agree to comply with applicable procedures and requirements established by this document.

5.2 Ethics and Data Integrity

TestAmerica is committed to ensuring the integrity of its data and meeting the quality needs of its clients. The elements of TestAmerica's Ethics and Data Integrity Program include:

- An Ethics Policy (Corporate Policy No. CW-L-P-004) and Employee Ethics Statements.
- Ethics and Compliance Officers (ECOs).
- A Training Program.
- Self-governance through disciplinary action for violations.
- A Confidential mechanism for anonymously reporting alleged misconduct and a means for conducting internal investigations of all alleged misconduct. (Corporate SOP No. CW-L-S-002)
- Procedures and guidance for recalling data if necessary (Corporate SOP No. CW-Q-S-005).
- Effective external and internal monitoring system that includes procedures for internal audits (Section 15).
- Produce results, which are accurate and include QA/QC information that meets client pre-defined Data Quality Objectives (DQOs).
- Present services in a confidential, honest and forthright manner.

- Provide employees with guidelines and an understanding of the Ethical and Quality Standards of our Industry.
- Operate our facilities in a manner that protects the environment and the health and safety of employees and the public.
- Obey all pertinent federal, state and local laws and regulations and encourage other members of our industry to do the same.
- Educate clients as to the extent and kinds of services available.
- Assert competency only for work for which adequate personnel and equipment are available and for which adequate preparation has been made.
- Promote the status of environmental laboratories, their employees, and the value of services rendered by them.

5.3 Quality System Documentation

The laboratory's Quality System is communicated through a variety of documents.

- Quality Assurance Manual – Each laboratory has a lab-specific quality assurance manual.
- Corporate SOPs and Policies – Corporate SOPs and Policies are developed for use by all relevant laboratories. They are incorporated into the laboratory's normal SOP distribution, training and tracking system. Corporate SOPs may be general or technical.
- Work Instructions – A subset of procedural steps, tasks or forms associated with an operation of a management system (e.g., checklists, preformatted bench sheets, forms).
- Laboratory SOPs – General and Technical
- Laboratory QA/QC Policy Memorandums

5.3.1 Order of Precedence

In the event of a conflict or discrepancy between policies, the order of precedence is as follows:

- Corporate Quality Management Plan (CQMP)
- Corporate SOPs and Policies
- Laboratory QA/QC Policy Memorandum
- Laboratory Quality Assurance Manual (QAM)
- Laboratory SOPs and Policies
- Other (Work Instructions (WI), memos, flow charts, etc.)

Note: The laboratory has the responsibility and authority to operate in compliance with regulatory requirements of the jurisdiction in which the work is performed. Where the CQMP conflicts with those regulatory requirements, the regulatory requirements of the jurisdiction shall hold primacy. The laboratory's QAM shall take precedence over the CQMP in those cases.

5.4 QA/QC Objectives for the Measurement of Data

Quality Assurance (QA) and Quality Control (QC) are activities undertaken to achieve the goal of producing data that accurately characterize the sites or materials that have been sampled. Quality Assurance is generally understood to be more comprehensive than Quality Control. Quality Assurance can be defined as the integrated system of activities that ensures that a product or service meets defined standards.

Quality Control is generally understood to be limited to the analyses of samples and to be synonymous with the term "analytical quality control". QC refers to the routine application of statistically based procedures to evaluate and control the accuracy of results from analytical measurements. The QC program includes procedures for estimating and controlling precision and bias and for determining reporting limits.

Request for Proposals (RFPs) and Quality Assurance Project Plans (QAPP) provide a mechanism for the client and the laboratory to discuss the data quality objectives in order to ensure that analytical services closely correspond to client needs. The client is responsible for developing the QAPP. In order to ensure the ability of the laboratory to meet the Data Quality Objectives (DQOs) specified in the QAPP, clients are advised to allow time for the laboratory to review the QAPP before being finalized. Additionally, the laboratory will provide support to the client for developing the sections of the QAPP that concern laboratory activities.

Historically, laboratories have described their QC objectives in terms of precision, accuracy, representativeness, comparability, completeness, selectivity and sensitivity (PARCCSS).

5.4.1 Precision

The laboratory objective for precision is to meet the performance for precision demonstrated for the methods on similar samples and to meet data quality objectives of the EPA and/or other regulatory programs. Precision is defined as the degree of reproducibility of measurements under a given set of analytical conditions (exclusive of field sampling variability). Precision is documented on the basis of replicate analysis, usually duplicate or matrix spike (MS) duplicate samples.

5.4.2 Accuracy

The laboratory objective for accuracy is to meet the performance for accuracy demonstrated for the methods on similar samples and to meet data quality objectives of the EPA and/or other regulatory programs. Accuracy is defined as the degree of bias in a measurement system. Accuracy may be documented through the use of laboratory control samples (LCS) and/or MS. A statement of accuracy is expressed as an interval of acceptance recovery about the mean recovery.

5.4.3 Representativeness

The laboratory objective for representativeness is to provide data which is representative of the sampled medium. Representativeness is defined as the degree to which data represent a characteristic of a population or set of samples and is a measurement of both analytical and field sampling precision. The representativeness of the analytical data is a function of the procedures used in procuring and processing the samples. The representativeness can be documented by the

relative percent difference between separately procured, but otherwise identical samples or sample aliquots.

The representativeness of the data from the sampling sites depends on both the sampling procedures and the analytical procedures. The laboratory may provide guidance to the client regarding proper sampling and handling methods in order to assure the integrity of the samples.

5.4.4 Comparability

The comparability objective is to provide analytical data for which the accuracy, precision, representativeness and reporting limit statistics are similar to these quality indicators generated by other laboratories for similar samples, and data generated by the laboratory over time.

The comparability objective is documented by inter-laboratory studies carried out by regulatory agencies or carried out for specific projects or contracts, by comparison of periodically generated statements of accuracy, precision and reporting limits with those of other laboratories.

5.4.5 Completeness

The completeness objective for data is 90% (or as specified by a particular project), expressed as the ratio of the valid data to the total data over the course of the project. Data will be considered valid if they are adequate for their intended use. Data usability will be defined in a QAPP, project scope or regulatory requirement. Data validation is the process for reviewing data to determine its usability and completeness. If the completeness objective is not met, actions will be taken internally and with the data user to improve performance. This may take the form of an audit to evaluate the methodology and procedures as possible sources for the difficulty or may result in a recommendation to use a different method.

5.4.6 Selectivity

Selectivity is defined as: The capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. Target analytes are separated from non-target constituents and subsequently identified/detected through one or more of the following, depending on the analytical method: extractions (separation), digestions (separation), interelement corrections (separation), use of matrix modifiers (separation), specific retention times (separation and identification), confirmations with different columns or detectors (separation and identification), specific wavelengths (identification), specific mass spectra (identification), specific electrodes (separation and identification), etc..

5.4.7 Sensitivity

Sensitivity refers to the amount of analyte necessary to produce a detector response that can be reliably detected (Method Detection Limit) or quantified (Reporting Limit).

5.5 Criteria for Quality Indicators

The laboratory maintains quality control limits in the Laboratory Information Management System that summarize the precision and accuracy acceptability limits for performed analyses. This summary includes an effective date, is updated each time new limits are generated and are managed by the laboratory's QA department. Unless otherwise noted, limits within these tables are laboratory generated. Some acceptability limits are derived from US EPA methods when they are required. Where US EPA method limits are not required, the laboratory has developed limits from evaluation of data from similar matrices. Criteria for development of control limits is contained in SOP TA-QA-0600 Control Charting and Establishing Method Warning and Action Limits.

5.6 Statistical Quality Control

Statistically-derived precision and accuracy limits are required by selected methods (such as SW-846) and programs, such as the Ohio Voluntary Action Plan (VAP). The laboratory routinely utilizes statistically-derived limits to evaluate method performance and determine when corrective action is appropriate. The analysts are instructed to use the current limits in the laboratory (dated and approved by the Technical Manager and QA Manager) and entered into the Laboratory Information Management System (LIMS). The Quality Assurance department maintains an archive of all limits used within the laboratory via the LIMS. If a method defines the QC limits, the method limits are used.

If a method requires the generation of historical limits, the lab develops such limits from recent data in the QC database of the LIMS following the guidelines described in Section 24. All calculations and limits are documented and dated when approved and effective. On occasion, a client requests contract-specified limits for a specific project.

Current QC limits are entered and maintained in the LIMS analyte database. As sample results and the related QC are entered into LIMS, the sample QC values are compared with the limits in LIMS to determine if they are within the acceptable range. The analyst then evaluates if the sample needs to be rerun or re-extracted/rerun or if a comment should be added to the report explaining the reason for the QC outlier.

5.6.1 QC Charts

As the QC limits are calculated, QC charts are generated showing warning and control limits for the purpose of evaluating trends. The QA Manager evaluates these to determine if adjustments need to be made or for corrective actions to methods. All findings are documented and kept on file. (Refer to SOP TA-QA-0600 Control Charting and Establishing Method Warning and Action Limits.)

5.7 Quality System Metrics

In addition to the QC parameters discussed above, the entire Quality System is evaluated on a monthly basis through the use of specific metrics (refer to Section 16). These metrics are used to drive continuous improvement in the laboratory's Quality System.

SECTION 6. DOCUMENT CONTROL

6.1 Overview

The QA Department is responsible for the control of documents used in the laboratory to ensure that approved, up-to-date documents are in circulation and out-of-date (obsolete) documents are archived or destroyed. The following documents, at a minimum, must be controlled:

- Laboratory Quality Assurance Manual
- Laboratory Standard Operating Procedures (SOP)
- Laboratory Policies
- Work Instructions and Forms
- Corporate Policies and Procedures distributed outside the intranet

Corporate Quality posts Corporate Manuals, SOPs, Policies, Work Instructions, White Papers and Training Materials on the company intranet site. These Corporate documents are only considered controlled when they are read on the intranet site. Printed copies are considered uncontrolled unless the laboratory physically distributes them as controlled documents. A detailed description of the procedure for issuing, authorizing, controlling, distributing, and archiving Corporate documents is found in Corporate SOP No. CW-Q-S-001, Corporate Document Control and Archiving. The laboratory's internal document control procedures are defined in SOPs TA-QA-0528, (Document Control) and TA-QA-0506 (Document Archiving).

The laboratory QA Department also maintains access to various references and document sources integral to the operation of the laboratory. This includes reference methods and regulations. Instrument manuals (hard or electronic copies) are also maintained by the laboratory.

The laboratory maintains control of records for raw analytical data and supporting records such as audit reports and responses, logbooks, standard logs, training files, MDL studies, Proficiency Testing (PT) studies, certifications and related correspondence, and nonconformance memos/corrective action reports. Raw analytical data consists of bound logbooks, instrument printouts, any other notes, magnetic media, electronic data and final reports.

6.2 Document Approval and Issue

The pertinent elements of a document control system for each document include a unique document title and number, pagination, the total number of pages of the item or an 'end of document' page, the effective date, revision number and the laboratory's name. The QA personnel are responsible for the maintenance of this system.

Controlled documents are authorized by the QA Department. In order to develop a new document, a technical manager submits an electronic draft to the QA Department for suggestions and approval before use. Upon approval, QA personnel add the identifying version information to the document and retains that document as the official document on file. That document is then provided to all applicable operational units (may include electronic access). Controlled documents are identified as such and records of their distribution are kept by the QA Department. Document control may be achieved by either electronic or hardcopy distribution.

The QA Department maintains a list of the official versions of controlled documents.

Quality System Policies and Procedures will be reviewed at a minimum of annually and revised as appropriate. Changes to documents occur when a procedural change warrants.

6.3 Procedures for Document Control Policy

For changes to the QA Manual, refer to SOP No. TA-QA-0528 (Document Control). Uncontrolled copies must not be used within the laboratory. Previous revisions and back-up data are stored by the QA department. Electronic copies are stored on the Public server in the QAM folder for the applicable revision.

For changes to SOPs, refer to SOP No. TA-QA-0500, Writing a Standard Operating Procedure SOP or list your labs SOP on this topic. The SOP identified above also defines the process of changes to SOPs.

Forms, worksheets, work instructions and information are organized by department in the QA office. There is a table of contents. Electronic versions are kept on a hard drive in the QA department; hard copies are kept in QA files. The procedure for the care of these documents is in SOP TA-QA-0528 (Document Control).

6.4 Obsolete Documents

All invalid or obsolete documents are removed, or otherwise prevented from unintended use. The laboratory has specific procedures as described above to accomplish this. In general, obsolete documents are collected from employees according to distribution lists and are marked obsolete on the cover or destroyed. At least one copy of the obsolete document is archived according to SOP No. TA-QA-0528 (Document Control).

SECTION 7. SERVICE TO THE CLIENT

7.1 Overview

The laboratory has established procedures for the review of work requests and contracts, oral or written. The procedures include evaluation of the laboratory's capability and resources to meet the contract's requirements within the requested time period. All requirements, including the methods to be used, must be adequately defined, documented and understood. For many environmental sampling and analysis programs, testing design is site or program specific and does not necessarily "fit" into a standard laboratory service or product. It is the laboratory's intent to provide both standard and customized environmental laboratory services to our clients.

A thorough review of technical and QC requirements contained in contracts is performed to ensure project success. The appropriateness of requested methods, and the lab's capability to perform them must be established. Projects, proposals and contracts are reviewed for adequately defined requirements and the laboratory's capability to meet those requirements. Alternate test methods that are capable of meeting the clients' requirements may be proposed by the lab. A review of the lab's capability to analyze non-routine analytes is also part of this review process.

All projects, proposals and contracts are reviewed for the client's requirements in terms of compound lists, test methodology requested, sensitivity (detection and reporting levels), accuracy, and precision requirements (% Recovery and RPD). The reviewer ensures that the laboratory's test methods are suitable to achieve these requirements and that the laboratory holds the appropriate certifications and approvals to perform the work. The laboratory and any potential subcontract laboratories must be certified, as required, for all proposed tests.

The laboratory must determine if it has the necessary physical, personnel and information resources to meet the contract, and if the personnel have the expertise needed to perform the testing requested. Each proposal is checked for its impact on the capacity of the laboratory's equipment and personnel. As part of the review, the proposed turnaround time will be checked for feasibility.

Electronic or hard copy deliverable requirements are evaluated against the laboratory's capacity for production of the documentation.

If the laboratory cannot provide all services but intends to subcontract such services, whether to another TestAmerica facility or to an outside firm, this will be documented and discussed with the client prior to contract approval. (Refer to Section 8 for Subcontracting Procedures.)

The laboratory informs the client of the results of the review if it indicates any potential conflict, deficiency, lack of accreditation, or inability of the lab to complete the work satisfactorily. Any discrepancy between the client's requirements and the laboratory's capability to meet those requirements is resolved in writing before acceptance of the contract. It is necessary that the contract be acceptable to both the laboratory and the client. Amendments initiated by the client and/or TestAmerica, are documented in writing.

All contracts, QAPPs, Sampling and Analysis Plans (SAPs), contract amendments, and documented communications become part of the project record.

The same contract review process used for the initial review is repeated when there are amendments to the original contract by the client, and the participating personnel are informed of the changes.

7.2 Review Sequence and Key Personnel

Appropriate personnel will review the work request at each stage of evaluation.

For routine projects and other simple tasks, a review by the Project Manager (PM) is considered adequate. The PM confirms that the laboratory has any required certifications, that it can meet the clients' data quality and reporting requirements and that the lab has the capacity to meet the clients turn around needs. It is recommended that, where there is a sales person assigned to the account, an attempt should be made to contact that sales person to inform them of the incoming samples.

For new, complex or large projects, the proposed contract is given to the Client Relationship Manager or Proposal Team, who will decide which lab will receive the work based on the scope of work and other requirements, including certification, testing methodology, and available capacity to perform the work. The contract review process is outlined in TestAmerica's Corporate SOP No. CA-L-P-002**,** Contract Compliance Policy.

This review encompasses all facets of the operation. The scope of work is distributed to the appropriate personnel, as needed based on scope of contract, to evaluate all of the requirements shown above (not necessarily in the order below):

- Contract Administrator
- VP of Operations
- Laboratory Project Manager
- Laboratory Directors and/or Corporate Technical Managers
- Laboratory Directors and/or Corporate Information Technology Managers
- Account Executives
- Laboratory and/or Corporate Quality
- Laboratory and/or Corporate Environmental Health and Safety Managers/Directors
- The Laboratory Director reviews the formal laboratory quote and makes final acceptance for their facility.

The Sales Director, Contract Administrator, Account Executive or Proposal Coordinator then submits the final proposal to the client.

In the event that one of the above personnel is not available to review the contract, his or her back-up will fulfill the review requirements.

The Contracts Department maintains copies of all signed contracts**.** The Laboratory Director also maintains copies of all signed contracts on site.

7.3 Documentation

Appropriate records are maintained for every contract or work request. All stages of the contract review process are documented and include records of any significant changes. The reviewed contracts or QAPPs, along with records identifying issues or changes (at a minimum the Additional Project Notes from the quote) will be scanned and stored on the Public server.

The contract will be distributed to and maintained by the appropriate sales/marketing personnel and the Account Executive. A copy of the contract and formal quote will be filed with the laboratory PM and the Laboratory Director.

Records are maintained of pertinent discussions with a client relating to the client's requirements or the results of the work during the period of execution of the contract. The PM keeps a phone log of conversations with the client and all actions agreed upon between the PM and the client and are officially documented with a follow-up email.

7.3.1 Project-Specific Quality Planning

Communication of contract specific technical and QC criteria is an essential activity in ensuring the success of site specific testing programs. To achieve this goal, a PM is assigned to each client. It is the PM's responsibility to ensure that project-specific technical and QC requirements are effectively evaluated and communicated to the laboratory personnel before and during the project. QA department involvement may be needed to assist in the evaluation of custom QC requirements.

PM's are the primary client contact and they ensure resources are available to meet project requirements. Although PM's do not have direct reports or staff in production, they coordinate opportunities and work with laboratory management and supervisory staff to ensure available resources are sufficient to perform work for the client's project. Project management is positioned between the client and laboratory resources.

Prior to work on a new project, the dissemination of project information and/or project opening meetings may occur to discuss schedules and unique aspects of the project. Items to be discussed may include the project technical profile, turnaround times, holding times, methods, analyte lists, reporting limits, deliverables, sample hazards, or other special requirements. The PM introduces new projects to the laboratory staff through project kick-off meetings or to the supervisory staff during production meetings. These meetings provide direction to the laboratory staff in order to maximize production and client satisfaction, while maintaining quality. In addition, project notes may be associated with each sample batch as a reminder upon sample receipt and analytical processing.

During the project, any change that may occur within an active project is agreed upon between the client/regulatory agency and the PM/laboratory. These changes (e.g., use of a non-standard method or modification of a method) and approvals must be documented prior to implementation. Documentation pertains to any document, e.g., letter, e-mail, variance, contract addendum, which has been signed by both parties.

Such changes are communicated to the laboratory during production or status meetings. These changes are also updated in the project notes and are introduced to the managers at these meetings. The laboratory staff is then introduced to the modified requirements via the PM or the individual laboratory Technical Manager. After the modification is implemented into the laboratory process, documentation of the modification is made in the case narrative of the data report(s).

The laboratory strongly encourages client visits to the laboratory and for formal/informal information sharing session with employees in order to effectively communicate ongoing client needs as well as project specific details for customized testing programs.

7.4 Special Services

The laboratory cooperates with clients and their representatives to monitor the laboratory's performance in relation to work performed for the client. It is the laboratory's goal to meet all client requirements in addition to statutory and regulatory requirements. The laboratory has procedures to ensure confidentiality to clients (Section 15 and 25).

Note: ISO/IEC 17025 states that a laboratory "shall afford clients or their representatives cooperation to clarify the client's request". This topic is discussed in Section 7.

The laboratory's standard procedures for reporting data are described in Section 25. Special services are also available and provided upon request. These services include:

- Reasonable access for our clients or their representatives to the relevant areas of the laboratory for the witnessing of tests performed for the client.
- Assist client-specified third party data validators as specified in the client's contract.

- Supplemental information pertaining to the analysis of their samples. Note: An additional charge may apply for additional data/information that was not requested prior to the time of sample analysis or previously agreed upon.

7.5 Client Communication

Project managers are the primary communication link to the clients. They shall inform their clients of any delays in project completion as well as any non-conformances in either sample receipt or sample analysis. Project management will maintain ongoing client communication throughout the entire client project.

Technical Managers are available to discuss any technical questions or concerns that the client may have.

7.6 Reporting

The laboratory works with our clients to produce any special communication reports required by the contract.

7.7 Client Surveys

The laboratory assesses both positive and negative client feedback. The results are used to improve overall laboratory quality and client service. TestAmerica's Sales and Marketing teams periodically develop lab- and client-specific surveys to assess client satisfaction.

SECTION 8. SUBCONTRACTING OF TESTS

8.1 Overview

For the purpose of this quality manual, the phrase subcontract laboratory refers to a laboratory external to the TestAmerica laboratories. The phrase "work sharing" refers to internal transfers of samples between the TestAmerica laboratories. The term outsourcing refers to the act of subcontracting tests.

When contracting with our clients, the laboratory makes commitments regarding the services to be performed and the data quality for the results to be generated. When the need arises to outsource testing for our clients because project scope, changes in laboratory capabilities, capacity or unforeseen circumstances, we must be assured that the subcontractors or work sharing laboratories understand the requirements and will meet the same commitments we have made to the client. Refer to TestAmerica's Corporate SOP's on Subcontracting Procedures (CW-L-S-004) and the Work Sharing Process (CA-C-S-001).

When outsourcing analytical services, the laboratory will assure, to the extent necessary, that the subcontract or work sharing laboratory maintains a program consistent with the requirements of this document, the requirements specified in TNI/ISO 17025 and/or the client's Quality Assurance Project Plan (QAPP). All QC guidelines specific to the client's analytical program are transmitted to the subcontractor and agreed upon before sending the samples to the subcontract facility. Additionally, work requiring accreditation will be placed with an appropriately accredited laboratory.

The laboratory performing the subcontracted work will be identified in the final report, as will non-TNI accredited work where required.

Project Managers (PMs), Managers of Project Managers, Client Relationship Managers or Account Executives (AE) for the Export Lab are responsible for obtaining client approval prior to outsourcing any samples. The laboratory will advise the client of a subcontract or work sharing arrangement in writing and when possible approval from the client shall be retained in the project folder. Standard TestAmerica Terms & Conditions include the flexibility to subcontract samples within the TestAmerica laboratories. Therefore, additional advance notification to clients for intra-laboratory subcontracting is not necessary unless specifically required by a client contract.

Note: In addition to the client, some regulating agencies (e.g., USDA) or contracts (e.g., DoD/DOE projects) may require notification prior to placing such work.

8.2 Qualifying and Monitoring Subcontractors

Whenever a PM, Account Executive (AE) or Client Relationship Manager becomes aware of a client requirement or laboratory need where samples must be outsourced to another laboratory, the other laboratory(s) shall be selected based on the following:

- Subcontractors specified by the client - In these circumstances, the client assumes responsibility for the quality of the data generated from the use of a subcontractor.
- Subcontractors reviewed by TestAmerica – Firms which have been reviewed by the company and are known to meet standards for accreditations (e.g., State, TNI and DoD/DOE); technical specifications; legal and financial information.

A listing of vendors is available on the TestAmerica intranet site.

All TestAmerica laboratories are pre-qualified for work sharing provided they hold the appropriate accreditations, can adhere to the project/program requirements, and the client approved sending samples to that laboratory. The client must provide acknowledgement that the samples can be sent to that facility (an e-mail is sufficient documentation or if acknowledgement is verbal, the date, time, and name of person providing acknowledgement must be documented). The originating laboratory is responsible for communicating all technical, quality, and deliverable requirements as well as other contract needs. (Corporate SOP No. CA-C-S-001, Work Sharing Process).

8.2.1 When the potential sub-contract laboratory has not been previously approved, PM, Account Executive (AE) or Client Relationship Manager may nominate a laboratory as a subcontractor based on need. The decision to nominate a laboratory must be approved by the Client Relations Manager (CRM) or Laboratory Director. The CRM or Laboratory Director requests that the QA Manager or PM begin the process of approving the subcontract laboratory as outlined in Corporate SOP No. CW-L-S-004, Subcontracting Procedures.

Once the appropriate accreditation and legal information is received by the laboratory, it is evaluated for acceptability (where applicable) and forwarded to the Corporate Quality Information Manager (QIM) for review. After the Corporate QIM reviews the documents for completeness, the information is forwarded to the Finance Department for formal signature and contracting with the laboratory. The approved vendor will be added to the approved subcontractor list on the intranet site and the finance group is concurrently notified for JD Edwards.

The client will assume responsibility for the quality of the data generated from the use of a subcontractor they have requested the lab to use. The qualified subcontractors on the intranet site are known to meet minimal standards. TestAmerica does not certify laboratories. The subcontractors on our approved list can only be recommended to the extent that we would use them.

8.3 Oversight and Reporting

8.3.1 The status and performance of qualified subcontractors will be monitored by the Corporate Quality department. Any problems identified will be brought to the attention of TestAmerica's Corporate Finance, Legal and Corporate Quality personnel.

- Complaints shall be investigated. Documentation of the complaint, investigation and corrective action will be maintained in the subcontractor's file on the intranet site. Complaints are posted using the Vendor Performance Report.
- Information shall be updated on the intranet when new information is received from the subcontracted laboratories.
- Subcontractors in good standing will be retained on the intranet listing. CSO personnel will notify all TestAmerica laboratories, Corporate Quality and Corporate Contracts if any laboratory requires removal from the intranet site. This notification will be posted on the intranet site and e-mailed to all CSO Personnel, Laboratory Directors, QA Managers and Sales Personnel.

Prior to initially sending samples to the subcontracted laboratory, the PM confirms their certification status to determine if it's current and scope-inclusive. The information is documented within the project records.

8.3.2 For continued use of a subcontractor, verification of certification is placed upon the subcontractor for the defined project. Samples are subcontracted under Chain of Custody with the program defined as 'Accreditation Required' and the following statement for verification upon sample receipt:

Note: Since laboratory accreditations are subject to change, TestAmerica Laboratories, Inc. places the ownership of method, analyte & accreditation compliance upon our subcontract laboratories. This sample shipment is forwarded under Chain of Custody. If the laboratory does not currently maintain accreditation in the State of Origin listed above for analytes/tests/matrix being analyzed, the samples must be shipped back to the TestAmerica laboratory or other instructions will be provided. Any changes to accreditation status should be brought to TestAmerica Laboratories, Inc. attention immediately. If all requested accreditations are current to date, return the signed Chain of Custody attesting to said compliance to TestAmerica Laboratories, Inc.

For TestAmerica laboratories, certifications can be viewed on the company's TotalAccess Database.

8.3.3 All subcontracted samples must be accompanied by a TestAmerica Chain of Custody (COC). A copy of the original COC sent by the client must be available in TALS for all samples workshared within TestAmerica. Client COCs are only forwarded to external subcontractors when samples are shipped directly from the project site to the subcontractor lab. Under routine circumstances, client COCs are not provided to external subcontractors.

Through communication with the subcontracted laboratory, the PM monitors the status of the subcontracted analyses, facilitates successful execution of the work, and ensures the timeliness and completeness of the analytical report.

Non-TNI accredited work must be identified in the subcontractor's report as appropriate. If TNI accreditation is not required, the report does not need to include this information.

Reports submitted from subcontractor laboratories are not altered and are included in their original form in the final project report. This clearly identifies the data as being produced by a subcontractor facility. If subcontract laboratory data is incorporated into the laboratories EDD (i.e., imported), the report must explicitly indicate which lab produced the data for which methods and samples.

Note: The results submitted by a TestAmerica work sharing laboratory may be transferred electronically and the results reported by the TestAmerica work sharing lab are identified on the final report. The report must explicitly indicate which lab produced the data for which methods and samples. The final report must include a copy of the completed COC for all work sharing reports.

8.4 Contingency Planning

The full qualification of a subcontractor may be waived to meet emergency needs; however, this decision & justification must be documented in the project files, and the 'Purchase Order Terms And Conditions For Subcontracted Laboratory Services' must be sent with the samples and COC.

In the event this provision is utilized, the laboratory (e.g., PM) will be required to verify and document the applicable accreditations of the subcontractor. All other quality and accreditation requirements will still be applicable, but the subcontractor need not have signed a subcontract with TestAmerica at this time

The use of any emergency subcontractor will require the PM to complete a JDE New Vendor Add Form in order to process payment to the vendor and add them to TALS. This form requires the user to define the subcontractor's category/s of testing and the reason for testing.

SECTION 9. PURCHASING SERVICES AND SUPPLIES

9.1 Overview

Evaluation and selection of suppliers and vendors is performed, in part, on the basis of the quality of their products, their ability to meet the demand for their products on a continuous and short term basis, the overall quality of their services, their past history, and competitive pricing. This is achieved through evaluation of objective evidence of quality furnished by the supplier, which can include certificates of analysis, recommendations, and proof of historical compliance with similar programs for other clients. To ensure that quality critical consumables and equipment conform to specified requirements, which may affect quality, all purchases from specific vendors are approved by a member of the supervisory or management staff. Capital expenditures are made in accordance with TestAmerica's Capital Expenditure, Controlled Purchase Requests and Fixed Asset Capitalization, SOP No. CW-F-S-007.

Contracts will be signed in accordance with TestAmerica's Company-Wide Authorization Matrix Policy, Policy No. CW-F-P-002. Request for Proposals (RFP's) will be issued where more

information is required from the potential vendors than just price. Process details are available in TestAmerica's Corporate Procurement and Contracts Policy (Policy No. CW-F-P-004). RFP's allow TestAmerica to determine if a vendor is capable of meeting requirements such as supplying all of the TestAmerica facilities, meeting required quality standards and adhering to necessary ethical and environmental standards. The RFP process also allows potential vendors to outline any additional capabilities they may offer

9.2 Glassware

Glassware used for volumetric measurements must be Class A or verified for accuracy according to laboratory procedure. Pyrex (or equivalent) glass should be used where possible. For safety purposes, thick-wall glassware should be used where available.

9.3 Reagents, Standards & Supplies

Purchasing guidelines for equipment, consumables, and reagents must meet the requirements of the specific method and testing procedures for which they are being purchased. Solvents and acids are pre-tested in accordance with TestAmerica's Corporate SOP on Solvent & Acid Lot Testing & Approval, SOP No. CA-Q-S-001. Approval information for the solvents and acids tested under SOP CA-Q-S-001 is stored on the TestAmerica Sharepoint, under Solvent Approvals. A master list of all tested materials, as well as the certificates of analysis for the materials, is stored in the same location.

9.3.1 Purchasing

Chemical reagents, solvents, glassware, and general supplies are ordered as needed to maintain sufficient quantities on hand. Materials used in the analytical process must be of a known quality. The wide variety of materials and reagents available makes it advisable to specify recommendations for the name, brand, and grade of materials to be used in any determination. This information is contained in the method SOP. The analyst completes the Material Request Sheet when requesting reagents, standards, or supplies that are not stocked in on-site consignment system that contains items approved for laboratory use.

The analyst must provide the master item number (from the master item list that has been approved by the Technical Manager), item description, package size, catalogue page number, and the quantity needed. If an item being ordered is not the exact item requested, approval must be obtained from the Technical Manager prior to placing the order. The authorized requisitioning agent places the order.

9.3.2 Receiving

It is the responsibility of the receiving clerk to receive the shipment. It is the responsibility of the analyst who ordered the materials to document the date materials where received. Once the ordered reagents or materials are received, the analyst compares the information on the label or packaging to the original order to ensure that the purchase meets the quality level specified. This is documented through the addition of the received date and initials to the information present on the daily order log.

The analyst verifies the lot numbers of received solvents and acids against the pre-approval lists. If a received material is listed as unapproved, or is not listed, it is sequestered and returned to the

vendor. Alternatively, the laboratory may test the material for the intended use, and if it is acceptable, document the approval on the approval list. Records of any testing performed locally are maintained on the shared "public" folder on the computer network.

Materials may not be released for use in the laboratory until they have been inspected, verified as suitable for use, and the inspection/verification has been documented.

Safety Data Sheets (SDSs) are available online through the Company's intranet website. Anyone may review these for relevant information on the safe handling and emergency precautions of on-site chemicals.

9.3.3 Specifications

Methods in use in the laboratory specify the grade of reagent that must be used in the procedure. If the quality of the reagent is not specified, analytical reagent grade will be used. It is the responsibility of the analyst to check the procedure carefully for the suitability of grade of reagent.

Chemicals must not be used past the manufacturer's expiration date and must not be used past the expiration time noted in a method SOP. If expiration dates are not provided, the laboratory may contact the manufacturer to determine an expiration date.

The laboratory assumes a five year expiration date on inorganic dry chemicals and solvents unless noted otherwise by the manufacturer or by the reference source method. Chemicals/solvents should not be used past the manufacturer's or SOPs expiration date unless 'verified' (refer to item 3 listed below).

- An expiration date **cannot** be extended if the dry chemical/solvent is discolored or appears otherwise physically degraded, the dry chemical/solvent must be discarded.
- Expiration dates can be extended if the dry chemical/solvent is found to be satisfactory based on acceptable performance of quality control samples (Continuing Calibration Verification (CCV), Blanks, Laboratory Control Sample (LCS), etc.).
- If the dry chemical/solvent is used for the preparation of standards, the expiration dates can be extended 6 months if the dry chemical/solvent is compared to an unexpired independent source in performing the method and the performance of the dry chemical/solvent is found to be satisfactory. The comparison must show that the dry chemical/solvent meets CCV limits. The comparison studies are maintained in the QA files**.**

Wherever possible, standards must be traceable to national or international standards of measurement or to national or international reference materials. Records to that effect are available to the user.

Compressed gases in use are checked for pressure and secure positioning daily. To prevent a tank from going to dryness or introducing potential impurities, the pressure should be closely watched as it decreases to approximately 15% of the original reading, at which point it should be replaced. For example, a standard sized laboratory gas cylinder containing 3,000 psig of gas should be replaced when it drops to approximately 500 psig. The quality of the gases must meet method or manufacturer specification or be of a grade that does not cause any analytical interference.

Water used in the preparation of standards or reagents must have a specific conductivity of less than 1- µmho/cm (or specific resistivity of greater than 1.0 megohm-cm) at 25°C. The *specific resistivity* is checked and recorded daily. If the water's specific *resistivity is less* than the specified limit, the Facility Manager and appropriate Technical Manager must be notified immediately in order to notify all departments, decide on cessation (based on intended use) of activities, and make arrangements for correction.

The laboratory may purchase reagent grade (or other similar quality) water for use in the laboratory. This water must be certified "clean" by the supplier for all target analytes or otherwise verified by the laboratory prior to use. This verification is documented.

Standard lots are verified before first time use if the laboratory switches manufacturers or has historically had a problem with the type of standard.

Purchased bottleware used for sampling must be certified clean and the certificates must be maintained. If uncertified sampling bottleware is purchased, all lots must be verified clean prior to use. This verification must be maintained.

Records of manufacturer's certification and traceability statements are stored as scanned images in the LIMS Reagent module. These records include date of receipt, lot number (when applicable), and expiration date (when applicable). Incorporation of the item into the record indicates that the analyst has compared the new certificate with the previous one for the same purpose and that no difference is noted, unless approved and so documented by the Technical Manager or QA Manager.

9.3.4 Storage

Reagent and chemical storage is important from the aspects of both integrity and safety. Light-sensitive reagents may be stored in brown-glass containers. Storage conditions are per the Corporate Environmental Health & Safety Manual (Corp. Doc. No. CW-E-M-001) and method SOPs or manufacturer instructions.

9.4 Purchase of Equipment / Instruments / Software

When a new piece of equipment is needed, either for additional capacity or for replacing inoperable equipment, the analyst or supervisor makes a supply request to the Technical Manager and/or the Laboratory Director. If they agree with the request, the procedures outlined in TestAmerica's Corporate Policy No. CA-T-P-001, Qualified Products List, are followed. A decision is made as to which piece of equipment can best satisfy the requirements. The appropriate written requests are completed and purchasing places the order.

Upon receipt of a new or used piece of equipment, an identification name is assigned and added to the equipment list. IT must also be notified so that they can synchronize the instrument for back-ups. Its capability is assessed to determine if it is adequate or not for the specific application. For instruments, a calibration curve is generated, followed by MDLs, Demonstration of Capabilities (DOCs), and other relevant criteria (refer to Section 19). For software, its operation must be deemed reliable and evidence of instrument verification must be retained by the QA Department. Software certificates supplied by the vendors are filed with the LIMS Administrator. The manufacturer's operation manual is retained at the bench.

9.5 Services

Service to analytical instruments (except analytical balances) is performed on an as needed basis. Routine preventative maintenance is discussed in Section 20. The need for service is determined by analysts and/or Technical Managers. The service providers that perform the services are approved by the Technical Manager.

Analytical balances are serviced and calibrated annually in accordance with SOP TA-QA-0014. The calibration and maintenance services are performed on-site, and the balances are returned to use immediately following successful calibration. When the calibration certificates are received (usually within two weeks of the service), they are reviewed, and documentation of the review is filed with the certificates. If the calibration was unsuccessful, the balance is immediately removed from service and segregated pending either further maintenance or disposal.

Calibration services for support equipment such as thermometers, weight sets, autopipettors, etc, are obtained from vendors with current and valid ISO 17025 accreditation for calibration of the specific piece of equipment. Prior to utilizing the vendor's services, the vendor's accreditation status is verified. Once the equipment has been calibrated, the calibration certificates are reviewed by the QA department, and documentation of the review is filed with the calibration certificates. The equipment is then returned to service within the laboratory

9.6 Suppliers

TestAmerica selects vendors through a competitive proposal / bid process, strategic business alliances or negotiated vendor partnerships (contracts). This process is defined in the Procurement & Contracts Policy (Policy No. CW-F-P-004). The level of control used in the selection process is dependent on the anticipated spending amount and the potential impact on TestAmerica business. Vendors that provide test and measuring equipment, solvents, standards, certified containers, instrument related service contracts or subcontract laboratory services shall be subject to more rigorous controls than vendors that provide off-the-shelf items of defined quality that meet the end use requirements. The JD Edwards purchasing system includes all suppliers/vendors that have been approved for use.

Evaluation of suppliers is accomplished by ensuring the supplier ships the product or material ordered and that the material is of the appropriate quality. This is documented by signing off on packing slips or other supply receipt documents. The purchasing documents contain the data that adequately describe the services and supplies ordered.

Any issues of vendor performance are to be reported immediately by the laboratory staff to the Corporate Purchasing Group by completing a Vendor Performance Report.

The Corporate Purchasing Group will work through the appropriate channels to gather the information required to clearly identify the problem and will contact the vendor to report the problem and to make any necessary arrangements for exchange, return authorization, credit, etc.

As deemed appropriate, the Vendor Performance Reports will be summarized and reviewed to determine corrective action necessary, or service improvements required by vendors.

The laboratory has access to a listing of all approved suppliers of critical consumables, supplies and services. This information is provided through the JD Edwards purchasing system.

9.6.1 New Vendor Procedure

TestAmerica employees who wish to request the addition of a new vendor must complete a J.D. Edwards Vendor Add Request Form.

New vendors are evaluated based upon criteria appropriate to the products or services provided as well as their ability to provide those products and services at a competitive cost. Vendors are also evaluated to determine if there are ethical reasons or potential conflicts of interest with TestAmerica employees that would make it prohibitive to do business with them as well as their financial stability. The QA Department and/or the Technology Manager are consulted with vendor and product selection that have an impact on quality.

SECTION 10. COMPLAINTS

10.1 Overview

The laboratory considers an effective client complaint handling processes to be of significant business and strategic value. Listening to and documenting client concerns captures 'client knowledge' that enables our operations to continually improve processes and client satisfaction. An effective client complaint handling process also provides assurance to the data user that the laboratory will stand behind its data, service obligations and products.

A client complaint is any expression of dissatisfaction with any aspect of our business services (e.g., communications, responsiveness, data, reports, invoicing and other functions) expressed by any party, whether received verbally or in written form. Client inquiries, complaints or noted discrepancies are documented, communicated to management, and addressed promptly and thoroughly.

The laboratory has procedures for addressing both external and internal complaints with the goal of providing satisfactory resolution to complaints in a timely and professional manner.

The nature of the complaint is identified, documented and investigated, and an appropriate action is determined and taken. In cases where a client complaint indicates that an established policy or procedure was not followed, the QA Department must evaluate whether a special audit must be conducted to assist in resolving the issue. A written confirmation or letter to the client, outlining the issue and response taken is recommended as part of the overall action taken.

The process of complaint resolution and documentation utilizes the procedures outlined in Section 12 (Corrective Actions) and laboratory SOP TA-QA-0529 (Client Complaint Resolution).

10.2 External Complaints

An employee that receives a complaint initiates the complaint resolution process by first documenting the complaint according to SOP TA-QA-0529.

Complaints fall into two categories: correctable and non-correctable. An example of a correctable complaint would be one where a report re-issue would resolve the complaint. An example of a non-correctable complaint would be one where a client complains that their data was repeatedly late.

Non-correctable complaints should be reviewed for preventive action measures to reduce the likelihood of future occurrence and mitigation of client impact.

The general steps in the complaint handling process are:

- Receiving and Documenting Complaints
- Complaint Investigation and Service Recovery
- Process Improvement

The laboratory shall inform the initiator of the complaint of the results of the investigation and the corrective action taken, if any.

10.3 Internal Complaints

Internal complaints include, but are not limited to: errors and non-conformances, training issues, internal audit findings, and deviations from methods. Corrective actions may be initiated by any staff member who observes a nonconformance and shall follow the procedures outlined in Section 12. In addition, Corporate Management, Sales and Marketing and IT may initiate a complaint by contacting the laboratory or through the corrective action system described in Section 12.

10.4 Management Review

The number and nature of client complaints is reported by the QA Manager to the laboratory and Quality Director in the QA Monthly report. Monitoring and addressing the overall level and nature of client complaints and the effectiveness of the solutions is part of the Annual Management Review (Section 16).

SECTION 11. CONTROL OF NON-CONFORMING WORK

11.1 Overview

When data discrepancies are discovered or deviations and departures from laboratory SOPs, policies and/or client requests have occurred, corrective action is taken immediately. First, the laboratory evaluates the significance of the nonconforming work. Then, a corrective action plan is initiated based on the outcome of the evaluation. If it is determined that the nonconforming work is an isolated incident, the plan could be as simple as adding a qualifier to the final results and/or making a notation in the case narrative. If it is determined that the nonconforming work is a systematic or improper practices issue, the corrective action plan could include a more in depth investigation and a possible suspension of an analytical method. In all cases, the actions taken are documented using the laboratory's corrective action system (refer to Section 12).

Due to the frequently unique nature of environmental samples, sometimes departures from documented policies and procedures are needed. When an analyst encounters such a situation, the problem is presented to the supervisor for resolution. The supervisor may elect to discuss it with the Technical Manager or have a representative contact the client to decide on a logical course of action. Once an approach is agreed upon, the analyst documents it using the laboratory's corrective action system described in Section 12. This information can then be supplied to the client in the form of a footnote or a case narrative with the report.

Project Management may encounter situations where a client may request that a special procedure be applied to a sample that is not standard lab practice. Based on a technical evaluation, the lab may accept or opt to reject the request based on technical or ethical merit. An example might be the need to report a compound that the lab does not normally report. The lab would not have validated the method for this compound following the procedures in Section 19. The client may request that the compound be reported based only on the calibration. Such a request would need to be approved by the Technical Manager and QA Manager, documented and included in the project folder. Deviations **must** also be noted on the final report with a statement that the compound is not reported in compliance with TNI (or the analytical method) requirements and the reason. Data being reported to a non-NELAC state would need to note the change made to how the method is normally run.

11.2 Responsibilities and Authorities

Under certain circumstances, the Laboratory Director, a Technical Manager, or a member of the QA team may authorize departures from documented procedures or policies. The departures may be a result of procedural changes due to the nature of the sample; a one-time procedure for a client; QC failures with insufficient sample to reanalyze, etc.. In most cases, the client will be informed of the departure prior to the reporting of the data. Any departures must be well documented using the laboratory's corrective action procedures. This information may also be documented in logbooks and/or data review checklists as appropriate**.** Any impacted data must be referenced in a case narrative and/or flagged with an appropriate data qualifier.

Any misrepresentation or possible misrepresentation of analytical data discovered by any laboratory staff member must be reported to facility Senior Management within 24-hours. The Senior Management staff is comprised of the Laboratory Director, the QA Manager, and the Technical Managers. The reporting of issues involving alleged violations of the company's Data Integrity or Manual Integration procedures must be conveyed to an Ethics and Compliance Officer (ECO), Exec. Director of Quality & EHS and the laboratory's Quality Director within 24 hours of discovery.

Whether an inaccurate result was reported due to calculation or quantitation errors, data entry errors, improper practices, or failure to follow SOPs, the data must be evaluated to determine the possible effect.

The Laboratory Director, QA Manager, ECOs, VP of Operations and the Quality Directors have the authority and responsibility to halt work, withhold final reports, or suspend an analysis for due cause as well as authorize the resumption of work.

11.3 Evaluation of Significance and Actions Taken

For each nonconforming issue reported, an evaluation of its significance and the level of management involvement needed is made. This includes reviewing its impact on the final data, whether or not it is an isolated or systematic issue, and how it relates to any special client requirements.

Corporate SOP entitled Data Recalls (CW-Q-S-005) is the procedure to be followed when it is discovered that erroneous or biased data may have been reported to clients or regulatory agencies.

Corporate SOP entitled Internal Investigations (CW-L-S-002) is the procedure to be followed for investigation and correction of situations involved alleged incidents of misconduct or violation of the company's ethics policy.

Laboratory level decisions are documented and approved using the laboratory's standard nonconformance/corrective action reporting in lieu of the data recall determination form contained in TestAmerica's Corporate SOP No. CW-Q-S-005.

11.4 Prevention of NonConforming Work

If it is determined that the nonconforming work could recur, further corrective actions must be made following the laboratory's corrective action system. On a weekly basis, the QA Department evaluates non-conformances to determine if any nonconforming work has been repeated multiple times. If so, the laboratory's corrective action process may be followed.

11.5 Method Suspension / Restriction (Stop Work Procedures)

In some cases, it may be necessary to suspend/restrict the use of a method or target compound which constitutes significant risk and/or liability to the laboratory. Suspension/restriction procedures can be initiated by any of the persons noted in Section 11.2, Paragraph 5.

Prior to suspension/restriction, confidentiality will be respected, and the problem with the required corrective and preventive action will be stated in writing and presented to the Laboratory Director and Operations Manager.

The Laboratory Director shall arrange for the appropriate personnel to meet with the QA Manager as needed. This meeting shall be held to confirm that there is a problem, that suspension/restriction of the method is required and will be concluded with a discussion of the steps necessary to bring the method/target or test fully back on line. In some cases, that may not be necessary if all appropriate personnel have already agreed there is a problem and there is agreement on the steps needed to bring the method, target or test fully back on line. The QA Manager will also initiate a corrective action report as described in Section 12 if one has not already been started. A copy of any meeting notes and agreed upon steps should be faxed or e-mailed by the laboratory to the appropriate VP of Operations and member of Corporate QA. This fax/e-mail acts as notification of the incident.

After suspension/restriction, the lab will hold all reports to clients pending review. No faxing, mailing or distributing through electronic means may occur. The report must not be posted for viewing on the internet. It is the responsibility of the Laboratory Director to hold all reporting and to notify all relevant laboratory personnel regarding the suspension/restriction (e.g., Project Management, Log-in, etc…). Clients will NOT generally be notified at this time. Analysis may proceed in some instances depending on the non-conformance issue.

Within 72 hours, the QA Manager will determine if compliance is now met and reports can be released, OR determine the plan of action to bring work into compliance, and release work. A team, with all principals involved (Laboratory Director, Technical Manager, QA Manager) can devise a start-up plan to cover all steps from client notification through compliance and release of reports. Project Management and the Directors of Client Services and Sales and Marketing must be notified if clients must be notified or if the suspension/restriction affects the laboratory's ability to accept work. The QA Manager must approve start-up or elimination of any restrictions after all corrective

action is complete. This approval is given by final signature on the completed corrective action report.

SECTION 12. CORRECTIVE ACTION

12.1 Overview

A major component of TestAmerica's Quality Assurance (QA) Program is the problem investigation and feedback mechanism designed to keep the laboratory staff informed on quality related issues and to provide insight to problem resolution. When nonconforming work or departures from policies and procedures in the quality system or technical operations are identified, the corrective action procedure provides a systematic approach to assess the issues, restore the laboratory's system integrity, and prevent reoccurrence. Corrective actions are documented using Non-Conformance Memo (NCM) and Corrective Action Reports (CAR) (refer to SOP No. TA-QA-0610 and Figure 12-1).

12.2 General

Problems within the quality system or within analytical operations may be discovered in a variety of ways, such as QC sample failures, internal or external audits, proficiency testing (PT) performance, client complaints, staff observation, etc.

The purpose of a corrective action system is to:

- Identify non-conformance events and assign responsibility(s) for investigating.
- Resolve non-conformance events and assign responsibility for any required corrective action.
- Identify systematic problems before they become serious.
- Identify and track client complaints and provide resolution.

12.2.1 Non-Conformance Memo (NCM) - is used to document the following types of corrective actions:

- Deviations from an established procedure or SOP
- QC outside of limits (non-matrix related)
- Isolated reporting / calculation errors
- Client complaints
- Discrepancies in materials / goods received vs. manufacturer packing slips.

12.2.2 Corrective Action Report (CAR) - is used to document the following types of corrective actions:

- Questionable trends that are found in the review of NCMs.
- Issues found while reviewing NCMs that warrant further investigation.
- Internal and external audit findings.
- Failed or unacceptable PT results.
- Corrective actions that cross multiple departments in the laboratory.

- Systematic reporting / calculation errors
- Client complaints
- Data recall investigations
- Identified poor process or method performance trends
- Excessive revised reports
- Health and Safety violations

This will provide background documentation to enable root cause analysis and preventive action.

12.3 Closed Loop Corrective Action Process

Any employee in the company can initiate a corrective action. There are four main components to a closed-loop corrective action process once an issue has been identified: Cause Analysis, Selection and Implementation of Corrective Actions (both short and long term), Monitoring of the Corrective Actions, and Follow-up. (refer to SOP No. TA-QA-0610 for more detail)

12.3.1 Cause Analysis

- Upon discovery of a non-conformance event, the event must be defined and documented. An NCM or CAR must be initiated, someone is assigned to investigate the issue and the event is investigated for cause. Table 12-1 provides some general guidelines on determining responsibility for assessment.
- The cause analysis step is the key to the process as a long term corrective action cannot be determined until the cause is determined.
- If the cause is not readily obvious, the Technical Manager, Laboratory Director, or QA Manager (or QA designee) is consulted.

12.3.2 Selection and Implementation of Corrective Actions

- Where corrective action is needed, the laboratory shall identify potential corrective actions. The action(s) most likely to eliminate the problem and prevent recurrence are selected and implemented. Responsibility for implementation is assigned.
- Corrective actions shall be to a degree appropriate to the magnitude of the problem identified through the cause analysis.
- Whatever corrective action is determined to be appropriate, the laboratory shall document and implement the changes. The NCM or CAR is used for this documentation.

12.3.3 Root Cause Analysis

Root Cause Analysis is a class of problem solving (investigative) methods aimed at identifying the basic or causal factor(s) that underlie variation in performance or the occurrence of a significant failure. The root cause may be buried under seemingly innocuous events, many steps preceding the perceived failure. At first glance, the immediate response is typically directed at a symptom and not the cause. Typically, root cause analysis would be best with three or more incidents to triangulate a weakness. Corporate SOP Root Cause Analysis (No. CA-Q-S-009) describes the procedure.

Systematically analyze and document the root causes of the more significant problems that are reported. Identify, track, and implement the corrective actions required to reduce the likelihood of

recurrence of significant incidents. Trend the root cause data from these incidents to identify root causes that, when corrected, can lead to dramatic improvements in performance by eliminating entire classes of problems.

Identify the one event associated with problem and ask why this event occurred. Brainstorm the root causes of failures; for example, by asking why events occurred or conditions existed; and then why the cause occurred 5 consecutive times until you get to the root cause. For each of these sub events or causes, ask why it occurred. Repeat the process for the other events associated with the incident.

Root cause analysis does not mean the investigation is over. Look at technique, or other systems outside the normal indicators. Often creative thinking will find root causes that ordinarily would be missed, and continue to plague the laboratory or operation.

12.3.4 Monitoring of the Corrective Actions

- The Technical Manager and QA Manager are responsible to ensure that the corrective action taken was effective.
- Ineffective actions are documented and re-evaluated until acceptable resolution is achieved. Technical Managers are accountable to the Laboratory Director to ensure final acceptable resolution is achieved and documented appropriately.
- Each NCM and CAR is entered into a database for tracking purposes and a monthly summary of all corrective actions is printed out for review to aid in ensuring that the corrective actions have taken effect.
- TestAmerica laboratories began using the Incident/Corrective Action Tracker (iCAT) database developed by the company in 2015. (Previously, a local database served this purpose.) An incident is an event triggering the need for one or more corrective actions as distinct from a corrective action, a potential deficiency stemming from an incident that requires investigation and possibly fixing. The database is independent of TALS, available to all local and corporate managers, and capable of notifying and tracking multiple corrective actions per event, dates, and personnel. iCAT allows associated document upload, categorization (such as, external/internal audit, client service concerns, data quality issues, proficiency testing, etc.), and trend analysis. Refer to Figure 12-1.
- The QA Manager reviews monthly NCMs and CARs for trends. Highlights are included in the QA monthly report (refer to Section 16). If a significant trend develops that adversely affects quality, an audit of the area is performed and corrective action implemented.
- Any out-of-control situations that are not addressed acceptably at the laboratory level may be reported to the Corporate Quality Director by the QA Manager, indicating the nature of the out-of-control situation and problems encountered in solving the situation.

12.3.5 Follow-up Audits

- Follow-up audits may be initiated by the QA Manager and shall be performed as soon as possible when the identification of a nonconformance casts doubt on the laboratory's compliance with its own policies and procedures, or on its compliance with state or federal requirements.
- These audits often follow the implementation of the corrective actions to verify effectiveness. An additional audit would only be necessary when a critical issue or risk to business is discovered.

(Also refer to Section 15.1.4, Special Audits.)

12.4 Technical Corrective Actions

In addition to providing acceptance criteria and specific protocols for technical corrective actions in the method SOPs, the laboratory has general procedures to be followed to determine when departures from the documented policies and procedures and quality control have occurred (refer to Section 11). The documentation of these procedures is through the use of an NCM.

Table 12-1 includes examples of general technical corrective actions. For specific criteria and corrective actions, refer to the analytical methods or specific method SOPs. The laboratory may also maintain Work Instructions on these items that are available upon request.

Table 12-1 provides some general guidelines for identifying the individual(s) responsible for assessing each QC type and initiating corrective action. The table also provides general guidance on how a data set should be treated if associated QC measurements are unacceptable. Specific procedures are included in Method SOPs, Work Instructions and QAM Sections 19 and 20. All corrective actions are reviewed monthly, at a minimum, by the QA Manager and highlights are included in the QA monthly report.

To the extent possible, samples shall be reported only if all quality control measures are acceptable. If the deficiency does not impair the usability of the results, data will be reported with an appropriate data qualifier and/or the deficiency will be noted in the case narrative. Where sample results may be impaired, the Project Manager is notified by an NCM and appropriate corrective action (e.g., reanalysis) is taken and documented**.**

12.5 Basic Corrections

When mistakes occur in records, each mistake shall be crossed-out, [not obliterated (e.g. no white-out), and the correct value entered alongside. All such corrections shall be initialed (or signed) and dated by the person making the correction. In the case of records stored electronically, the original “uncorrected” file must be maintained intact and a second “corrected” file is created.

This same process applies to adding additional information to a record. All additions made later than the initial must also be initialed (or signed) and dated.

When corrections are due to reasons other than obvious transcription errors, the reason for the corrections (or additions) shall also be documented.

Figure 12-1.

Example - Non Conformance Memo

NCM	TestAmerica Seattle - 145339
Project	WWTP
Job/Client	580-66230-1 ABC Inc.
Lab Section	GC/MS Semi VOA
Method	625
NCM Type	Deficiency - CCV - %D, High, Sample ND, Sample IDs Included
Affected Items	580-66230-B-1-A Client Sample-B1 CCVIS 580-239305/3
Narrative for Job 580-66230-1	The continuing calibration verification (CCV) associated with batch 580-239305 recovered above the upper control limit for Bis(2-ethylhexyl) phthalate. The samples associated with this CCV were non-detects for the affected analytes; therefore, the data have been reported. The following sample is impacted: Client Sample-B1 (580-66230-1) and (CCVIS 580-239305/3).
Internal Comments	[INTERNALCOMMENTS]

Example – Corrective Action Report

iCAT id:	Created On:	Created By:
Subject:	Client:	Project (if applicable):
Laboratory Function:	Corrective Action Type:	Finding Number:
Finding Reference:	Priority:	Assigned To:
Response Due to QA:	Planned Issue Closure Date:	Date Closed:
Follow-Up Assigned To:		Date Follow-Up Due:

Corrective Action Requested:

Investigation/Response:

Root Cause Analysis:

Corrective Action:

Table 12-1. Example – General Corrective Action Procedures

QC Activity (Individual Responsible for Initiation/Assessment)	Acceptance Criteria	Recommended Corrective Action
Initial Instrument Blank (Analyst)	- Instrument response < MDL.	- Prepare another blank. - If same response, determine cause of contamination: reagents, environment, instrument equipment failure, etc..
Initial Calibration Standards (Analyst, Technical Manager(s))	- Correlation coefficient > 0.99 or standard concentration value. - % Recovery within acceptance range. - See details in Method SOP.	- Reanalyze standards. - If still unacceptable, remake standards and recalibrate instrument.
Independent Calibration Verification (Second Source) (Analyst, Technical Manager(s))	- % Recovery within control limits.	- Remake and reanalyze standard. - If still unacceptable, then remake calibration standards or use new primary standards and recalibrate instrument.
Continuing Calibration Standards (Analyst, Data Reviewer)	% Recovery within control limits.	- Reanalyze standard. - If still unacceptable, then recalibrate and rerun affected samples.
Laboratory Control Sample (LCS) (Analyst, Data Reviewer)	- % Recovery within limits specified in LIMS.	- Batch must be re-prepared and re-analyzed. This includes any allowable marginal exceedance. When not using marginal exceedances, the following exceptions apply: 1) when the acceptance criteria for the positive control are exceeded high (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported with data qualifying codes; 2) when the acceptance criteria for the positive control are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level with data qualifying codes. **Note:** If there is insufficient sample or the holding time cannot be met, contact client and report with flags.

QC Activity (Individual Responsible for Initiation/Assessment)	Acceptance Criteria	Recommended Corrective Action
Matrix Spike / Matrix Spike Duplicate (MS/MSD) (Analyst, Data Reviewer)	- % Recovery within limits documented in LIMS.	- If the acceptance criteria for duplicates or matrix spikes are not met because of matrix interferences, the acceptance of the analytical batch is determined by the validity of the LCS. - If the LCS is within acceptable limits the batch is acceptable. - The results of the duplicates, matrix spikes and the LCS are reported with the data set. - For matrix spike or duplicate results outside criteria, the data for that sample shall be reported with qualifiers.
Surrogates (Analyst, Data Reviewer)	- % Recovery within limits of method or within three standard deviations of the historical mean.	- Individual sample must be repeated. Place comment in LIMS. - Surrogate results outside criteria shall be reported with qualifiers.
Method Blank (MB) (Analyst, Data Reviewer)	< Reporting Limit [1]	- Reanalyze blank. - If still positive, determine source of contamination. If necessary, reprocess (i.e. digest or extract) entire sample batch. Report blank results. - Qualify the result(s) if the concentration of a targeted analyte in the MB is at or above the reporting limit AND is > 1/10 of the amount measured in the sample.
Proficiency Testing (PT) Samples (QA Manager, Technical Manager(s)	- Criteria supplied by PT Supplier.	- Any failures or warnings must be investigated for cause. Failures may result in the need to repeat a PT sample to show the problem is corrected.
Internal / External Audits (QA Manager, Technical Manager(s), Laboratory Director)	- Defined in Quality System documentation such as SOPs, QAM, etc..	- Non-conformances must be investigated through CAR system and necessary corrections must be made.

QC Activity (Individual Responsible for Initiation/Assessment)	Acceptance Criteria	Recommended Corrective Action
Reporting / Calculation Errors (Depends on issue – possible individuals include: Analysts, Data Reviewers, Project Managers, Technical Managers, QA Manager, Corporate QA, Corporate Management)	- SOP CW-L-S-002, Internal Investigation of Potential Data Discrepancies and Determination for Data Recall.	- Corrective action is determined by type of error. Follow the procedures in SOP CW-L-S-002 or Lab SOP TA-QA-0610 Laboratory Corrective Action Procedures.
Client Complaints (Project Managers, Lab Director, Sales and Marketing)	-	- Corrective action is determined by the type of complaint. For example, a complaint regarding an incorrect address on a report will result in the report being corrected and then follow-up must be performed on the reasons the address was incorrect (e.g., database needs to be updated).
QA Monthly Report (Refer to Section 16 for an example) (QA Manager, Lab Director, Technical Manager(s))	- QAM, SOPs.	- Corrective action is determined by the type of issue. For example, CARs for the month are reviewed and possible trends are investigated.
Health and Safety Violation (Safety Officer, Lab Director, Technical Manager(s))	- Environmental Health and Safety (EHS) Manual.	- Non-conformance is investigated and corrected through CAR system.

Note:
1. Except as noted below for certain compounds, the method blank should be below the detection limit or for DoD/DOE projects the method blank should be below ½ the RL. Concentrations up to five times the reporting limit will be allowed for the ubiquitous laboratory and reagent contaminants: methylene chloride, toluene, acetone, 2-butanone and phthalates **provided** they appear in similar levels in the reagent blank and samples. This allowance presumes that the detection limit is significantly below any regulatory limit to which the data are to be compared and that blank subtraction will not occur. For benzene and ethylene dibromide (EDB) and other analytes for which regulatory limits are extremely close to the detection limit, the method blank must be below the method detection limit.

SECTION 13. PREVENTIVE ACTION / IMPROVEMENT

13.1 Overview

The laboratory's preventive action programs improve or eliminate potential causes of nonconforming product and/or nonconformance to the quality system. This preventive action process is a proactive and continuous process of improvement activities that can be initiated through feedback from clients, employees, business providers, and affiliates. The QA Department has the overall responsibility to ensure that the preventive action process is in place, and that relevant information on actions is submitted for management review.

Dedicating resources to an effective preventive action system emphasizes the laboratory's commitment to its Quality Program. It is beneficial to identify and address negative trends before they develop into complaints, problems and corrective actions. Additionally, the laboratory continually strives to improve customer service and client satisfaction through continuous improvements to laboratory systems.

Opportunities for improvement may be discovered through any of the following:

- review of the monthly QA Metrics Report,
- trending NCMs,
- review of control charts and QC results,
- trending proficiency testing (PT) results,
- performance of management system reviews,
- trending client complaints,
- review of processing operations, or
- staff observations.

The monthly Management Systems Metrics Report shows performance indicators in all areas of the laboratory and quality system. These areas include revised reports, corrective actions, audit findings, internal auditing and data authenticity audits, client complaints, PT samples, holding time violations, SOPs, ethics training, etc. The metrics report is reviewed monthly be the laboratory management, Corporate QA and TestAmerica's Executive Committee. These metrics are used ~~to~~ in evaluating the management and quality system performance on an ongoing basis and provide a tool for identifying areas for improvement.

Items identified as continuous improvement opportunities to the management system may be issued as goals from the annual management systems review, recommendations from internal audits, white papers, Lesson Learned, Technical Services audit report, Technical Best Practices, or as Corporate or management initiatives.

The laboratory's corrective action process is integral to implementation of preventive actions. A critical piece of the corrective action process is the implementation of actions to prevent further occurrence of a non-compliance event. Historical review of corrective action and non-conformances provides a valuable mechanism for identifying preventive action opportunities.

13.1.1 The following elements are part of a preventive action/process improvement system:

- Identification of an opportunity for preventive action or process improvement.

- Process for the preventive action or improvement.
- Define the measurements of the effectiveness of the process once undertaken.
- Execution of the preventive action or improvement.
- Evaluation of the plan using the defined measurements.
- Verification of the effectiveness of the preventive action or improvement.
- Close-Out by documenting any permanent changes to the Quality System as a result of the Preventive Action or Process Improvement. Documentation of Preventive Action/Process Improvement is incorporated into the monthly QA reports, corrective action process and management review.

13.1.2 Any Preventive Actions/Process Improvement undertaken or attempted shall be taken into account during the annual Management Systems Review (Section 16). A highly detailed report is not required; however, a summary of successes and failures within the preventive action program is sufficient to provide management with a measurement for evaluation.

13.2 Management of Change

The Management of Change process is designed to manage significant events and changes that occur within the laboratory. Through these procedures, the potential risks inherent with a new event or change are identified and evaluated. The risks are minimized or eliminated through pre-planning and the development of preventive measures. The types of changes covered under this system include: Facility Changes, Major Accreditation Changes, Addition or Deletion to Division's Capabilities or Instrumentation, Key Personnel Changes, Laboratory Information Management System (LIMS) changes. This process is discussed in further detail in SOP TA-QA-0530, Management of Change.

SECTION 14. CONTROL OF RECORDS

The laboratory maintains a records management system appropriate to its needs and that complies with applicable standards or regulations as required. The system produces unequivocal, accurate records that document all laboratory activities. The laboratory retains all original observations, calculations and derived data, calibration records and a copy of the analytical report for a minimum of five years after it has been issued. Exceptions for programs with longer retention requirements are discussed in Section 14.1.2.

14.1 Overview

The laboratory has established procedures for identification, collection, indexing, access, filing, storage, maintenance and disposal of quality and technical records. A record index is listed in Table 14-1. More detailed information on retention of specific records is provided in CW-L-P-001, Records Retention Policy and CW-L-WI-001, TestAmerica Records Retention/Storage Schedule. Quality records are maintained by the QA department in a database, which is backed up as part of the regular laboratory backup. Records are of two types; either electronic or hard copy paper formats depending on whether the record is computer or hand generated (some records may be in both formats, in this instance the electronic copy will be considered to be the vital record). Technical records are maintained by the Technical Managers.

Table 14-1. Record Index[1]

	Record Types [1]:	Retention Time:
Technical Records	- Raw Data - Logbooks[2] - Standards - Certificates - Analytical Records - MDLs/IDLs/DOCs - Lab Reports	5 Years from analytical report issue*
Official Documents	- Quality Assurance Manual (QAM) - Work Instructions - Policies - SOPs - Policy Memorandums - Manuals - Published Methods	Indefinitely
QA Records	- Certifications - Method and Software Validation / Verification Data	Indefinitely
QA Records	- Internal & External Audits/Responses - Corrective/Preventive Actions - Management Reviews - Data Investigation	5 Years from archival* **Data Investigation:** 5 years or the life of the affected raw data storage whichever is greater (beyond 5 years if ongoing project or pending investigation)
Project Records	- Sample Receipt & COC Documents - Contracts and Amendments - Correspondence - QAPP - SAP - Telephone Logbooks - Lab Reports	5 Years from analytical report issue*
Administrative Records	Financial and Business Operations	Refer to CW-L-WI-001
	EH&S Manual, Permits	Indefinitely
	Disposal Records	Indefinitely
	Employee Handbook	Indefinitely
	Personnel files, Employee Signature & Initials, Administrative Training Records (e.g., Ethics)	Refer to HR Manual
	Administrative Policies	Indefinitely
	Technical Training Records	7 years
	Legal Records	Indefinitely
	HR Records	Refer to CW-L-WI-001
	IT Records	Refer to CW-L-WI-001
	Corporate Governance Records	Refer to CW-L-WI-001
	Sales & Marketing	5 years
	Real Estate	Indefinitely

[1] Record Types encompass hardcopy and electronic records.
[2] Examples of Logbook types: Maintenance, Instrument Run, Preparation (standard and samples), Standard and Reagent Receipt, Archiving, Balance Calibration, Temperature (hardcopy or electronic records).
* Exceptions listed in Table 14-2.

14.1.1 All records are stored and retained in such a way that they are secure and readily retrievable at the laboratory or the Iron Mountain data storage facility that provide a suitable environment to prevent damage or deterioration and to prevent loss. All records shall be protected against fire, theft, loss, environmental deterioration, and vermin. In the case of electronic records, electronic or magnetic sources, storage media are protected from deterioration caused by magnetic fields and/or electronic deterioration.

Access to the data is limited to laboratory and company employees and shall be documented with an access log**.** Records archived off-site are stored in a secure location where a record is maintained of any entry into the storage facility. Whether on-site or off-site storage is used, logs are maintained in each storage box to note removal and return of records. Retention of records are maintained on-site at the laboratory for at least 6 months after their generation and moved offsite for the remainder of the required storage time. Records are maintained for a minimum of five years unless otherwise specified by a client or regulatory requirement.

For raw data and project records, record retention shall be calculated from the date the project report is issued. For other records, such as Controlled Documents, QA, or Administrative Records, the retention time is calculated from the date the record is formally retired. Records related to the programs listed in Table 14-2 have lengthier retention requirements and are subject to the requirements in Section 14.1.3.

14.1.2 Programs with Longer Retention Requirements

Some regulatory programs have longer record retention requirements than the standard record retention time. These are detailed in Table 14-2 with their retention requirements. In these cases, the longer retention requirement is enacted. If special instructions exist such that client data cannot be destroyed prior to notification of the client, the container or box containing that data is marked as to who to contact for authorization prior to destroying the data.

Table 14-2. Example: Special Record Retention Requirements

Program	[1]Retention Requirement
Drinking Water – All States	10 years (lab reports and raw data) 10 years - Radiochemistry (project records)
Drinking Water Lead and Copper Rule	12 years (project records)
Alaska	10 years
Navy Facilities Engineering Service Center (NFESC)	10 years
TSCA - 40 CFR Part 792	10 years after publication of final test rule or negotiated test agreement

[1]Note: Extended retention requirements must be noted with the archive documents or addressed in facility-specific records retention procedures.

14.1.3 The laboratory has procedures to protect and back-up records stored electronically and to prevent unauthorized access to or amendment of these records. All analytical data is maintained as hard copy or in a secure readable electronic format. For analytical reports that are maintained as copies in PDF format, refer to Section 19.14.1 for more information. Additional information can also

be reference in SOP TA-QA-0506 Archiving Data and Reports.

14.1.4 The record keeping system allows for historical reconstruction of all laboratory activities that produced the analytical data, as well as rapid recovery of historical data. The history of the sample from when the laboratory took possession of the samples must be readily understood through the documentation. This shall include inter-laboratory transfers of samples and/or extracts.

- The records include the identity of personnel involved in sampling, sample receipt, preparation, or testing. All analytical work contains the initials (at least) of the personnel involved. The laboratory's copy of the COC is stored with the invoice and the work order sheet generated by the LIMS. The chain of custody would indicate the name of the sampler. If any sampling notes are provided with a work order, they are kept with this package.

- All information relating to the laboratory facilities equipment, analytical test methods, and related laboratory activities, such as sample receipt, sample preparation, or data verification are documented.

- The record keeping system facilitates the retrieval of all working files and archived records for inspection and verification purposes (e.g., set format for naming electronic files, set format for what is included with a given analytical data set as per SOP TA-QA-0506 Archiving Reports and Report File Maintenance). Instrument data is stored sequentially by instrument. A given day's analyses are maintained in the order of the analysis. Run logs are maintained for each instrument or method; a copy of each day's run log or instrument sequence is stored with the data to aid in re-constructing an analytical sequence. Where an analysis is performed without an instrument, bound logbooks or bench sheets are used to record and file data. Standard and reagent information is recorded in logbooks or entered into the LIMS for each method as required.

- Changes to hardcopy records shall follow the procedures outlined in Section 12 and 19. Changes to electronic records in LIMS or instrument data are recorded in audit trails.

- The reason for a signature or initials on a document is clearly indicated in the records such as "sampled by," "prepared by," "reviewed by", or "analyzed by".

- All generated data except those that are generated by automated data collection systems, are recorded directly, promptly and legibly in permanent dark ink.

- Hard copy data may be scanned into PDF format for record storage as long as the scanning process can be verified in order to ensure that no data is lost and the data files and storage media must be tested to verify the laboratory's ability to retrieve the information prior to the destruction of the hard copy that was scanned. The procedure for this verification can be found in SOP TA-QA-0506 Archiving Reports and Report File Maintenance.

- Also refer to Section 19.14.1 'Computer and Electronic Data Related Requirements'**.**

14.2 Technical and Analytical Records

14.2.1 The laboratory retains records of original observations, derived data and sufficient information to establish an audit trail, calibration records, staff records and a copy of each analytical

report issued, for a minimum of five years unless otherwise specified by a client or regulatory requirement. The records for each analysis shall contain sufficient information to enable the analysis to be repeated under conditions as close as possible to the original. The records shall include the identity of laboratory personnel responsible for the performance of each analysis and reviewing results.

14.2.2 Observations, data and calculations are recorded real-time and are identifiable to the specific task.

14.2.3 Changes to hardcopy records shall follow the procedures outlined in Section 12 and 19. Changes to electronic records in LIMS or instrument data are recorded in audit trails.

The essential information to be associated with analysis, such as strip charts, tabular printouts, computer data files, analytical notebooks, and run logs, include:

- laboratory sample ID code**;**
- Date of analysis; Time of Analysis is also required if the holding time is seventy-two (72) hours or less, or when time critical steps are included in the analysis (e.g., drying times, incubations, etc.); instrumental analyses have the date and time of analysis recorded as part of their general operations. Where a time critical step exists in an analysis, location for such a time is included as part of the documentation in a specific logbook or on a benchsheet or in the LIMS.
- Instrumentation identification and instrument operating conditions/parameters. Operating conditions/parameters are typically recorded in instrument maintenance logs where available.
- analysis type**;**
- all manual calculations and manual integrations**;**
- analyst's or operator's initials/signature**;**
- sample preparation including cleanup, separation protocols, incubation periods or subculture, ID codes, volumes, weights, instrument printouts, meter readings, calculations, reagents**;**
- test results**;**
- standard and reagent origin, receipt, preparation, and use**;**
- calibration criteria, frequency and acceptance criteria**;**
- data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions**;**
- quality control protocols and assessment**;**
- electronic data security, software documentation and verification, software and hardware audits, backups, and records of any changes to automated data entries; and
- Method performance criteria including expected quality control requirements. These are indicated both in the LIMS and on specific analytical report formats**.**

14.2.4 All logbooks used during receipt, preparation, storage, analysis, and reporting of samples or monitoring of support equipment shall undergo a documented supervisory or peer review on a monthly basis.

14.3 Laboratory Support Activities

In addition to documenting all the above-mentioned activities, the following are retained QA records and project records (previous discussions in this section relate where and how these data are stored):

- all original raw data, whether hard copy or electronic, for calibrations, samples and quality control measures, including analysts' work sheets and data output records (chromatograms, strip charts, and other instrument response readout records)**;**
- a written description or reference to the specific test method used which includes a description of the specific computational steps used to translate parametric observations into a reportable analytical value**;**
- copies of final reports**;**
- archived SOPs**;**
- correspondence relating to laboratory activities for a specific project**;**
- all corrective action reports, audits and audit responses**;**
- proficiency test results and raw data; and
- results of data review, verification, and crosschecking procedures.

14.3.1 Sample Handling Records

Records of all procedures to which a sample is subjected while in the possession of the laboratory are maintained. These include but are not limited to records pertaining to:

- sample preservation including appropriateness of sample container and compliance with holding time requirement;
- sample identification, receipt, acceptance or rejection and login;
- sample storage and tracking including shipping receipts, sample transmittal / COC forms; and
- procedures for the receipt and retention of samples, including all provisions necessary to protect the integrity of samples.

14.4 Administrative Records

The laboratory also maintains the administrative records in either electronic or hard copy form. Refer to Table 14-1.

14.5 Records Management, Storage and Disposal

All records (including those pertaining to test equipment), certificates and reports are safely stored, held secure and in confidence to the client. Certification related records are available upon request.

All information necessary for the historical reconstruction of data is maintained by the laboratory. Records that are stored only on electronic media must be supported by the hardware and software necessary for their retrieval.

Records that are stored or generated by computers or personal computers have hard copy, write-protected backup copies, or an electronic audit trail controlling access**.**

The laboratory has a record management system (a.k.a., document control) for control of laboratory notebooks, instrument logbooks, standards logbooks, and records for data reduction, validation, storage and reporting. Laboratory notebooks are issued on a per analysis basis, and are numbered sequentially. All data are recorded sequentially within a series of sequential notebooks. Bench sheets are filed sequentially. Standards are maintained in the LIMS – no logbooks are used to record that data**.** Records are considered archived when noted as such in the records management system (a.k.a., document control.)

14.5.1 Transfer of Ownership

In the event that the laboratory transfers ownership or goes out of business, the laboratory shall ensure that the records are maintained or transferred according to client's instructions. Upon ownership transfer, record retention requirements shall be addressed in the ownership transfer agreement and the responsibility for maintaining archives is clearly established. In addition, in cases of bankruptcy, appropriate regulatory and state legal requirements concerning laboratory records must be followed. In the event of the closure of the laboratory, all records will revert to the control of the corporate headquarters. Should the entire company cease to exist, as much notice as possible will be given to clients and the accrediting bodies who have worked with the laboratory during the previous 5 years of such action.

14.5.2 Records Disposal

Records are removed from the archive and destroyed after 5 years unless otherwise specified by a client or regulatory requirement. On a project specific or program basis, clients may need to be notified prior to record destruction. Records are destroyed in a manner that ensures their confidentiality such as shredding, mutilation or incineration. (Refer to Tables 14-1 and 14-2).

Electronic copies of records must be destroyed by erasure or physically damaging off-line storage media so no records can be read.

If a third party records management company is hired to dispose of records, a "Certificate of Destruction" is required.

SECTION 15. AUDITS

15.1 Internal Audits

Internal audits are performed to verify that laboratory operations comply with the requirements of the lab's quality system and with the external quality programs under which the laboratory operates. Audits are planned and organized by the QA staff. Personnel conducting the audits should be independent of the area being evaluated. Auditors will have sufficient authority, access to work areas, and organizational freedom necessary to observe all activities affecting quality and to report the assessments to laboratory management and**,** when requested**,** to corporate management.

Audits are conducted and documented as described in the TestAmerica Corporate SOP on performing Internal Auditing, SOP No. CW-Q-S-003. The types and frequency of routine internal

audits are described in Table 15-1. Special or ad hoc assessments may be conducted as needed under the direction of the QA staff.

Table 15-1. Types of Internal Audits and Frequency

Description	Performed by	Frequency
Quality Systems Audits	QA Department, QA approved designee, or Corporate QA	All areas of the laboratory annually
Method Audits QA Technical Audits	Joint responsibility: QA Manager or designee Technical Manager or Designee (Refer to CW-Q-S-003)	Technical Audits Frequency: 50% of methods annually
SOP Method Compliance	Joint responsibility: a) QA Manager or designee b) Technical Manager or Designee (Refer to CW-Q-S-003)	SOP Compliance Review Frequency: Every 2 years 100% of SOPs annually for methods and administrative SOPs related to DoD/DOE programs
Special	QA Department or Designee	Surveillance or spot checks performed as needed, e.g., to confirm corrective actions from other audits.
Performance Testing	Analysts with QA oversight	Two successful per year for each TNI-field of testing or as dictated by regulatory requirements

15.1.1 Annual Quality Systems Audit

An annual quality systems audit is required to ensure compliance to analytical methods and SOPs, TestAmerica's Data Integrity and Ethics Policies, TNI quality systems, client and state requirements, and the effectiveness of the internal controls of the analytical process, including but not limited to data review, quality controls, preventive action and corrective action. The completeness of earlier corrective actions is assessed for effectiveness & sustainability. The audit is divided into sections for each operating or support area of the lab, and each section is comprehensive for a given area. The area audits may be performed on a rotating schedule throughout the year to ensure adequate coverage of all areas. This schedule may change as situations in the laboratory warrant.

15.1.2 QA Technical Audits

QA technical audits assess data authenticity and analyst integrity. These audits are based on client projects, associated sample delivery groups, and the methods performed. Reported results are compared to raw data to verify the authenticity of results. The validity of calibrations and QC results are compared to data qualifiers, footnotes, and case narratives. Documentation is assessed by examining run logs and records of manual integrations. Manual calculations are checked. Where possible, electronic audit miner programs (e.g., Chrom AuditMiner) are used to identify unusual manipulations of the data deserving closer scrutiny. QA technical audits will include all methods within a two-year period. All analysts should be reviewed over the course of a two year period through at least one QA Technical Audit

15.1.3 SOP Method Compliance

Compliance of all SOPs with the source methods and compliance of the operational groups with the SOPs will be assessed by the Technical Manager or qualified designee at least every two years, annually for methods and administrative SOPs related to DoD/DOE programs. It is also recommended that the work of each newly hired analyst is assessed within 3 months of working independently, (e.g., completion of method IDOC). In addition, as analysts add methods to their capabilities, (new IDOC) reviews of the analyst work products will be performed within 3 months of completing the documented training.

15.1.4 Special Audits

Special audits are conducted on an as needed basis, generally as a follow up to specific issues such as client complaints, corrective actions, PT results, data audits, system audits, validation comments, regulatory audits or suspected ethical improprieties. Special audits are focused on a specific issue, and report format, distribution, and timeframes are designed to address the nature of the issue.

15.1.5 Performance Testing

The laboratory participates semi-annually in performance audits conducted through the analysis of PT samples provided by a third party. The laboratory generally participates in the following types of PT studies: UST, Drinking Water, Non Potable Water, and Solid Hazardous Waste.

It is TestAmerica's policy that PT samples be treated as typical samples in the production process. Furthermore, where PT samples present special or unique problems, in the regular production process they may need to be treated differently, as would any special or unique request submitted by any client. The QA Manager must be consulted and in agreement with any decisions made to treat a PT sample differently due to some special circumstance.

Written responses to unacceptable PT results are required. In some cases it may be necessary for blind QC samples to be submitted to the laboratory to show a return to control.

15.2 External Audits

External audits are performed when certifying agencies or clients conduct on-site inspections or submit performance testing samples for analysis. It is TestAmerica's policy to cooperate fully with regulatory authorities and clients. The laboratory makes every effort to provide the auditors with access to personnel, documentation, and assistance. Laboratory supervisors are responsible for providing corrective actions to the QA Manager who coordinates the response for any deficiencies discovered during an external audit. Audit responses are due in the time allotted by the client or agency performing the audit. When requested, a copy of the audit report and the labs corrective action plan will be forwarded to Corporate Quality.

The laboratory cooperates with clients and their representatives to monitor the laboratory's performance in relation to work performed for the client. The client may only view data and systems related directly to the client's work. All efforts are made to keep other client information confidential.

15.2.1 Confidential Business Information (CBI) Considerations

During on-site audits, auditors may come into possession of information claimed as business

confidential. A business confidentiality claim is defined as "a claim or allegation that business information is entitled to confidential treatment for reasons of business confidentiality or a request for a determination that such information is entitled to such treatment." When information is claimed as business confidential, the laboratory must place on (or attach to) the information at the time it is submitted to the auditor, a cover sheet, stamped or typed legend or other suitable form of notice, employing language such as "trade secret", "proprietary" or "company confidential". Confidential portions of documents otherwise non-confidential must be clearly identified. CBI may be purged of references to client identity by the responsible laboratory official at the time of removal from the laboratory. However, sample identifiers may not be obscured from the information. Additional information regarding CBI can be found in within the 2009 TNI standards.

15.3 Audit Findings

Audit findings are documented using the corrective action process and database. The laboratory's corrective action responses for both types of audits may include action plans that could not be completed within a predefined timeframe. In these instances, a completion date must be set and agreed to by operations management and the QA Manager.

Developing and implementing corrective actions to findings is the responsibility of the Technical Manager where the finding originated. Findings that are not corrected by specified due dates are reported monthly to management in the QA monthly report. When requested, a copy of the audit report and the labs corrective action plan will be forwarded to Corporate Quality.

If any audit finding casts doubt on the effectiveness of the operations or on the correctness or validity of the laboratory's test results, the laboratory shall take timely corrective action, and shall notify clients in writing if the investigations show that the laboratory results have been affected. Once corrective action is implemented, a follow-up audit is scheduled to ensure that the problem has been corrected.

Clients must be notified promptly in writing, of any event such as the identification of defective measuring or test equipment that casts doubt on the validity of results given in any test report or amendment to a test report. The investigation must begin within 24-hours of discovery of the problem and all efforts are made to notify the client within two weeks after the completion of the investigation.

SECTION 16. MANAGEMENT REVIEWS

16.2 Quality Assurance Report

A comprehensive QA Report shall be prepared each month by the laboratory's QA Department and forwarded to the Laboratory Director, Technical Managers, their Quality Director as well as the VP of Operations. All aspects of the QA system are reviewed to evaluate the suitability of policies and procedures. During the course of the year, the Laboratory Director, VP of Operations or Corporate QA may request that additional information be added to the report.

On a monthly basis, Corporate QA compiles information from all the monthly laboratory reports. The Corporate Quality Directors prepare a report that includes a compilation of all metrics and notable information and concerns regarding the QA programs within the laboratories. The report also

includes a listing of new regulations that may potentially impact the laboratories. This report is presented to the Senior Management Team and VPs of Operations.

16.3 Annual Management Review

The senior lab management team (Laboratory Director, Technical Managers, QA Manager) conducts a review annually of its quality systems and LIMS to ensure its continuing suitability and effectiveness in meeting client and regulatory requirements and to introduce any necessary changes or improvements. It will also provide a platform for defining goals, objectives and action items that feed into the laboratory planning system. Corporate Operations and Corporate QA personnel is be included in this meeting at the discretion of the Laboratory Director. The LIMS review consists of examining any audits, complaints or concerns that have been raised through the year that are related to the LIMS. The laboratory will summarize any critical findings that can not be solved by the lab and report them to Corporate IT.

This management systems review (Corporate SOP No. CW-Q-S-004 & Work Instruction No. CA-Q-WI-020) uses information generated during the preceding year to assess the “big picture” by ensuring that routine actions taken and reviewed on a monthly basis are not components of larger systematic concerns. The monthly review should keep the quality systems current and effective, therefore, the annual review is a formal senior management process to review specific existing documentation. Significant issues from the following documentation are compiled or summarized by the QA Manager prior to the review meeting:

- Matters arising from the previous annual review.
- Prior Monthly QA Reports issues.
- Laboratory QA Metrics.
- Review of report reissue requests.
- Review of client feedback and complaints.
- Issues arising from any prior management or staff meetings.
- Minutes from prior senior lab management meetings. Issues that may be raised from these meetings include:
    - Adequacy of staff, equipment and facility resources.
    - Adequacy of policies and procedures.
    - Future plans for resources and testing capability and capacity.
- The annual internal double blind PT program sample performance (if performed),
- Compliance to the Ethics Policy and Data Integrity Plan. Including any evidence/incidents of inappropriate actions or vulnerabilities related to data Integrity.

A report is generated by the QA Manager and management. The report is distributed to the appropriate VP of Operation and the Quality Director. The report includes, but is not limited to:

- The date of the review and the names and titles of participants.
- A reference to the existing data quality related documents and topics that were reviewed.

- Quality system or operational changes or improvements that will be made as a result of the review [e.g., an implementation schedule including assigned responsibilities for the changes (Action Table)].

Changes to the quality systems requiring update to the laboratory QA Manual shall be included in the next revision of the QA Manual.

16.4 Potential Integrity Related Managerial Reviews

Potential integrity issues (data or business related) must be handled and reviewed in a confidential manner until such time as a follow-up evaluation, full investigation, or other appropriate actions have been completed and issues clarified. TestAmerica's Corporate Data Investigations SOP shall be followed (SOP No. CW-L-S-002). All investigations that result in finding of inappropriate activity are documented and include any disciplinary actions involved, corrective actions taken, and all appropriate notifications of clients.

TestAmerica's President and CEO, Executive VP of Operations, VP of Client & Technical Services, VPs of Operations and Quality Directors receive a monthly report from the VP-QA/EHS summarizing any current data integrity or data recall investigations. The VPs of Operations are also made aware of progress on these issues for their specific labs.

SECTION 17. PERSONNEL

17.1 Overview

The laboratory's management believes that its highly qualified and professional staff is the single most important aspect in assuring a high level of data quality and service. The staff consists of professionals and support personnel as outlined in the organization chart in Figure 4-1.

All personnel must demonstrate competence in the areas where they have responsibility. Any staff that is undergoing training shall have appropriate supervision until they have demonstrated their ability to perform their job function on their own. Staff shall be qualified for their tasks based on appropriate education, training, experience and/or demonstrated skills as required.

The laboratory employs sufficient personnel with the necessary education, training, technical knowledge and experience for their assigned responsibilities.

All personnel are responsible for complying with all QA/QC requirements that pertain to the laboratory and their area of responsibility. Each staff member must have a combination of experience and education to adequately demonstrate a specific knowledge of their particular area of responsibility. Technical staff must also have a general knowledge of lab operations, test methods, QA/QC procedures and records management.

Laboratory management is responsible for formulating goals for lab staff with respect to education, training and skills and ensuring that the laboratory has a policy and procedures for identifying training needs and providing training of personnel. The training shall be relevant to the present and anticipated responsibilities of the lab staff.

The laboratory only uses personnel that are employed by or under contract to, the laboratory. Contracted personnel, when used, must meet competency standards of the laboratory and work in accordance to the laboratory's quality system.

17.2 Education and Experience Requirements for Technical Personnel

The laboratory makes every effort to hire analytical staffs that possess a college degree (AA, BA, BS) in an applied science with some chemistry in the curriculum. Exceptions can be made based upon the individual's experience and ability to learn. Selection of qualified candidates for laboratory employment begins with documentation of minimum education, training, and experience prerequisites needed to perform the prescribed task. Minimum education and training requirements for TestAmerica employees are outlined in job descriptions and are generally summarized for analytical staff in the table below.

The laboratory maintains job descriptions for all personnel who manage, perform or verify work affecting the quality of the environmental testing the laboratory performs. Job Descriptions are located on the TestAmerica intranet site's Human Resources web-page (Also see Section 4 for position descriptions/responsibilities).

Experience and specialized training are occasionally accepted in lieu of a college degree (basic lab skills such as using a balance, colony counting, aseptic or quantitation techniques, etc., are also considered).

As a general rule for analytical staff:

Specialty	Education	Experience
Extractions, Digestions, some electrode methods (pH, DO, Redox, etc.), or Titrimetric and Gravimetric Analyses	H.S. Diploma	On the job training (OJT)
GFAA, CVAA, FLAA, Single component or short list Chromatography (e.g., Fuels, BTEX-GC, IC	A college degree in an applied science or 2 years of college and at least 1 year of college chemistry	Or 2 years prior analytical experience is required
ICP, ICPMS, Long List or complex chromatography (e.g., Pesticides, PCB, Herbicides, HPLC, etc.), GCMS	A college degree in an applied science or 2 years of college chemistry	or 5 years of prior analytical experience
Spectra Interpretation	A college degree in an applied science or 2 years of college chemistry	And 2 years relevant experience Or 5 years of prior analytical experience

Specialty	Education	Experience
Technical Managers – **General**	Bachelors Degree in an applied science or engineering with 24 semester hours in chemistry An advanced (MS, PhD.) degree may substitute for one year of experience	And 2 years experience in environmental analysis of representative analytes for which they will oversee
Technical Managers – **Wet Chem** only (no advanced instrumentation)	Associates degree in an applied science or engineering or 2 years of college with 16 semester hours in chemistry	And 2 years relevant experience

When an analyst does not meet these requirements, they can perform a task under the direct supervision of a qualified analyst, peer reviewer or Technical Manager, and are considered an analyst in training. The person supervising an analyst in training is accountable for the quality of the analytical data and must review and approve data and associated corrective actions.

17.3 Training

The laboratory is committed to furthering the professional and technical development of employees at all levels.

Orientation to the laboratory's policies and procedures, in-house method training, and employee attendance at outside training courses and conferences all contribute toward employee proficiency. Below are examples of various areas of required employee training:

Required Training	Time Frame	Employee Type
Environmental Health & Safety	Prior to lab work	All
Ethics – New Hires	1 week of hire	All
Ethics – Comprehensive	90 days of hire	All
Data Integrity	30 days of hire	Technical and PMs
Quality Assurance	90 days of hire	All
Ethics – Comprehensive Refresher	Annually	All
Initial Demonstration of Capability (DOC)	Prior to unsupervised method performance	Technical

The laboratory maintains records of relevant authorization/competence, education, professional qualifications, training, skills and experience of technical personnel (including contracted personnel) as well as the date that approval/authorization was given. These records are kept on file at the laboratory. Also refer to "Demonstration of Capability" in Section 19.

The training of technical staff is kept up to date by:

- Each employee must have documentation in their training file that they have read, understood and agreed to follow the most recent version of the laboratory QA Manual and SOPs in their area of responsibility. This documentation is updated as SOPs are updated.
- Documentation from any training courses or workshops on specific equipment, analytical techniques or other relevant topics are maintained in their training file.
- Documentation of proficiency (refer to Section 19).
- An Ethics Agreement signed by each staff member (renewed each year) and evidence of annual ethics training.
- A Confidentiality Agreement signed by each staff member signed at the time of employment.
- Human Resources maintains documentation and attestation forms on employment status & records; benefit programs; timekeeping/payroll; and employee conduct (e.g., ethics violations). This information is maintained in the employee's secured personnel file.

Evidence of successful training could include such items as:

- Adequate documentation of training within operational areas, including one-on-one technical training for individual technologies, and particularly for people cross-trained.
- Analysts knowledge to refer to QA Manual for quality issues.
- Analysts following SOPs, i.e., practice matches SOPs.
- Analysts regularly communicate to supervisors and QA if SOPs need revision, rather than waiting for auditors to find problems.

Further details of the laboratory's training program are described in the Employee Training SOP (TA-QA-0608).

17.4 Data Integrity and Ethics Training Program

Establishing and maintaining a high ethical standard is an important element of a Quality System. Ethics and data integrity training is integral to the success of TestAmerica and is provided for each employee at TestAmerica. It is a formal part of the initial employee orientation within 1 week of hire followed by technical data integrity training within 30 days, comprehensive training within 90 days, and an annual refresher for all employees. Senior management at each facility performs the ethics training for their staff.

In order to ensure that all personnel understand the importance TestAmerica places on maintaining high ethical standards at all times; TestAmerica has established a Corporate Ethics Policy (Policy No. CW-L-P-004) and an Ethics Statement. All initial and annual training is documented by signature on the signed Ethics Statement demonstrating that the employee has participated in the training and understands their obligations related to ethical behavior and data integrity.

Violations of this Ethics Policy will not be tolerated. Employees who violate this policy will be subject to disciplinary actions up to and including termination. Criminal violations may also be referred to the Government for prosecution. In addition, such actions could jeopardize TestAmerica's ability to

do work on Government contracts, and for that reason, TestAmerica has a Zero Tolerance approach to such violations.

Employees are trained as to the legal and environmental repercussions that result from data misrepresentation. Key topics covered in the presentation include:

- Organizational mission and its relationship to the critical need for honesty and full disclosure in all analytical reporting.
- Ethics Policy
- How and when to report ethical/data integrity issues. Confidential reporting.
- Record keeping.
- Discussion regarding data integrity procedures.
- Specific examples of breaches of ethical behavior (e.g. peak shaving, altering data or computer clocks, improper macros, etc., accepting/offering kickbacks, illegal accounting practices, unfair competition/collusion)
- Internal monitoring. Investigations and data recalls.
- Consequences for infractions including potential for immediate termination, debarment, or criminal prosecution.
- Importance of proper written narration / data qualification by the analyst and project manager with respect to those cases where the data may still be usable but are in one sense or another partially deficient.

Additionally, a data integrity hotline (1-800-736-9407) is maintained by TestAmerica and administered by the Corporate Quality Department.

SECTION 18. ACCOMMODATIONS AND ENVIRONMENTAL CONDITIONS

18.1 Overview

The laboratory is a 20,000 ft^2 secure laboratory facility with controlled access and designed to accommodate an efficient workflow and to provide a safe and comfortable work environment for employees. All visitors sign in and are escorted by laboratory personnel. Access is controlled by various measures.

The laboratory is equipped with structural safety features. Each employee is familiar with the location, use, and capabilities of general and specialized safety features associated with their workplace. The laboratory provides and requires the use of protective equipment including safety glasses, protective clothing, gloves, etc., OSHA and other regulatory agency guidelines regarding required amounts of bench and fume hood space, lighting, ventilation (temperature and humidity controlled at fixed laboratory), access, and safety equipment are met or exceeded.

Traffic flow through sample preparation and analysis areas is minimized to reduce the likelihood of contamination. Adequate floor space and bench top area is provided to allow unencumbered sample preparation and analysis space. Sufficient space is also provided for storage of reagents and media, glassware, and portable equipment. Ample space is also provided for refrigerated sample storage

before analysis and archival storage of samples after analysis. The fixed laboratory HVAC and deionized water systems are designed to minimize potential trace contaminants.

The laboratory is separated into specific areas for sample receiving, sample preparation, volatile organic sample analysis, non-volatile organic sample analysis, inorganic sample analysis and administrative functions.

18.2 Environment

Laboratory accommodation, test areas, energy sources, lighting are adequate to facilitate proper performance of tests. The fixed facility is equipped with heating, ventilation, and air conditioning (HVAC) systems appropriate to the needs of environmental testing performed at this laboratory.

The environment in which these activities are undertaken does not invalidate the results or adversely affect the required accuracy of any measurements.

The laboratory provides for the effective monitoring, control and recording of environmental conditions that may affect the results of environmental tests as required by the relevant specifications, methods, and procedures. Such environmental conditions include temperature levels in the laboratory.

When any of the method or regulatory required environmental conditions change to a point where they may adversely affect test results, analytical testing will be discontinued until the environmental conditions are returned to the required levels.

Environmental conditions of the facility housing the computer network and LIMS are regulated to protect against raw data loss.

18.3 Work Areas

There is effective separation between neighboring areas when the activities therein are incompatible with each other. Examples include:

- Volatile organic chemical handling areas, including sample preparation and waste disposal, and volatile organic chemical analysis areas.

Access to and use of all areas affecting the quality of analytical testing is defined and controlled by secure access to the laboratory building as described below in the Building Security section.

Adequate measures are taken to ensure good housekeeping in the laboratory and to ensure that any contamination does not adversely affect data quality. These measures include regular cleaning to control dirt and dust within the laboratory. Work areas are available to ensure an unencumbered work area. Work areas include:

- Access and entryways to the laboratory.
- Sample receipt areas.
- Sample storage areas.
- Chemical and waste storage areas.

- Data handling and storage areas.
- Sample processing areas.
- Sample analysis areas.

18.4 Floor Plan

The fixed laboratory floor plan can be found in Appendix 1.

18.5 Building Security

Building keys are distributed to employees as necessary.

Visitors to the laboratory sign in and out in a visitor's logbook. A visitor is defined as any person who visits the laboratory who is not an employee of the laboratory. In addition to signing into the laboratory, the Environmental, Health and Safety Manual contains requirements for visitors and vendors. There are specific safety forms that must be reviewed and signed. Visitors (with the exception of company employees) are escorted by laboratory personnel at all times, or the location of the visitor is noted in the visitor's logbook.

SECTION 19. TEST METHODS AND METHOD VALIDATION

19.1 Overview

The laboratory uses methods that are appropriate to meet our clients' requirements and that are within the scope of the laboratory's capabilities. These include sampling, handling, transport, storage and preparation of samples, and, where appropriate, an estimation of the measurement of uncertainty as well as statistical techniques for analysis of environmental data.

Instructions are available in the laboratory for the operation of equipment as well as for the handling and preparation of samples. All instructions, Standard Operating Procedures (SOPs), reference methods and manuals relevant to the working of the laboratory are readily available to all staff. Deviations from published methods are documented (with justification) in the laboratory's approved SOPs. SOPs are submitted to clients for review at their request. Significant deviations from published methods require client approval and regulatory approval where applicable.

19.2 Standard Operating Procedures (SOPS)

The laboratory maintains SOPs that accurately reflect all phases of the laboratory such as assessing data integrity, corrective actions, handling customer complaints as well as all analytical methods and sampling procedures. The method SOPs are derived from the most recently promulgated/approved, published methods and are specifically adapted to the laboratory facility. Modifications or clarifications to published methods are clearly noted in the SOPs. All SOPs are controlled in the laboratory.

- All SOPs contain a revision number, effective date, and appropriate approval signatures. Controlled copies are available to all staff.

- Procedures for writing an SOP are incorporated by reference to TestAmerica's Corporate SOP entitled 'Writing a Standard Operating Procedure', No. CW-Q-S-002 and the laboratory's SOP TA-QA-0500 Standard Operating Procedures.
- SOPs are reviewed at a minimum of every 2 years (annually for DoD/DOE SOPs), and where necessary, revised to ensure continuing suitability and compliance with applicable requirements.

19.3 Laboratory Methods Manual

For each test method, the laboratory shall have available the published referenced method as well as the laboratory developed SOP.

Note: If more stringent standards or requirements are included in a mandated test method or regulation than those specified in this manual, the laboratory shall demonstrate that such requirements are met. If it is not clear which requirements are more stringent, the standard from the method or regulation is to be followed. Any exceptions or deviations from the referenced methods or regulations are noted in the specific analytical SOP.

The laboratory maintains an SOP Index for both technical and non-technical SOPs. Technical SOPs are maintained to describe a specific test method. Non-technical SOPs are maintained to describe functions and processes not related to a specific test method.

19.4 Selection of Methods

Since numerous methods and analytical techniques are available, continued communication between the client and laboratory is imperative to assure the correct methods are utilized. Once client methodology requirements are established, this and other pertinent information is summarized by the Project Manager. These mechanisms ensure that the proper analytical methods are applied when the samples arrive for log-in. For non-routine analytical services (e.g., special matrices, non-routine compound lists), the method of choice is selected based on client needs and available technology. The methods selected should be capable of measuring the specific parameter of interest, in the concentration range of interest, and with the required precision and accuracy.

19.4.1 Sources of Methods

Routine analytical services are performed using standard EPA-approved methodology. In some cases, modification of standard approved methods may be necessary to provide accurate analyses of particularly complex matrices. When the use of specific methods for sample analysis is mandated through project or regulatory requirements, only those methods shall be used.

When clients do not specify the method to be used or methods are not required, the methods used will be clearly validated and documented in an SOP and available to clients and/or the end user of the data.

The analytical methods used by the laboratory are those currently accepted and approved by the U. S. EPA and the state or territory from which the samples were collected. Reference methods include:

- Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; 40CFR Part 136 as amended by Method Update Rule; *August 28, 2017.*

- Methods for Chemical Analysis of Water and Wastes, EPA 600 (4-79-020), 1983.
- Methods for the Determination of Inorganic Substances in Environmental Samples, EPA-600/R-93/100, August 1993.
- Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, June 1991. Supplement I: EPA-600/R-94/111, May 1994.
- NIOSH Manual of Analytical Methods, 4th ed., August 1994.
- Standard Methods for the Examination of Water and Wastewater, 18th/19th /20th/ on-line edition; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C.
- Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996; Final Update IV, January 2008.
- Annual Book of ASTM Standards, American Society for Testing & Materials (ASTM), Philadelphia, PA.
- National Status and Trends Program, National Oceanographic and Atmospheric Administration, Volume I-IV, 1985-1994.
- Code of Federal Regulations (CFR) 40, Parts 136, 141, 172, 173, 178, 179 and 261
- Plumb, Jr., R.H. 1981, Procedures for Handling and Chemical Analysis of Sediment and Water Samples, Technical Report EPA/C E-81-1. US Army Engineering Waterways Experiment Station, Vicksburg, MS.
- Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound, April 2003.
- Recommended Guidelines for Measuring Organic Compounds in Puget Sound Waters, Sediment and Tissue Samples, April 1997.
- Recommended Guidelines for Measuring Metals in Puget Sound Waters, Sediment and Tissue Samples, April 1997.

The laboratory reviews updated versions to all the aforementioned references for adaptation based upon capabilities, instrumentation, etc., and implements them as appropriate. As such, the laboratory strives to perform only the latest versions of each approved method as regulations allow or require.

Other reference procedures for non-routine analyses may include methods established by specific states (e.g., Underground Storage Tank methods), ASTM or equipment manufacturers. Sample type, source, and the governing regulatory agency requiring the analysis will determine the method utilized.

The laboratory shall inform the client when a method proposed by the client may be inappropriate or out of date. After the client has been informed, and they wish to proceed contrary to the laboratory's recommendation, it will be documented.

19.4.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. In general, this demonstration does not test the performance of the method in real world samples, but in an applicable and available clean matrix sample. If the method is for the testing of analytes that are not conducive to spiking, demonstration of capability may be performed on quality control samples.

A demonstration of capability (Analyst DOC, Lab SOP # TA-QA-0617) is performed whenever there is a change in instrument type (e.g., new instrumentation), method or personnel (e.g., analyst hasn't performed the test within the last 12 months).

Note: The laboratory shall have a DOC for all analytes included in the methods that the laboratory performs, and proficiency DOCs for each analyst shall include all analytes that the laboratory routinely performs. Addition of non-routine analytes does not require new DOCs for all analysts if those analysts are already qualified for routine analytes tested using identical chemistry and instrument conditions.

The initial demonstration of capability must be thoroughly documented and approved by the Technical Manager and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in accordance with the laboratories archiving procedures.

The laboratory must have an approved SOP, demonstrate satisfactory performance, and conduct an MDL study (when applicable). There may be other requirements as stated within the published method or regulations (i.e., retention time window study).

Note: In some instances, a situation may arise where a client requests that an unusual analyte be reported using a method where this analyte is not normally reported. If the analyte is being reported for regulatory purposes, the method must meet all procedures outlined within this QA Manual (SOP, MDL, and Demonstration of Capability). If the client states that the information is not for regulatory purposes, the result may be reported as long as the following criteria are met:

- The instrument is calibrated for the analyte to be reported using the criteria for the method and ICV/CCV criteria are met (unless an ICV/CCV is not required by the method or criteria are per project DQOs).
- The laboratory's nominal or default reporting limit (RL) is equal to the quantitation limit (QL), must be at or above the lowest non-zero standard in the calibration curve and must be reliably determined. Project RLs are client specified reporting levels which may be higher than the QL. Results reported below the QL must be qualified as estimated values. Also see Section 19.6.1.3, Relationship of Limit of Detection (LOD) to Quantitation Limit (QL).
- The client request is documented and the lab informs the client of its procedure for working with unusual compounds. The final report must be footnoted: Reporting Limit based on the low standard of the calibration curve.

19.4.3 Initial Demonstration of Capability (IDOC) Procedures

19.4.3.1 The spiking standard used must be prepared independently from those used in instrument calibration.

19.4.3.2 The analyte(s) shall be diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified by a method or the laboratory SOP.

19.4.3.3 At least four aliquots shall be prepared (including any applicable clean-up procedures) and analyzed according to the test method (either concurrently or over a period of days).

19.4.3.4 Using all of the results, calculate the mean recovery in the appropriate reporting units and the standard deviations for each parameter of interest.

19.4.3.5 When it is not possible to determine the mean and standard deviations, such as for presence, absence and logarithmic values, the laboratory will assess performance against criteria described in the Method SOP.

19.4.3.6 Compare the information obtained above to the corresponding acceptance criteria for precision and accuracy in the test method (if applicable) or in laboratory generated acceptance criteria (LCS or interim criteria) if there is no mandatory criteria established. If any one of the parameters do not meet the acceptance criteria, the performance is unacceptable for that parameter.

19.4.3.7 When one or more of the tested parameters fail at least one of the acceptance criteria, the analyst must proceed according to either option listed below:

- Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with 19.4.3.3 above.
- Beginning with 19.4.3.3 above, repeat the test for all parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 19.4.3.1 above.

Note: Results of successive LCS analyses can be used to fulfill the DOC requirement.

A certification statement (refer to Figure 19-1 as an example) shall be used to document the completion of each initial demonstration of capability. A copy of the certification is archived in the analyst's training folder.

Methods on line prior to the effective date of this Section shall be updated to the procedures outlined above as new analysts perform their demonstration of capability. A copy of the new record will replace that which was used for documentation in the past. At a minimum, the precision and accuracy of four mid-level laboratory control samples must have been compared to the laboratory's quality control acceptance limits.

19.5 Laboratory Developed Methods and Non-Standard Methods

Any new method developed by the laboratory must be fully defined in an SOP and validated by qualified personnel with adequate resources to perform the method. Method specifications and the relation to client requirements must be clearly conveyed to the client if the method is a non-standard method (not a published or routinely accepted method). The client must also be in agreement to the use of the non-standard method.

19.6 Validation of Methods

Validation is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled.

All non-standard methods, laboratory designed/developed methods, standard methods used outside of their scope, and major modifications to published methods must be validated to confirm they are fit for their intended use. The validation will be as extensive as necessary to meet the needs of the

given application. The results are documented with the validation procedure used and contain a statement as to the fitness for use.

19.6.1 Method Validation and Verification Activities for All New Methods

While method validation can take various courses, the following activities can be required as part of method validation. Method validation records are designated QC records and are archived accordingly.

19.6.1.1 Determination of Method Selectivity – Method selectivity is the demonstrated ability to discriminate the analyte(s) of interest from other compounds in the specific matrix or matrices from other analytes or interference. In some cases to achieve the required selectivity for an analyte, a confirmation analysis is required as part of the method.

19.6.1.2 Determination of Method Sensitivity – Sensitivity can be both estimated and demonstrated. Whether a study is required to estimate sensitivity depends on the level of method development required when applying a particular measurement system to a specific set of samples. *Detection limit studies are conducted as described in Section 19.7 below*. Where *other protocols for* estimations and/or demonstrations of sensitivity are required by regulation or client agreement, these shall be followed.

19.6.1.3 Relationship of Limit of Detection (LOD) to the *Limit of Quantitation (LOQ)* – An important characteristic of expression of sensitivity is the *distinction between the LOD and the LOQ*. The LOD is the minimum level at which the presence of an analyte can be reliably concluded. The *LOQ* is the minimum concentration of analyte that can be quantitatively determined with acceptable precision and bias, *equivalent to the laboratory's routine reporting limit (RL).* For most instrumental measurement systems, there is a region where semi-quantitative data is generated around the LOD (both above and below the estimated MDL or LOD) and below the *LOQ*. In this region, detection of an analyte may be confirmed but quantification of the analyte is unreliable within the accuracy and precision guidelines of the measurement system. When an analyte is detected below the *LOQ*, and the presence of the analyte is confirmed by meeting the qualitative identification criteria for the analyte, the analyte can be reliably reported, but the amount of the analyte can only be estimated. If data is to be reported in this region, it must be done so with a qualification that denotes the semi-quantitative nature of the result.

19.6.1.4 Determination of Interferences – A determination that the method is free from interferences in a blank matrix is performed.

19.6.1.5 Determination of Range – Where appropriate to the method, the quantitation range is determined by comparison of the response of an analyte in a curve to established or targeted criteria. Generally the upper quantitation limit is defined by highest acceptable calibration concentration. The lower quantitation limit or QL cannot be lower than the lowest non-zero calibration level, and can be constrained by required levels of bias and precision.

19.6.1.6 Determination of Accuracy and Precision – Accuracy and precision studies are generally performed using replicate analyses, with a resulting percent recovery and measure of reproducibility (standard deviation, relative standard deviation) calculated and measured against a set of target criteria.

19.6.1.7 Documentation of Method – The method is formally documented in an SOP. If the method is a minor modification of a standard laboratory method that is already documented in an SOP, an SOP Attachment describing the specific differences in the new method is acceptable in place of a separate SOP.

19.6.1.8 Continued Demonstration of Method Performance – Continued demonstration of Method Performance is addressed in the SOP. Continued demonstration of method performance is generally accomplished by batch specific QC samples such as LCS, method blanks or PT samples.

19.7 Method Detection Limits (MDL) / Limits of Detection (LOD)

The MDL is the minimum measured quantity of a substance that can be reported with 99% confidence that the concentration is distinguishable from method blank results, consistent with 40CFR Part 136 Appendix B, August, 2017. The MDL is equivalent to the TNI LOD, and is also equivalent to the DoD/DOE Quality Systems Manual (QSM) DL. The working or final MDL is the higher of the MDL value determined from spikes (MDLs) and the MDL value determined from blanks (MDLb). An initial MDL study shall be performed during the method validation process and when the method is altered in a way that can reasonably be expected to change its sensitivity. On-going data are collected during each quarter in which samples are being analyzed. At least once every 13 months the MDLs and MDLb are re-calculated and re-evaluated using data collected during the preceeding period. Details of TestAmerica's procedure for conducting MDL studies are given in SOP # CA-Q-S-006).

19.8 Verification of Detection Reporting Limits

If it is found during the re-evaluation of detection limit results that more than 5% of the spiked samples do not return positive numeric results that meet all method qualitative identification criteria, then then spiking level shall be increased and the initial MDL study performed at the new spiking concentration. For DoD/DOE labs, additional requirements are given in Attachment 2 of SOP # CA-Q-S-006.

19.9 Instrument Detection Limits (IDL)

The IDL is sometimes used to assess the reasonableness of the MDLs or in some cases required by the analytical method or program requirements. IDLs are most used in metals analyses, but may be useful in demonstration of instrument performance in other areas.

IDLs are calculated to determine an instrument's sensitivity independent of any preparation method. IDLs are calculated either using 7 replicate spike analyses, like MDL but without sample preparation, or by the analysis of 10 instrument blanks and calculating 3 x the absolute value of the standard deviation.

19.10 Limit of Quantitation (LOQ)

The LOQ shall be at a concentration equivalent to the lowest calibration standard concentration, with the exceptin of methods using a single-point calibration, and shall be greater than the MDL. The LOQ is verified by preparing and analyzing spikes at concentrations two (2) times or less than the selected LOQ, employing the complete analytical process. For DoD/DOE labs, additional requirements are given in Attachment 2 of SOP # CA-Q-S-006.

19.10 Retention Time Windows

Most organic analyses and some inorganic analyses use chromatography techniques for qualitative and quantitative determinations. For every chromatography analysis or as specific in the reference method, each analyte will have a specific time of elution from the column to the detector. This is known as the analytes retention time. The variance in the expected time of elution is defined as the retention time window. As the key to analyte identification in chromatography, retention time windows must be established on every column for every analyte used for that method. These records are kept with the files associated with an instrument for later quantitation of the analytes. Complete details are available in the laboratory SOPs.

19.11 Evaluation of Selectivity

The laboratory evaluates selectivity by following the checks within the applicable analytical methods, which include mass spectral tuning, second column confirmation, ICP interelement interference checks, chromatography retention time windows, sample blanks, spectrochemical, atomic absorption profiles, co-precipitation evaluations and specific electrode response factors.

19.12 Estimation of Uncertainty of Measurement

19.12.1 Uncertainty is "a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand" (as defined by the International Vocabulary of Basic and General Terms in Metrology, ISO Geneva, 1993, ISBN 92-67-10175-1). Knowledge of the uncertainty of a measurement provides additional confidence in a result's validity. Its value accounts for all the factors which could possibly affect the result, such as adequacy of analyte definition, sampling, matrix effects and interferences, climatic conditions, variances in weights, volumes, and standards, analytical procedure, and random variation. Some national accreditation organizations require the use of an "expanded uncertainty": the range within which the value of the measurand is believed to lie within at least a 95% confidence level with the coverage factor k=2.

19.12.2 Uncertainty is not error. Error is a single value, the difference between the true result and the measured result. On environmental samples, the true result is never known. The measurement is the sum of the unknown true value and the unknown error. Unknown error is a combination of systematic error, or bias, and random error. Bias varies predictably, constantly, and independently from the number of measurements. Random error is unpredictable, assumed to be Gaussian in distribution, and reducible by increasing the number of measurements.

19.12.3 The minimum uncertainty associated with results generated by the laboratory can be determined by using the Laboratory Control Sample (LCS) accuracy range for a given analyte. The LCS limits are used to assess the performance of the measurement system since they take into consideration all of the laboratory variables associated with a given test over time (except for variability associated with the sampling and the variability due to matrix effects). The percent recovery of the LCS is compared either to the method-required LCS accuracy limits or to the statistical, historical, in-house LCS accuracy limits.

19.12.4 To calculate the uncertainty for the specific result reported, multiply the result by the decimal of the lower end of the LCS range percent value for the lower end of the uncertainty range, and multiply the result by the decimal of the upper end of the LCS range percent value for the upper end of the uncertainty range. These calculated values represent uncertainties at approximately the 99% confidence level with a coverage factor of k = 3. As an example, for a reported result of 1.0

mg/l with an LCS recovery range of 50 to 150%, the estimated uncertainty in the result would be 1.0 +/- 0.5 mg/l.

19.12.5 In the case where a well recognized test method specifies limits to the values of major sources of uncertainty of measurement (e.g., 524.2, 525, etc.) and specifies the form of presentation of calculated results, no further discussion of uncertainty is required.

19.13 Sample Reanalysis Guidelines

Because there is a certain level of uncertainty with any analytical measurement, a sample re-preparation (where appropriate) and subsequent analysis (hereafter referred to as 'reanalysis') may result in either a higher or lower value from an initial sample analysis. There are also variables that may be present (e.g., sample homogeneity, analyte precipitation over time, etc.) that may affect the results of a reanalysis. Based on the above comments, the laboratory will reanalyze samples at a client's request with the following caveats. Client specific Contractual Terms & Conditions for reanalysis protocols may supersede the following items.

- Homogenous samples: If a reanalysis agrees with the original result to within the RPD limits for MS/MSD or Duplicate analyses, or within $\pm$ 1 reporting limit for samples $\leq$ 5x the reporting limit, the original analysis will be reported. At the client's request, both results may be reported on the same report but not on two separate reports.

- If the reanalysis does not agree (as defined above) with the original result, then the laboratory will investigate the discrepancy and reanalyze the sample a third time for confirmation if sufficient sample is available.

- Any potential charges related to reanalysis are discussed in the contract terms and conditions or discussed at the time of the request. The client will typically be charged for reanalysis unless it is determined that the lab was in error.

- Due to the potential for increased variability, reanalysis may not be applicable to Non-homogenous, Encore, and Sodium Bisulfate preserved samples. See the Area Technical Manager or Laboratory Director if unsure.

19.14 Control of Data

The laboratory has policies and procedures in place to ensure the authenticity, integrity, and accuracy of the analytical data generated by the laboratory.

19.14.1 Computer and Electronic Data Related Requirements

The three basic objectives of our computer security procedures and policies are shown below. More detail is outlined in SOP TA-IT-0523 Data Integrity and Security. The laboratory is currently running the TALS system which is a custom in-house developed LIMS system that has been highly customized to meet the needs of the laboratory. It is referred to as LIMS for the remainder of this section. The LIMS utilizes Sequel Server which is an industry standard relational database platform. It is referred to as Database for the remainder of this section.

19.14.1.1 **Maintain the Database Integrity** – Assurance that data is reliable and accurate through data verification (review) procedures, password-protecting access, anti-virus protection, data change requirements, as well as an internal LIMS permissions procedure.

- LIMS Database Integrity is achieved through data input validation, internal user controls, and data change requirements.
- Spreadsheets and other software developed in-house must be verified with documentation through hand calculations prior to use. Cells containing calculations must be lock-protected and controlled.
- Instrument hardware and software adjustments are safeguarded through maintenance logs, audit trails and controlled access.

19.14.1.2 **Ensure Information Availability** – Protection against loss of information or service is ensured through scheduled back-ups, stable file server network architecture, secure storage of media, line filter, Uninterruptible Power Supply (UPS), and maintaining older versions of software as revisions are implemented.

19.14.1.3 **Maintain Confidentiality** – Ensure data confidentiality through physical access controls such as password protection or website access approval when electronically transmitting data.

19.14.2 Data Reduction

The complexity of the data reduction depends on the analytical method and the number of discrete operations involved (e.g., extractions, dilutions, instrument readings and concentrations). The analyst calculates the final results from the raw data or uses appropriate computer programs to assist in the calculation of final reportable values.

For manual data entry, e.g., Wet Chemistry, the data is reduced by the analyst and then verified by the Department Manager or alternate analyst prior to updating the data in LIMS. The spreadsheets, or any other type of applicable documents, are signed by both the analyst and alternate reviewer to confirm the accuracy of the manual entry(s).

Manual integration of peaks will be documented and reviewed and the raw data will be flagged in accordance with the TestAmerica Corporate SOP No. CA-Q-S-002, Acceptable Manual Integration Practices.

Analytical results are reduced to appropriate concentration units specified by the analytical method, taking into account factors such as dilution, sample weight or volume, etc. Blank correction will be applied only when required by the method or per manufacturer's indication; otherwise, it should not be performed. Calculations are independently verified by appropriate laboratory staff. Calculations and data reduction steps for various methods are summarized in the respective analytical SOPs or program requirements.

19.14.2.1 All raw data must be retained in the worklist folder, computer file (if appropriate), and/or run log. All criteria pertinent to the method must be recorded. The documentation is recorded at the time observations or calculations are made and must be signed or initialed/dated (month/day/year). It must be easily identifiable who performed which tasks if multiple people were involved.

19.14.2.2 In general, concentration results are reported in milligrams per liter (mg/L) or micrograms per liter (µg/l) for liquids and milligrams per kilogram (mg/Kg) or micrograms per kilogram (µg/Kg) for

solids. For values greater than 10,000 mg/L, results can be reported in percent, i.e., 10,000 mg/l = 1%. Units are defined in each lab SOP.

19.14.2.3 In reporting, the analyst or the instrument output records the raw data result using values of known certainty plus one uncertain digit. If final calculations are performed external to LIMS, the results should be entered in LIMS with at least three significant figures. In general, results are reported to 2 significant figures on the final report.

19.14.2.4 For those methods that do not have an instrument printout or an instrumental output compatible with the LIMS System, the raw results and dilution factors are entered directly into LIMS by the analyst, and the software calculates the final result for the analytical report. LIMS has a defined significant figure criterion for each analyte.

19.14.2.5 The laboratory strives to import data directly from instruments or calculation spreadsheets to ensure that the reported data are free from transcription and calculation errors. For those analyses with an instrumental output compatible with the LIMS, the raw results and dilution factors are transferred into LIMS electronically after reviewing the quantitation report, and removing unrequested or poor spectrally-matched compounds. The analyst prints a copy of what has been entered to check for errors. This printout and the instrument's printout of calibrations, concentrations, retention times, chromatograms, and mass spectra, if applicable, are retained with the data file. The data file is stored in a monthly folder on the instrument computer; periodically, this file is transferred to the server and, eventually, to a tape file.

19.14.3 Logbook / Worksheet Use Guidelines

Logbooks and worksheets are filled out 'real time' and have enough information on them to trace the events of the applicable analysis/task. (e.g. calibrations, standards, analyst, sample ID, date, time on short holding time tests, temperatures when applicable, calculations are traceable, etc.)

- Corrections are made following the procedures outlined in Section 12.
- Logbooks are controlled by the QA department. A record is maintained of all logbooks in the lab.
- Unused portions of pages must be "Z"'d out, signed and dated.
- Worksheets are created with the approval of the Technical Manager and QA Manager at the facility. The QA Manager controls all worksheets following the procedures in Section 6.

19.14.4 Review / Verification Procedures

Review procedures are outlined in several SOPs (e.g. SOP TA-QA-0001, Sample Receipt and Log-in, SOP TA-QA-0511, Project Management and SOP TA-QA-0635, Data Review)
to ensure that reported data are free from calculation and transcription errors and that QC parameters have been reviewed and evaluated before data is reported. The laboratory also utilizes corporate SOP CA-Q-S-002 Acceptable Manual Integration Practices to ensure the authenticity of the data. The general review concepts are discussed below, more specific information can be found in the SOPs.

19.14.4.1 Log-In Review - The data review process starts at the sample receipt stage. Sample control personnel review chain-of-custody forms and project instructions from the project management group. This is the basis of the sample information and analytical instructions entered

into the LIMS. The log-in instructions are reviewed by the personnel entering the information, and a second level review is conducted by the project management staff.

19.14.4.2 First Level Data Review - The next level of data review occurs with the analysts. As data are generated, analysts review their work to ensure that the results meet project and SOP requirements. First level reviews include inspection of all raw data (e.g., instrument output for continuous analyzers, chromatograms, spectra, and manual integrations), evaluation of calibration/calibration verification data in the day's analytical run, evaluation of QC data, and reliability of sample results. The analyst transfers data into LIMS, data qualifiers are added as needed. All first level reviews are documented.

19.14.4.3 Second Level Data Review – All analytical data are subject to review by a second qualified analyst or supervisor. Second level reviews include inspection of all raw data (e.g., instrument output, chromatograms, and spectra) including 100% of data associated with any changes made by the primary analyst, such as manual integrations or reassignment of peaks to different analytes, or elimination of false negative analytes. The second review also includes evaluation of initial calibration/calibration verification data in the day's analytical run, evaluation of QC data, reliability of sample results, qualifiers and NCM narratives. Manual calculations are checked in second level review. All second level reviews are documented.

Issues that deem further review include the following:

- QC data are outside the specified control limits for accuracy and precision
- Reviewed sample data does not match with reported results
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration
- Transcription errors
- Results outside of calibration range

19.14.4.4 Unacceptable analytical results may require reanalysis of the samples. Any problems are brought to the attention of the Laboratory Director, Project Manager, Quality Director/Manager, Technical Manager, or Supervisor for further investigation. Corrective action is initiated whenever necessary.

19.14.4.5 The results are then entered or directly transferred into the computer database and a hard copy (or .pdf) is printed for the client.

19.14.4.6 As a final review prior to the release of the report, the Project Manager reviews the results for appropriateness and completeness. This review and approval ensures that client requirements have been met and that the final report has been properly completed. The process includes, but is not limited to, verifying that the COC is followed, cover letters / narratives are present, flags are appropriate, and project specific requirements are met. The Project Manager may also evaluate the validity of results for different test methods given expected chemical relationships.

19.14.4.7 Any project that requires a data package is subject to a tertiary data review for transcription errors and acceptable quality control requirements. The Project Manager then signs the final report. The accounting personnel also check the report for any clerical or invoicing errors. When complete, the report is sent out to the client.

19.14.4.8 A visual summary of the flow of samples and information through the laboratory, as well as data review and validation, is presented in Figure 19-2.

19.14.5 Manual Integrations

Computerized data systems provide the analyst with the ability to re-integrate raw instrument data in order to optimize the interpretation of the data. Though manual integration of data is an invaluable tool for resolving variations in instrument performance and some sample matrix problems, when used improperly, this technique would make unacceptable data appear to meet quality control acceptance limits. Improper re-integrations lead to legally indefensible data, a poor reputation, or possible laboratory decertification. Because guidelines for re-integration of data are not provided in the methods and most methods were written prior to widespread implementation of computerized data systems, the laboratory trains all analytical staff on proper manual integration techniques using TestAmerica' s Corporate SOP (CA-Q-S-002).

19.14.5.1 The analyst must adjust baseline or the area of a peak in some situations, for example when two compounds are not adequately resolved or when a peak shoulder needs to be separated from the peak of interest. The analyst must use professional judgment and common sense to determine when manual integrating is required. Analysts are encouraged to ask for assistance from a senior analyst or manager when in doubt.

19.14.5.2 Analysts shall not increase or decrease peak areas for the sole purpose of achieving acceptable QC recoveries that would have otherwise been unacceptable. The intentional recording or reporting of incorrect information (or the intentional omission of correct information) is against company principles and policy and is grounds for immediate termination.

19.14.5.3 Client samples, performance evaluation samples, and quality control samples are all treated equally when determining whether or not a peak area or baseline should be manually adjusted.

19.14.5.4 All manual integrations receive a second level review. Manual integrations must be indicated on an expanded scale "after" chromatograms such that the integration performed can be easily evaluated during data review. Expanded scale "before" chromatograms are also required for all manual integrations on QC parameters (calibrations, calibration verifications, laboratory control samples, internal standards, surrogates, etc.) unless the laboratory has another documented corporate approved procedure in place that can demonstrate an active process for detection and deterrence of improper integration practices.

Figure 19-1. Example - Demonstration of Capability Documentation

Analyst Demonstration of Capability

TestAmerica Seattle

Preparation Method(s):
Analytical Method(s):
Matrix:
Method Description:

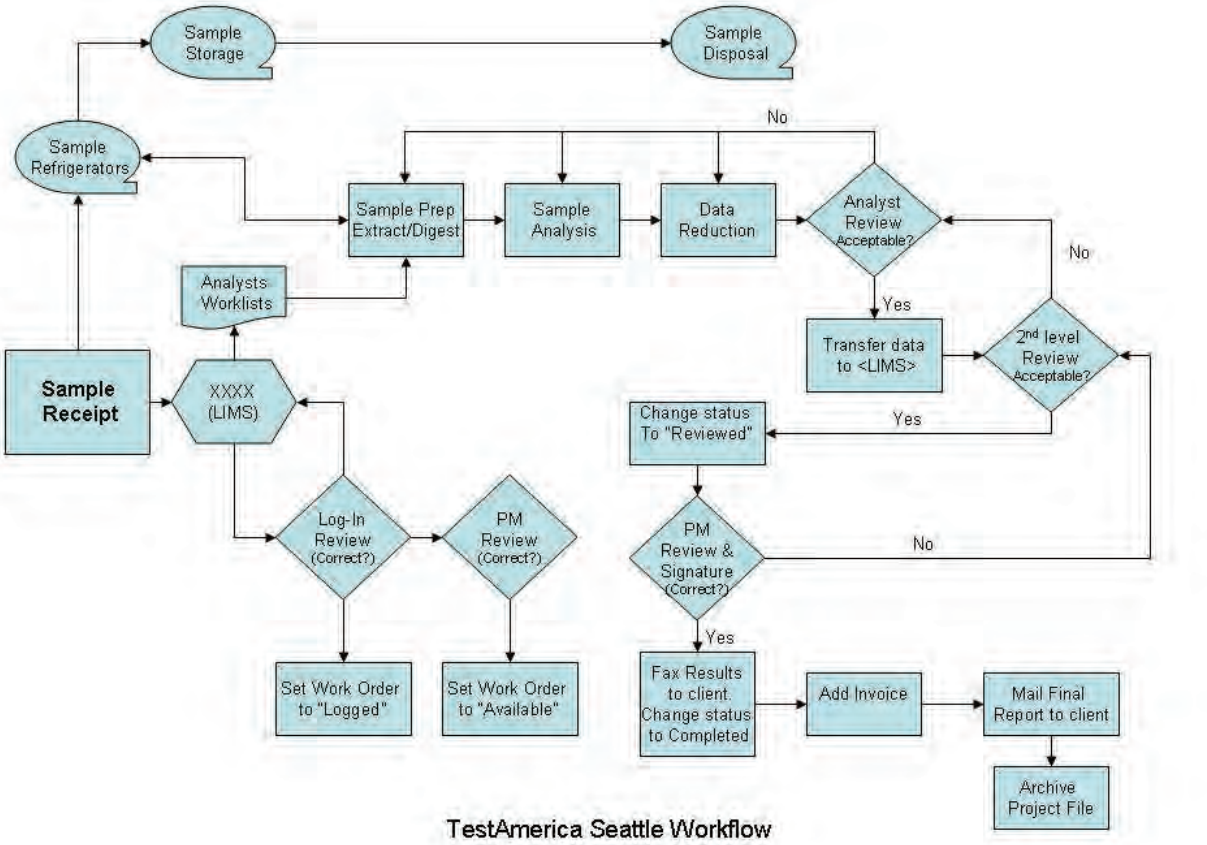
Preparation SOP No:

We, the undersigned, CERTIFY that:

1. The analyst identified above, using the cited test method with the specifications in the cited SOP, which is in use at this facility for the analyses of samples under the laboratory's Quality Assurance Plan, has completed the Demonstration of Capability (DOC).
2. The test method(s) was performed by the analyst identified on this certificate.
3. A copy of test method(s) and laboratory SOPs are available for all personnel on-site.
4. The data associated with the demonstration of capability are true, accurate, complete, and self-explanatory.
5. All raw data necessary to reconstruct and validate these analyses have been retained at the facility. The associated information is organized and available for review.

Department Manager	Signature	Date
Quality Assurance Officer	Signature	Date

Figure 19-2. Example: Work Flow



SECTION 20. EQUIPMENT and CALIBRATIONS

20.1 Overview

The laboratory purchases the most technically advanced analytical instrumentation for sample analyses. Instrumentation is purchased on the basis of accuracy, dependability, efficiency and sensitivity. Each laboratory is furnished with all items of sampling, preparation, analytical testing and measurement equipment necessary to correctly perform the tests for which the laboratory has capabilities. Each piece of equipment is capable of achieving the required accuracy and complies with specifications relevant to the method being performed. Before being placed into use, the equipment (including sampling equipment) is calibrated and checked to establish that it meets its intended specification. The calibration routines for analytical instruments establish the range of quantitation. Calibration procedures are specified in laboratory SOPs. A list of laboratory instrumentation is presented in Table 20-1. A list of software is provided in Table 20-2.

The safe handling and transport of laboratory equipment for mobile lab operations is covered in TestAmerica Seattle's SOP TA-MOB-0003.

Equipment is only operated by authorized and trained personnel. Manufacturer instructions for equipment use are readily accessible to all appropriate laboratory personnel.

20.2 Preventive Maintenance

The laboratory follows a well-defined maintenance program to ensure proper equipment operation and to prevent the failure of laboratory equipment or instrumentation during use. This program of preventive maintenance helps to avoid delays due to instrument failure.

Routine preventive maintenance procedures and frequency, such as cleaning and replacements, should be performed according to the procedures outlined in the manufacturer's manual. Qualified personnel must also perform maintenance when there is evidence of degradation of peak resolution, a shift in the calibration curve, loss of sensitivity, or failure to continually meet one of the quality control criteria.

Table 20-3 lists examples of scheduled routine maintenance. It is the responsibility of each Technical Manager to ensure that instrument maintenance logs are kept for all equipment in his/her department. Preventative maintenance procedures are also outlined in analytical SOPs or instrument manuals. (Note: for some equipment, the log used to monitor performance is also the maintenance log. Multiple pieces of equipment may share the same log as long as it is clear as to which instrument is associated with an entry.)

Instrument maintenance logs are controlled and are used to document instrument problems, instrument repair and maintenance activities. Maintenance logs shall be kept for all major pieces of equipment. Instrument maintenance logs may also be used to specify instrument parameters.

- Documentation must include all major maintenance activities such as contracted preventive maintenance and service and in-house activities such as the replacement of electrical components, lamps, tubing, valves, columns, detectors, cleaning and adjustments.
- Each entry in the instrument log includes the Analyst's initials, the date, a detailed description of the problem (or maintenance needed/scheduled), a detailed explanation of the solution or

maintenance performed, and a verification that the equipment is functioning properly (state what was used to determine a return to control. e.g. CCV run on 'date' was acceptable, or instrument recalibrated on 'date' with acceptable verification, etc.) must also be documented in the instrument records.

- When maintenance or repair is performed by an outside agency, service receipts detailing the service performed can be affixed into the logbooks adjacent to pages describing the maintenance performed. This stapled in page must be signed across the page entered and the logbook so that it is clear that a page is missing if only half a signature is found in the logbook.

If an instrument requires repair (subjected to overloading or mishandling, gives suspect results, or otherwise has shown to be defective or outside of specified limits) it shall be taken out of operation and tagged as out-of-service or otherwise isolated until such a time as the repairs have been made and the instrument can be demonstrated as operational by calibration and/or verification or other test to demonstrate acceptable performance. The laboratory shall examine the effect of this defect on previous analyses.

In the event of equipment malfunction that cannot be resolved, service shall be obtained from the instrument vendor manufacturer, or qualified service technician, if such a service can be tendered. If on-site service is unavailable, arrangements shall be made to have the instrument shipped back to the manufacturer for repair. Back up instruments, which have been approved, for the analysis shall perform the analysis normally carried out by the malfunctioning instrument. If the back up is not available and the analysis cannot be carried out within the needed timeframe, the samples shall be subcontracted.

If an instrument is sent out for service or transferred to another facility, it must be recalibrated and verified (including new initial MDL study) prior to return to lab operations.

20.3 Support Equipment

This section applies to all devices that may not be the actual test instrument, but are necessary to support laboratory operations. These include but are not limited to: balances, ovens, refrigerators, freezers, incubators, water baths, temperature measuring devices, thermal/pressure sample preparation devices and volumetric dispensing devices if quantitative results are dependent on their accuracy, as in standard preparation and dispensing or dilution into a specified volume. All raw data records associated with the support equipment are retained to document instrument performance.

20.3.1 Weights and Balances

The accuracy of the balances used in the laboratory is checked every working day, before use. All balances are placed on stable counter tops.

Each balance is checked prior to initial serviceable use with at least two certified ASTM type 1 weights spanning its range of use (weights that have been calibrated to ASTM type 1 weights may also be used for daily verification). ASTM type 1 weights used only for calibration of other weights (and no other purpose) are inspected for corrosion, damage or nicks at least annually and if no damage is observed, they are calibrated at least every 5 years by an outside calibration laboratory. Any weights (including ASTM Type 1) used for daily balance checks or other purposes are recalibrated/recertified annually to NIST standards (this may be done internally if laboratory maintains "calibration only" ASTM type 1 weights).

All balances are serviced annually by a qualified service representative, who supplies the laboratory with a certificate that identifies traceability of the calibration to the NIST standards.

All of this information is recorded in logs, and the recalibration/recertification certificates are kept on file in the QA office. Refer to SOP TA-QA-0014 Selecting and Using Balances for details.

20.3.2 pH, Conductivity, and Turbidity Meters

The pH meters used in the laboratory are accurate to ± 0.1 pH units, and have a scale readability of at least 0.05 pH units. The meters automatically compensate for the temperature, and are calibrated with at least two working range buffer solutions before each use.

Conductivity meters are also calibrated before each use with a known standard to demonstrate the meters do not exceed an error of 1% or one umhos/cm.

Turbidity meters are also calibrated before each use. All of this information is documented in logs.

Consult pH and Conductivity, and Turbidity SOPs for further information.

20.3.3 Thermometers

All thermometers are calibrated ***at a specific frequency*** with a NIST-traceable thermometer**.** ***Liquid-in-glass devices are calibrated annually. IR thermometers, digital probes and thermocouples are calibrated quarterly.***

- If the temperature measuring device is used over a range of 10℃ or less, then a single point verification within the range of use is acceptable;
- If the temperature measuring device is used over a range of greater than 10℃, then the verification must bracket the range of use.

The mercury NIST thermometer is recalibrated every five years and the digital NIST thermometer is recalibrated every year (unless thermometer has been exposed to temperature extremes or apparent separation of internal liquid) by an approved outside service and the provided certificate of traceability is kept on file. The NIST thermometer(s) have increments of 1 degree (0.5 degree or less increments are required for drinking water microbiological laboratories), and have ranges applicable to method and certification requirements. The NIST traceable thermometer is used for no other purpose than to calibrate other thermometers.

All of this information is documented in logbooks. Monitoring method-specific temperatures, including incubators, heating blocks, water baths, and ovens, is documented in method-specific logbooks. More information on this subject can be found in the SOP TA-QA-0024 Use, Calibration, and Maintenance of Laboratory Thermometers.

20.3.4 Refrigerators/Freezer Units, Waterbaths, Ovens and Incubators

The temperatures of all refrigerator units and freezers used for sample and standard storage are monitored each working day. Sample storage is monitored 7 days a week for DoD/DOE labs.

Ovens, water baths and incubators are monitored on days of use.

Each piece of equipment has a unique identification number, and is assigned a unique thermometer for monitoring.

Sample storage refrigerator temperatures are kept between > 0ºC and ≤ 6 ºC.

Specific temperature settings/ranges for other refrigerators, ovens, water baths, and incubators can be found in method specific SOPs.

All of this information is documented in Daily Temperature Logbooks and method-specific logbooks.

20.3.5 Autopipettors, Dilutors, and Syringes

Mechanical volumetric dispensing devices including burettes (except Class A Glassware and Glass microliter syringes) are given unique identification numbers and the delivery volumes are verified gravimetrically, at a minimum, on a *daily* basis.

For those dispensers that are not used for analytical measurements, a label is applied to the device stating that it is not calibrated. Any device not regularly verified can not be used for any quantitative measurements. Refer to SOP TA-QA-0016 Volumetric Verification.

Micro-syringes are purchased from Hamilton Company. Each syringe is traceable to NIST. The laboratory keeps on file an "Accuracy and Precision Statement of Conformance" from Hamilton attesting established accuracy.

20.4 Instrument Calibrations

Calibration of analytical instrumentation is essential to the production of quality data. Strict calibration procedures are followed for each method. These procedures are designed to determine and document the method detection limits, the working range of the analytical instrumentation and any fluctuations that may occur from day to day.

Sufficient raw data records are retained to allow an outside party to reconstruct all facets of the initial calibration. Records contain, but are not limited to, the following: calibration date, method, instrument, analyst(s) initials or signatures, analysis date, analytes, concentration, response, type of calibration (Avg RF, curve, or other calculations that may be used to reduce instrument responses to concentration.)

Sample results must be quantitated from the initial calibration and may not be quantitated from any continuing instrument calibration verification unless otherwise required by regulation, method or program.

If the initial calibration results are outside of the acceptance criteria, corrective action is performed and any affected samples are reanalyzed if possible. If the reanalysis is not possible, any data associated with an unacceptable initial calibration will be reported with appropriate data qualifiers (refer to Section 12).

Note: Instruments are calibrated initially and as needed after that and at least annually.

20.4.1 Calibration Standards

Calibration standards are prepared using the procedures indicated in the Reagents and Standards section of the determinative method SOP. If a reference method does not specify the number of calibration standards, a minimum of 3 calibration points will be used.

Standards for instrument calibration are obtained from a variety of sources. All standards are traceable to national or international standards of measurement, or to national or international standard reference materials.

The lowest concentration calibration standard that is analyzed during an initial calibration must be at or below the stated reporting limit for the method based on the final volume of extract (or sample).

The other concentrations define the working range of the instrument/method or correspond to the expected range of concentrations found in actual samples that are also within the working range of the instrument/method. Results of samples not bracketed by initial instrument calibration standards (within calibration range to at least the same number of significant figures used to report the data) must be reported as having less certainty, e.g., defined qualifiers or flags (additional information may be included in the case narrative). The exception to these rules is ICP and ICPMS methods which define the working range with periodic linear dynamic range studies, rather than through the range of concentrations of daily calibration standards.

All initial calibrations are verified with a standard obtained from a second source and traceable to a national standard, when available (or vendor certified different lot if a second source is not available). This verification occurs immediately after the calibration curve has been analyzed, and before the analysis of any samples.

20.4.1.1 Calibration Verification

The calibration relationship established during the initial calibration must be verified initially and at least daily as specified in the laboratory method SOPs in accordance with the referenced analytical methods and in the 2009 TNI Standard. The process of calibration verification applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models. Initial calibration verification is with a standard source secondary (second source standard) to the calibration standards, but continuing calibration verifications may use the same source standards as the calibration curve.

Note: The process of calibration verification referred to here is fundamentally different from the approach called "calibration" in some methods. As described in those methods, the calibration factors or response factors calculated during calibration are used to update the calibration factors or response factors used for sample quantitation. This approach, while employed in other EPA programs, amounts to a daily single-point calibration.

All target analytes and surrogates, including those reported as non-detects, must be included in periodic calibration verifications for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met, i.e., RPD, per 2009 TNI Std. EL-V1M4 Sec. 1.7.2.

All samples must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). The frequency is found in the determinative methods or SOPs.

Generally, the initial calibrations must be verified at the beginning of each 12-hour analytical shift during which samples are analyzed. (Some methods may specify more or less frequent verifications). The 12-hour analytical shift begins with the injection of the calibration verification standard (or the MS tuning standard in MS methods). The shift ends after the completion of the analysis of the last sample, QC, or standard that can be injected within 12 hours of the beginning of the shift.

A continuing instrument calibration verification (CCV) must be repeated at the beginning and, for methods that have quantitation by external calibration models, at the end of each analytical batch. Some methods have more frequent CCV requirements see specific SOPs. Most Inorganic methods require the CCV to be analyzed after ever 10 samples or injections, including matrix or batch QC samples.

Note: If an internal standard calibration is being used then bracketing standards are not required, only daily verifications are needed *(unless otherwise specified in the source method).* The results from these verification standards must meet the calibration verification criteria and the retention time criteria (if applicable).

If the results of a CCV are outside the established acceptance criteria and analysis of a second consecutive (and immediate) CCV fails to produce results within acceptance criteria, corrective action shall be performed. Once corrective actions have been completed & documented, the laboratory shall demonstrate acceptable instrument / method performance by analyzing two consecutive CCVs, or a new initial instrument calibration shall be performed.

Sample analyses and reporting of data may not occur or continue until the analytical system is calibrated or calibration verified. However, data associated with an unacceptable calibration verification may be fully useable under the following special conditions: **and reported based upon discussion and approval of the client:**

a). when the acceptance criteria for the CCV are exceeded high (i.e., high bias) and the associated samples within the batch are non-detects, then those non-detects may be reported with a footnote or case narrative explaining the high bias. Otherwise the samples affected by the unacceptable CCV shall be re-analyzed after a new calibration curve has been established, evaluated and accepted; or

b). when the acceptance criteria for the CCV are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable CCV shall be re-analyzed after a new calibration curve has been established, evaluated and accepted.

Samples reported by the 2 conditions identified above will be appropriately flagged.

20.4.1.2 Verification of Linear and Non-Linear Calibrations

Calibration verification for calibrations involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of

the verification standard. (These calculations are available in the laboratory method SOPs. Verification standards are evaluated based on the % Difference from the average CF or RF of the initial calibration or based on % Drift or % Recovery if a linear or quadratic curve is used.

Regardless of whether a linear or non-linear calibration model is used, if initial verification criterion is not met, then no sample analyses may take place until the calibration has been verified or a new initial calibration is performed that meets the specifications listed in the method SOPs. If the calibration cannot be verified after the analysis of a single verification standard, then adjust the instrument operating conditions and/or perform instrument maintenance, and analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, then a new initial calibration is performed.

- When the acceptance criteria for the calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

- When the acceptance criteria for the calibration verification are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise, the samples affected by the unacceptable verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted. Alternatively, a reporting limit standard may be analyzed to demonstrate that the laboratory can still support non-detects at their reporting limit.

20.5 Tentatively Identified Compounds (TICs) – GC/MS Analysis

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

Note: If the TIC compound is not part of the client target analyte list but is calibrated by the laboratory and is both qualitatively and/or quantitatively identifiable, it should not be reported as a TIC. If the compound is reported on the same form as true TICs, it should be qualified and/or narrated that the reported compound is qualitatively and quantitatively (if verification in control) reported compared to a known standard that is in control (where applicable).

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification.

20.6 GC/MS Tuning

Prior to any GCMS analytical sequence, including calibration, the instrument parameters for the tune and subsequent sample analyses within that sequence must be set.

Prior to tuning/auto-tuning the mass spec, the parameters may be adjusted within the specifications set by the manufacturer or the analytical method. These generally don't need any adjustment but it

may be required based on the current instrument performance. If the tune verification does not pass it may be necessary to clean the source or perform additional maintenance. Any maintenance is documented in the maintenance log.

Table 20-1. Example: Instrumentation List

GC	GC/MS	ICP	ICPMS	CVAA	AutoAnalyzer	IC	TOC
13	15	1	2	2	2	2	2

Table 20-2. Example: Software List

Lab Section	Software Title and Version
All (Data Processing and Reporting)	LIMS - TALS (TestAmerica) Ver 1.0.1.330 or higher
ECD, Fuels 8270 and VOA (Data Processing)	CHROM (TestAmerica) Ver 1.2 or higher
Data Acquistion	
ECD	Environmental Chemstation G1701DA Version D.00.01.27
	Envronmental Chemstation MSD Chemstation D.02.00.275
FUELS	Environmental Chemstation G1701DA Version D.00.01.27
	EnviroQuant ChemStation G1701BA Version B.01.00.
8270	Environmental ChemStation MSD ChemStation D.01.00 Build 75 26-Aug-2003.
	Environmental Chemstation G1701DA Version D.00.01.27 08-Nov-2002
	Environmental ChemStation MSD ChemStation E.01.00.237
	EnviroQuant ChemStation G1702BA Version B.01.00.
	Varian Saturn Software Data System
	Finnigan Magnum
	Finnigan GCQ
VOA	Environmental ChemStation MSD ChemStation D.01.00.275.
	EnviroQuant Chemstation G1701BA Version B.01.00.
	Environmental ChemStation MSD ChemStation E.02.00.493.
	Environmental ChemStation MSD ChemStation D.02.00.275.
	Environmental ChemStation MSD ChemStation D.03.00.552.
	Environmental ChemStation G1701DA Version D.00.01.27.
	EnviroQuant ChemStation G1701AA Version A.03.00.
	Environmental ChemStation G1701CA Version C.00.00 21-Dec-1999
Metals	ELAN Version 3.0 Hotfix 3 (Build 3, 0, 6, 48d)
	Agilent G1834B ICP-MS ChemStation B.03.03
	Perkin Elmer WinLab32 for ICP Version 4.0.0.0305
	Thermo iTeVA – Analyst Version 2.2.0.51
	Perkin Elmer WinLab32 for ICP Version 4.0.0.0305
	WinHg Runner 1.4 CT Rev 0.286
Wet Chem	
Lachat QuikChem	Omnion Program version 3.0.220.04
Astoria Pacific	EnviroQuant Chemstation G1701BA Version B.01.00
Dionex DX-500	Dionex Peaknet Run PeakNet 5.11
Dionex ICS 2000	Chromeleon Client Version 6.60 Build1428
Mitsubishi TOX-100	TOX-100 Versions 2.17 Mitsubishi Chemical Corp
OI Analytical	OI Analytical WinTOC for Solids 3.0
Teledyne Tekmar	TOCTalk Ver 4.2.105.
LECO C632	*LECO C632 Carbon Determination Ver 1.60*

Table 20-3. Example: Schedule of Routine Maintenance

Instrument	Procedure	Frequency
Leeman Mercury Analyzer	Check tubing for wear Fill rinse tank with 10% HCl Change drying tube Fill reductant bottle with 10% Stannous Chloride	Daily Daily As required Daily
ICP	Check pump tubing Check liquid argon supply Check fluid level in waste container Check filters Clean or replace filters Check torch Check sample spray chamber for debris Clean and align nebulizer Check entrance slit for debris Change printer ribbon Replace pump tubing	Daily Daily Daily Weekly As required Daily Monthly Monthly Monthly As required As required
ICP MS	Change pump tubing Clean torch Check / clean nebulizer Clean cones Check air filters Check multiplier voltages & do cross calibration Replace sample uptake tubing Check rotary pump oil Check oil mist filters Check chiller water level	Weekly Weekly Weekly Daily Weekly Weekly Monthly Monthly Monthly Monthly
Ion chromatograph	Check seals for leakage Replace seals/valves/lamps Replace suppressor Replace column Clean source/analyzer	Daily As required As required As required As required
UV-Vis Spectrophotometer	Clean ambient flow cell Precision check/alignment of flow cell Wavelength verification check	As required As required Semi-annually
TOC Analyzer	Check gas flow Check fluid level (IC reservoirs) Replace “O” rings Check needle Replace scrubbers (halogen and CO_2) Replace catalyst	Daily Daily As required Daily Yearly As required
Auto Analyzers	Clean sampler Check all tubing Clean inside of colorimeter Clean pump well and pump rollers Clean wash fluid receptacle Oil rollers/chains/side rails Clean optics and cells	Daily Daily Daily Quarterly Weekly Weekly Quarterly

Instrument	Procedure	Frequency
Hewlett Packard GC/MS	Ion gauge tube degassing Pump oil-level check Pump oil changing Analyzer bake-out Analyzer cleaning Resolution adjustment COMPUTER SYSTEM AND PRINTER: Air filter cleaning Change data system air filter Printer head carriage lubrication Paper sprocket cleaning Drive belt lubrication	As required Monthly Annually As required As required As required As required As required As required As required As required
Gas Chromatograph	Compare standard response to previous day or since last initial calibration Check carrier gas flow rate in column Check temp. of detector, inlet, column oven Septum replacement Check system for gas leaks with SNOOP Check for loose/frayed wires and insulation ½"Bake injector/column Change/remove sections of guard column Replace connectors/liners Change/replace column(s)	Daily Daily via use of known compound retention Daily As required W/cylinder change as required Monthly As Required As Required As Required As Required
Electron Capture Detector (ECD)	Detector wipe test (Ni-63) Detector cleaning	Semi-annually As required
Flame Ionization Detector (FID)	Detector cleaning	As required
Balances	Class "S" traceable weight check Clean pan and check if level Field service	Daily, when used Daily At least Annually
Conductivity Meter	0.01M KCl calibration Conductivity cell cleaning	Daily As required
Turbidimeter	Check light bulb	Daily, when used
Deionized/Distilled Water	Conductivity Point Sources Daily conductivity check Check deionizer light Monitor for VOA's System cleaning Replace cartridge & large mixed bed resins	SOP TA-QA-0162 Daily Daily As required As required
Drying Ovens	Temperature monitoring Temperature adjustments	Daily As required
Refrigerators/ Freezers	Temperature monitoring Temperature adjustment Defrosting/cleaning	Daily As required As required
Vacuum Pumps/ Air Compressor	Drained Belts checked Lubricated	Weekly Monthly Semi-annually
pH/Specific Ion Meter	Calibration/check slope Clean electrode	Daily As required

Instrument	Procedure	Frequency
BOD Incubator	Temperature monitoring Coil and incubator cleaning	Daily Monthly
Centrifuge	Check brushes and bearings	Every 6 months or as needed
Water baths	Temperature monitoring Water replaced	Daily Monthly or as needed
Zero Headspace Extractors	Verify rotation speed Check for leakage Vendor repair	As required Annually As required
TCLP Extractors	Verify rotation speed	Quarterly

SECTION 21. MEASUREMENT TRACEABILITY

21.1 Overview

Traceability of measurements shall be assured using a system of documentation, calibration, and analysis of reference standards. Laboratory equipment that are peripheral to analysis and whose calibration is not necessarily documented in a test method analysis or by analysis of a reference standard shall be subject to ongoing certifications of accuracy. At a minimum, these must include procedures for checking specifications of ancillary equipment: balances, thermometers, temperature, Deionized (DI) and Reverse Osmosis (RO) water systems, automatic pipettes and other volumetric measuring devices. (Refer to Section 20.3). With the exception of Class A Glassware, quarterly accuracy checks are performed for all mechanical volumetric devices. Microsyringes are verified at least semi-annually or disposed of after 6 months of use. Wherever possible, subsidiary or peripheral equipment is checked against standard equipment or standards that are traceable to national or international standards. Class A Glassware and glass microliter syringes should be routinely inspected for chips, acid etching or deformity (e.g., bent needle). If the Class A glassware or syringe is suspect, the accuracy of the glassware will be assessed prior to use.

21.2 NIST-Traceable Weights and Thermometers

Reference standards of measurement shall be used for calibration only and for no other purpose, unless it can be shown that their performance as reference standards would not be invalidated.

For NIST-traceable weights and thermometers, the laboratory requires that all calibrations be conducted by a calibration laboratory accredited by A2LA, NVLAP (National Voluntary Laboratory Accreditation Program), or another accreditation organization that is a signatory to a MRA (Mutual Recognition Arrangement) of one or more of the following cooperations – ILAC (International Laboratory Accreditation Cooperation) or APLAC (Asia –Pacific Laboratory Accreditation Cooperation). A calibration certificate and scope of accreditation is kept on file at the laboratory.

21.3 Reference Standards / Materials

Reference standards/materials, where commercially available, are traceable to certified reference materials. Commercially prepared reference standards, to the extent available, are purchased from vendors that are accredited to ISO Guide 34 and ISO/IEC Guide 17025. All reference standards from commercial vendors shall be accompanied with a certificate that includes at least the following information:

- Manufacturer
- Analytes or parameters calibrated
- Identification or lot number
- Calibration method
- Concentration with associated uncertainties
- Purity

If a standard cannot be purchased from a vendor that supplies a Certificate of Analysis, the purity of the standard is documented by analysis. The receipt of all reference standards must be documented. Reference standards are labeled with a unique Standard Identification Number and

expiration date. All documentation received with the reference standard is retained as a QC record and references the Standard Identification Number.

All reference, primary and working standards/materials, whether commercially purchased or laboratory prepared, must be checked regularly to ensure that the variability of the standard or material from the 'true' value does not exceed method requirements. The accuracy of calibration standards is checked by comparison with a standard from a second source. In cases where a second standard manufacturer is not available, a vendor certified different lot is acceptable for use as a second source. The appropriate Quality Control (QC) criteria for specific standards are defined in laboratory SOPs. In most cases, the analysis of an Initial Calibration Verification (ICV) or LCS (where there is no sample preparation) is used as the second source confirmation. These checks are generally performed as an integral part of the analysis method (e.g. calibration checks, laboratory control samples).

All standards and materials must be stored and handled according to method or manufacturer's requirements in order to prevent contamination or deterioration. Refer to the Corporate Environmental Health & Safety Manual or laboratory SOPs. For safety requirements, please refer to method SOPs and the laboratory Environmental Health and Safety Manual.

Standards and reference materials shall not be used after their expiration dates unless their reliability is verified by the laboratory and their use is approved by the Quality Assurance Manager. The laboratory has documented contingency procedures for re-verifying expired standards.

21.4 Documentation and Labeling of Standards, Reagents, and Reference Materials

Reagents must be at a minimum the purity required in the test method. The date of reagent receipt and the expiration date are documented. The lots for most of the common solvents and acids are tested for acceptability prior to company wide purchase. [Refer to TestAmerica's Corporate SOP (CA-Q-S-001), Solvent and Acid Lot Testing and Approval.]

All manufacturer or vendor supplied Certificate of Analysis or Purity must be retained, stored appropriately, and readily available for use and inspection. These records are maintained in the LIMS. Records must be kept of the date of receipt and date of expiration of standards, reagents and reference materials. In addition, records of preparation of laboratory standards, reagents, and reference materials must be retained, stored appropriately, and be readily available for use and inspection. These records are maintained in the LIMS. For detailed information on documentation and labeling, please refer to SOP TA-QA-0619, Preparation, Storage, and Verification of Standards.

Commercial materials purchased for preparation of calibration solutions, spike solutions, etc.., are usually accompanied with an assay certificate or the purity is noted on the label. If the assay purity is 96% or better, the weight provided by the vendor may be used without correction. If the assay purity is less than 96% a correction will be made to concentrations applied to solutions prepared from the stock commercial material.

21.4.1 All standards, reagents, and reference materials must be labeled in an unambiguous manner. Standards are logged into the laboratory's LIMS system, and are assigned a unique identification number. The following information is typically recorded in the electronic database within the LIMS.

- Standard ID
- Description of Standard
- Department
- Preparer's name
- Final volume and number of vials prepared
- Solvent type and lot number
- Preparation Date
- Expiration Date
- Standard source type (stock or daughter)
- Standard type (spike, surrogate, other)
- Parent standard ID (if applicable)
- Parent Standard Analyte Concentration (if applicable)
- Parent Standard Amount used (if applicable)
- Component Analytes
- Final concentration of each analyte
- Comment box (text field)

Records are maintained electronically for standard and reference material preparation. These records show the traceability to purchased stocks or neat compounds. These records also include method of preparation, date of preparation, expiration date and preparer's name or initials. Preparation procedures are provided in the Method SOPs.

21.4.2 All standards, reagents, and reference materials must be clearly labeled with a minimum of the following information:

- Expiration Date (include prep date for reagents)
- Standard ID (from LIMS)
- Special Health/Safety warnings if applicable

Records must also be maintained of the date of receipt for commercially purchased items or date of preparation for laboratory prepared items. Special Health/Safety warnings must also be available to the analyst. This information is maintained in the LIMS and MSD Sheets**.**

21.4.3 In addition, the following information may be helpful:

- Date opened (for multi-use containers, if applicable)
- Description of standard (if different from manufacturer's label or if standard was prepared in the laboratory)
- Recommended Storage Conditions
- Concentration (if applicable)
- Initials of analyst preparing standard or opening container

All containers of prepared reagents must include an expiration date and an ID number to trace back to preparation.

Procedures for preparation of reagents can be found in the Method SOPs.

Standard ID numbers must be traceable through associated logbooks, worksheets and raw data.

All reagents and standards must be stored in accordance to the following priority: 1) with the manufacturer's recommendations; 2) with requirements in the specific analytical methods as specified in laboratory SOP TA-QA-0619, Preparation, Storage, and Verification of Standards.

SECTION 22. SAMPLING

22.1 Overview

The laboratory does not provide sampling services. The laboratory's responsibility in the sample collection process lies in supplying the sampler with the necessary coolers, reagent water, sample containers, preservatives, sample labels, custody seals, COC forms, ice, and packing materials required to properly preserve, pack, and ship samples to the laboratory

22.2 Sampling Containers

The laboratory offers clean sampling containers for use by clients. These containers are obtained from reputable container manufacturers and meet EPA specifications as required. Certificates of cleanliness for bottles and preservatives are provided by the supplier and are maintained at the laboratory. Alternatively, the certificates may be maintained by the supplier and available to the laboratory on-line.

22.2.1 Preservatives

Upon request, preservatives are provided to the client in pre-cleaned sampling containers. In some cases containers may be purchased pre-preserved from the container supplier. Whether prepared by the laboratory or bought pre-preserved, the grades of the preservatives are at a minimum:

- Hydrochloric Acid – Reagent ACS (Certified VOA Free) or equivalent
- Methanol – Purge and Trap grade
- Nitric Acid – Instra-Analyzed or equivalent
- Sodium Bisulfate – ACS Grade or equivalent
- Sodium Hydroxide – Instra-Analyzed or equivalent
- Sulfuric Acid – Instra-Analyzed or equivalent
- Sodium Thiosulfate – ACS Grade or equivalent

22.3 Definition of Holding Time

The date and time of sampling documented on the COC form establishes the day and time zero. As a general rule, when the maximum allowable holding time is expressed in "days" (e.g., 14 days, 28 days), the holding time is based on calendar day measured. Holding times expressed in "hours" (e.g., 6 hours, 24 hours, etc.) are measured from date and time zero. Holding times for analysis

include any necessary reanalysis. However, there are some programs that determine holding time compliance based on the date and specific time of analysis compared to the time of sampling regardless of how long the holding time is.

22.4 Sampling Containers, Preservation Requirements, Holding Times

The preservation and holding time criteria specified in the laboratory SOPs are derived from the source documents for the methods. If method required holding times or preservation requirements are not met, the reports will be qualified using a flag, footnote or case narrative. As soon as possible or "ASAP" is an EPA designation for tests for which rapid analysis is advised, but for which neither EPA nor the laboratory have a basis for a holding time.

22.5 Sample Aliquots / Subsampling

Taking a representative sub-sample from a container is necessary to ensure that the analytical results are representative of the sample collected in the field. The size of the sample container, the quantity of sample fitted within the container, and the homogeneity of the sample need consideration when sub-sampling for sample preparation. It is the laboratory's responsibility to take a representative subsample or aliquot of the sample provided for analysis.

Analysts should handle each sample as if it is potentially dangerous. At a minimum, safety glasses, gloves, and lab coats must be worn when preparing aliquots for analysis.

Guidelines on taking sample aliquots & subsampling are located in SOP TA-QA-0028, Subsampling of Solid Samples.

SECTION 23. HANDLING OF SAMPLES

Sample management procedures at the laboratory ensure that sample integrity and custody are maintained and documented from sampling/receipt through disposal.

23.1 Chain of Custody (COC)

The COC form is the written documented history of any sample and is initiated when bottles are sent to the field, or at the time of sampling. This form is completed by the sampling personnel and accompanies the samples to the laboratory where it is received and stored under the laboratory's custody. The purpose of the COC form is to provide a legal written record of the handling of samples from the time of collection until they are received at the laboratory. It also serves as the primary written request for analyses from the client to the laboratory. The COC form acts as a purchase order for analytical services when no other contractual agreement is in effect. An example of a COC form may be found in Figure 23-1.

23.1.1 Field Documentation

The information the sampler needs to provide at the time of sampling on the container label is:

- Sample identification
- Date and time
- Preservative

During the sampling process, the COC form is completed and must be legible (see Figure 23-1). This form includes information such as:

- Client name, address, phone number and fax number (if available)
- Project name and/or number
- The sample identification
- Date, time and location of sampling
- Sample collectors name
- The matrix description
- The container description
- The total number of each type of container
- Preservatives used
- Analysis requested
- Requested turnaround time (TAT)
- Any special instructions
- Purchase Order number or billing information (e.g. quote number) if available
- The date and time that each person received or relinquished the sample(s), including their signed name.

When the sampling personnel deliver the samples directly to TestAmerica personnel, the samples are stored in a cooler with ice, as applicable, and remain solely in the possession of the client's field technician until the samples are delivered to the laboratory personnel. The sample collector must assure that each container is in his/her physical possession or in his/her view at all times, or stored in such a place and manner to preclude tampering. The field technician relinquishes the samples in writing on the COC form to the sample control personnel at the laboratory or to a TestAmerica courier. When sampling personnel deliver the samples through a common carrier (Fed-Ex, UPS), the CoC relinquished date/time is completed by the field personnel and samples are released to the carrier. Samples are only considered to be received by the lab when personnel at the fixed laboratory facility have physical contact with the samples.

Note: Independent couriers are not required to sign the COC form. The COC is usually kept in the sealed sample cooler. The receipt from the courier is stored in log-in by date; it lists all receipts each date.

23.2 Sample Receipt

Samples are received at the laboratory by designated sample receiving personnel and a unique laboratory project identification number is assigned. Each sample container shall be assigned a unique sample identification number that is cross-referenced to the client identification number such that traceability of test samples is unambiguous and documented. Each sample container is affixed with a durable sample identification label. Sample acceptance, receipt, tracking and storage procedures are summarized in the following sections.

23.2.1 Laboratory Receipt

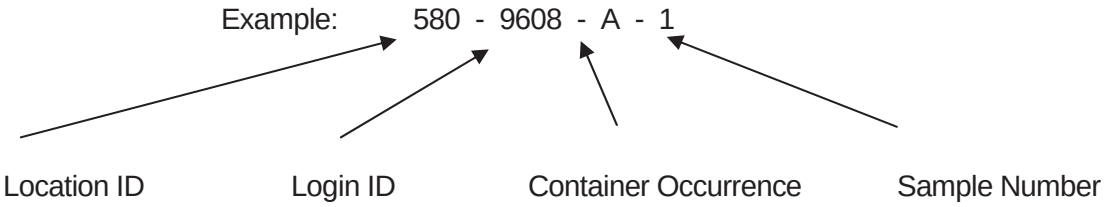
When samples arrive at the laboratory, sample receiving personnel inspect the coolers and samples. The integrity of each sample must be determined by comparing sample labels or tags with the COC and by visual checks of the container for possible damage. Any non-conformance, irregularity, or compromised sample receipt must be documented on an NCM or the login Checklist in LIMS and brought to the immediate attention of the client. The COC, shipping documents, documentation of any non-conformance, irregularity, or compromised sample receipt, record of client contact, and resulting instructions become part of the project record.

23.2.1.1 Unique Sample Identification

Note: Example LIMS IDs are from TALS.

All samples that are processed through the laboratory receive a unique sample identification to ensure that there can be no confusion regarding the identity of such samples at anytime. This system includes identification for all samples, subsamples and subsequent extracts and/or digestates.

The laboratory assigns a unique identification (e.g., Sample ID) code to each sample container received at the laboratory. This Primary ID is made up of the following information (consisting of 4 components):



The *above* example *states the TestAmerica Laboratory Location ID* (*Location* 580), the Login ID (9608) which is unique to a particular client/job occurrence, the container code (A) indicating t is the first container ("A") of Sample *Number* (1).

If the primary container goes through a prep step that creates a "new" container, then the new container is considered secondary and gets another ID. An example of this being a client sample in a 1-Liter amber bottle is sent through a Liquid/Liquid Extraction and an extraction vial is created from this step. The vial would be a SECONDARY container. The secondary ID has 5 components.

Example: 580 - 9608 - A - 1 - **A** ← **Secondary Container Occurrence**

Example: 580-9608-A-1-A, would indicate the PRIMARY container listed above that went through a step that created the 1st occurrence of a Secondary container.

With this system, a client sample can literally be tracked throughout the laboratory in every step from receipt to disposal.

23.3 Sample Acceptance Policy

The laboratory has a written sample acceptance policy (Figure 23-2) that clearly outlines the circumstances under which samples shall be accepted or rejected. These include:

- a COC filled out completely;
- samples must be properly labeled;
- proper sample containers with adequate volume for the analysis (Sampling Guide) and necessary QC;
- samples must be preserved according to the requirements of the requested analytical method (Sampling Guide);
- sample holding times must be adhered to (Sampling Guide);
- the project manager will be notified if any sample is received in damaged condition.

Data from samples which do not meet these criteria are flagged and the nature of the variation from policy is defined.

23.3.1 After inspecting the samples, the sample receiving personnel sign and date the COC form, make any necessary notes of the samples' conditions and store them in appropriate refrigerators or storage locations.

23.3.2 Any deviations from these checks that question the suitability of the sample for analysis, or incomplete documentation as to the tests required will be resolved by consultation with the client. If the sample acceptance policy criteria are not met, the laboratory shall either:

- Retain all correspondence and/or records of communications with the client regarding the disposition of rejected samples, or

- Fully document any decision to proceed with sample analysis that does not meet sample acceptance criteria.

Once sample acceptance is verified, the samples are logged into the LIMS according SOP TA-QA-0001 (Sample Receiving and Login).

23.4 Sample Storage

In order to avoid deterioration, contamination or damage to a sample during storage and handling, from the time of receipt until all analyses are complete, samples are stored in refrigerators, freezers or protected locations suitable for the sample matrix. Aqueous samples for metals testing are typically stored at ambient temperature**.** In addition, samples to be analyzed for volatile organic parameters are stored in separate refrigerators designated for volatile organic parameters only. Samples are never to be stored with reagents, standards or materials that may create contamination.

To ensure the integrity of the samples during storage, refrigerator blanks are maintained in the volatile sample refrigerators and analyzed every two weeks. The refrigerator blanks are logged into the LIMS and treated as normal samples with the data stored and archived in the LIMS.

Analysts and technicians retrieve the sample container allocated to their analysis from the designated storage location and place them on carts, analyze the sample, and return the remaining sample or empty container to the storage location from which it originally came. All unused portions of samples, including empty sample containers, are returned to designated storage location. All samples are kept in the designated storage locations for a *minimum of two from receipt*, which meets or exceeds most sample holding times. After two weeks the samples *may be* moved to dry room temperature, sample archive area where they are stored for a *minimum of four weeks from invoicing* before they are disposed of. This *minimum of six* week holding period allows samples to be checked if a discrepancy or question arises. Special arrangements may be made to store samples for longer periods of time. This extended holding period allows additional metal analyses to be performed on the archived sample and assists clients in dealing with legal matters or regulatory issues**.**

Access to the laboratory is controlled such that sample storage need not be locked at all times unless a project specifically demands it. Samples are accessible to laboratory personnel only. Visitors to the laboratory are prohibited from entering the refrigerator and laboratory areas unless accompanied by an employee of TestAmerica.

23.5 Hazardous Samples and Foreign Soils

To minimize exposure to personnel and to avoid potential accidents, hazardous and foreign soil samples are stored in isolated areas designated for hazardous waste or foreign soil samples only. All hazardous samples are either returned to the client or disposed of appropriately through a hazardous waste disposal firm that lab-packs all hazardous samples and removes them from the laboratory. Foreign soil samples are sent out for incineration by a USDA-approved waste disposal facility.

23.6 Sample Shipping

In the event that the laboratory needs to ship samples, the samples are placed in a cooler with enough ice to ensure the samples remain just above freezing and at or below 6.0°C during transit. The samples are carefully surrounded by packing material to avoid breakage (yet maintain appropriate temperature). A trip blank is enclosed for those samples requiring water/solid volatile organic analyses (see Note). The chain-of-custody form is signed by the sample control technician and attached to the shipping paperwork. Samples are generally shipped overnight express or hand-delivered by a TestAmerica courier to maintain sample integrity. All personnel involved with shipping and receiving samples must be trained to maintain the proper chain-of-custody documentation and to keep the samples intact and on ice. The Environmental, Health and Safety Manual contains additional shipping requirements.

Note: If a client does not request trip blank analysis on the COC or other paperwork, the laboratory will not analyze the trip blanks that were supplied. However, in the interest of good client service, the laboratory will advise the client at the time of sample receipt that it was noted that they did not request analysis of the trip blank; and that the laboratory is providing the notification to verify that they are not inadvertently omitting a key part of regulatory compliance testing.

23.7 Sample Disposal

Samples should be retained for a minimum of 30 days after the project *invoice* is sent, however, provisions may be made for earlier disposal of samples once the holding time is exceeded. Some samples are required to be held for longer periods based on regulatory or client requirements (e.g., 60 days after project *invoice* is sent). The laboratory must follow the longer sample retention requirements where required by regulation or client agreement. Several possibilities for sample disposal exist: the sample may be consumed completely during analysis, the sample may be returned to the customer or location of sampling for disposal, or the sample may be disposed of in accordance with the laboratory's waste disposal procedures (SOP: TA-EHS-0036). All procedures in the laboratory Environmental, Health and Safety Manual are followed during disposal. Samples are normally maintained in the laboratory no longer than ninety days from receipt unless otherwise requested. Unused portions of samples found or suspected to be hazardous according to state or federal guidelines may be returned to the client upon completion of the analytical work.

If a sample is part of a known litigation, the affected legal authority, sample data user, and/or submitter of the sample must participate in the decision about the sample's disposal. All documentation and correspondence concerning the disposal decision process must be kept on file. Pertinent information includes the date of disposal, nature of disposal (such as sample depletion, hazardous waste facility disposal or return to client), names of individuals who conducted the arrangements and physically completed the task. The laboratory will remove or deface sample labels prior to disposal unless this is accomplished through the disposal method (e.g., samples are incinerated). A Waste Disposal Record should be completed.

Figure 23-1. Example: Chain of Custody (COC)

Seattle
5755 8th Street East
Tacoma, WA 98424
253-922-2310

Chain of Custody Record

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica Laboratories, Inc.

Client Contact	Project Manager:	Site Contact:	Date:	COC No:
Your Company Name here	Tel/Fax:	Lab Contact:	Carrier:	_____ of _____ COCs
Address	Analysis Turnaround Time			Job No:
City/State/Zip	Calendar (C) or Work Days (W) _____			
(xxx) xxx-xxxx Phone	TAT if different from Below _____			
(xxx) xxx-xxxx FAX	☐ 2 weeks			SDG No:
Project Name:	☐ 1 week			
Site:	☐ 2 days			
P O #	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type	Matrix	# of Cont.	Filtered Sample																Sample Specific Notes:

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification
☐ *Non-Hazard* ☐ *Flammable* ☐ *Skin Irritant* *Poison B* ☐ *Unknown* ☐

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)
☐ *Return To Client* ☐ *Disposal By Lab* ☐ *Archive For* _____ *Months*

Special Instructions/QC Requirements & Comments:

Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:

Figure 23-2. Example: Sample Acceptance Policy

All incoming work will be evaluated against the criteria listed below. Where applicable, data from any samples that do not meet the criteria listed below will be noted on the laboratory report defining the nature and substance of the variation. In addition the client will be notified either by telephone, fax or e-mail ASAP after the receipt of the samples.

1) Samples must arrive with labels intact with a Chain of Custody filled out completely. The following information must be recorded.

   - Client name, address, phone number and fax number (if available)
   - Project name and/or number
   - The sample identification
   - Date, time and location of sampling
   - The collectors name
   - The matrix description
   - The container description
   - The total number of each type of container
   - Preservatives used
   - Analysis requested
   - Requested turnaround time (TAT)
   - Any special instructions
   - Purchase Order number or billing information (e.g. quote number) if available
   - The date and time that each person received or relinquished the sample(s), including their signed name.
   - Information must be legible

2) Samples must be properly labeled.
   - Use durable labels (labels provided by TestAmerica are preferred)
   - Include a unique identification number
   - Include sampling date and time & sampler ID
   - Include preservative used.
   - Use indelible ink
   - Information must be legible

3) Proper sample containers with adequate volume for the analysis and necessary QC are required for each analysis requested. See Lab Sampling Guide.

4) Samples must be preserved according to the requirements of the requested analytical method (See Sampling Guide**.**

5) Most analytical methods require chilling samples to 4^{o} C (other than water samples for metals analysis). For these methods, the criteria are met if the samples are chilled to below 6^{o} C and above freezing (0^{o}C). For methods with other temperature criteria (e.g. some bacteriological methods require $\leq$ 10 ^{o}C), the samples must arrive within $\pm$ 2^{o} C of the required temperature or within the method specified range. **Note:** Samples that are hand delivered to the laboratory immediately after collection may not have had time to cool sufficiently. In this case the samples will be considered acceptable as long as there is evidence that the chilling process has begun (arrival on ice).

5i.) Samples that are delivered to the laboratory on the same day they are collected may not meet the requirements of Section 5. In these cases, the samples shall be considered acceptable if the samples were received on ice.

5ii.) If sample analysis is begun within fifteen (15) minutes of collection, thermal preservation is not required.

5iii.)Thermal preservation is not required in the field if the laboratory receives and refrigerates the sample within fifteen (15) minutes of collection.

- Chemical preservation (pH) will be verified prior to analysis and documented, either in sample control or at the analyst's level. The project manager will be notified immediately if there is a discrepancy. If analyses will still be performed, all affected results will be flagged to indicate improper preservation.

- For Volatile Organic analyses in drinking water (Methods 502.2 or 524.2). Residual chlorine must be neutralized prior to preservation. If there is prior knowledge that the samples are not chlorinated, state it on the COC and use the VOA vials pre-preserved with HCl. The following are other options for a sampler and laboratory where the presence of chlorine is not known:
  - 1. Test for residual chlorine in the field prior to sampling.
    - If no chlorine is present, the samples are to be preserved using HCl as usual.
    - If chlorine is present, add either ascorbic acid or sodium thiosulfate prior to adding HCl.
  - 2. Use VOA vials pre-preserved with sodium thiosulfate or ascorbic acid and add HCl after filling the VOA vial with the sample.

- **FOR WATER SAMPLES TESTED FOR CYANIDE (by Standard Methods or EPA 335)**
  - In the Field: Samples are to be tested for Sulfide using lead acetate paper prior to the addition of Sodium Hydroxide (NaOH). If sulfide is present, the sample must be treated with Cadmium Chloride and filtered prior to the addition of NaOH.
    - If the sulfide test and treatment is not performed in the field, the lab will test the samples for sulfide using lead acetate paper at the time of receipt and if sulfide is present in the sample, the client will be notified and given the option of retaking the sample and treating in the field per the method requirements or the laboratory can analyze the samples as delivered and qualify the results in the final report.
  - It is the responsibility of the client to notify the laboratory if thiosulfate, sulfite, or thiocyanate are known or suspected to be present in the sample. This notification may be on the chain of custody. The samples may need to be subcontracted to a laboratory that performs a UV digestion. If the lab does not perform the UV digestion on samples that contain these compounds, the results must be qualified in the final report.
  - The laboratory must test the sample for oxidizing agents (e.g. Chlorine) prior to analysis and treat according to the methods prior to distillation. (ascorbic acid or sodium arsenite are the preferred choice).

6) Sample Holding Times

- TestAmerica will make every effort to analyze samples within the regulatory holding time. Samples must be received in the laboratory with enough time to perform the sample analysis. Except for short holding time samples (< 48hr HT), sample must be received with at least 48 hrs (working days) remaining on the holding time for us to ensure analysis.

- Analyses that are designated as "field" analyses (Odor, pH, Dissolved Oxygen, Disinfectant Residual; a.k.a. Residual Chlorine, and Redox Potential) should be analyzed ASAP by the field sampler prior to delivering to the lab (within 15 minutes). However, if the analyses are to be performed in the

laboratory, TestAmerica will make every effort to analyze the samples within 24 hours from receipt of the samples in the testing laboratory. Samples for "field" analyses received after 4:00 pm on Friday or on the weekend will be analyzed no later than the next business day after receipt (Monday unless a holiday). Samples will remain refrigerated and sealed until the time of analysis. The actual times of all "field" sample analyses are noted on the "Short Hold Time Detail Report" in the final report. Samples analyzed in the laboratory will be qualified on the final report with an 'H' to indicate holding time exceedance.

7) All samples submitted for Volatile Organic analyses must have a Trip Blank submitted at the same time. TestAmerica will supply a blank with the bottle order.

8) The project manager will be notified if any sample is received in damaged condition. TestAmerica will request that a sample be resubmitted for analysis.

9) Recommendations for packing samples for shipment.

- Pack samples in Ice rather than "Blue" ice packs.
- Soil samples should be placed in plastic zip-lock bags. The containers often have dirt around the top and do not seal very well and are prone to intrusion from the water from melted ice.
- Water samples would be best if wrapped with bubble-wrap or paper (newspaper, or paper towels work) and then placed in plastic zip-lock bags.
- Fill extra cooler space with bubble wrap.

Figure 23-3. Example: Cooler Receipt Form

Login Sample Receipt Checklist

Client: Client X

Job Number: 580-43036-1

Login Number: 43036
List Number: 1
Creator: Blankinship, Tom X

List Source: TestAmerica Seattle

Question	Answer	Comment
Radioactivity wasn't checked or is </= background as measured by a survey meter.	True	
The cooler's custody seal, if present, is intact.	True	
Sample custody seals, if present, are intact.	True	
The cooler or samples do not appear to have been compromised or tampered with.	True	
Samples were received on ice.	True	
Cooler Temperature is acceptable.	True	
Cooler Temperature is recorded.	True	
COC is present.	True	
COC is filled out in ink and legible.	True	
COC is filled out with all pertinent information.	True	
Is the Field Sampler's name present on COC?	True	
There are no discrepancies between the containers received and the COC.	True	
Samples are received within Holding Time.	True	
Sample containers have legible labels.	True	
Containers are not broken or leaking.	True	
Sample collection date/times are provided.	True	
Appropriate sample containers are used.	True	
Sample bottles are completely filled.	True	
Sample Preservation Verified.	True	
There is sufficient vol. for all requested analyses, incl. any requested MS/MSDs	True	
Containers requiring zero headspace have no headspace or bubble is <6mm (1/4").	N/A	
Multiphasic samples are not present.	True	
Samples do not require splitting or compositing.	True	
Residual Chlorine Checked.	N/A	

TestAmerica Seattle

SECTION 24. ASSURING THE QUALITY OF TEST RESULTS

24.1 Overview

In order to assure our clients of the validity of their data, the laboratory continuously evaluates the quality of the analytical process. The analytical process is controlled not only by instrument calibration as discussed in Section 20, but also by routine process quality control measurements (e.g. Blanks, Laboratory Control Samples (LCS), Matrix Spikes (MS), duplicates (DUP), surrogates, Internal Standards (IS)). These quality control checks are performed as required by the method or regulations to assess precision and accuracy. Quality control samples are to be treated in the exact same manner as the associated field samples being tested. In addition to the routine process quality control samples, Proficiency Testing (PT) Samples (concentrations unknown to laboratory) are analyzed to help ensure laboratory performance.

24.2 Controls

Sample preparation or pre-treatment is commonly required before analysis. Typical preparation steps include homogenization, grinding, solvent extraction, sonication, acid digestion, distillation, reflux, evaporation, drying and ashing. During these pre-treatment steps, samples are arranged into discreet manageable groups referred to as preparation (prep) batches. Prep batches provide a means to control variability in sample treatment. Control samples are added to each prep batch to monitor method performance and are processed through the entire analytical procedure with investigative/field samples.

24.3 Negative Controls

Table 24-1. Example – Negative Controls

Control Type	Details
Method Blank (MB)	are used to assess preparation and analysis for possible contamination during the preparation and processing steps.
	The specific frequency of use for method blanks during the analytical sequence is defined in the specific standard operating procedure for each analysis. Generally it is 1 for each batch of samples; not to exceed 20 environmental samples.
	The method blank is prepared from a clean matrix similar to that of the associated samples that is free from target analytes (e.g., Reagent water, Ottawa sand, glass beads, etc.) and is processed along with and under the same conditions as the associated samples. The method blank goes through all of the steps of the process (including as necessary: filtration, clean-ups, etc.).
	Reanalyze or qualify associated sample results when the concentration of a targeted analyte in the blank is at or above the reporting limit as established by the method or by regulation, AND is greater than 1/10 of the amount measured in the sample.
Calibration Blanks	are prepared and analyzed along with calibration standards where applicable. They are prepared using the same reagents that are used to prepare the standards. In some analyses the calibration blank may be included in the calibration curve.
Instrument Blanks	are blank reagents or reagent water that may be processed during an analytical sequence in order to assess contamination in the analytical system. In general, instrument blanks are used to differentiate between contamination caused by the analytical system and that caused by the sample handling or sample prep process. Instrument blanks may also be inserted throughout the analytical sequence to minimize the effect of carryover from samples with high analyte content.

Table 24-1. Example – Negative Controls

Control Type	Details
Trip Blank [1]	are required to be submitted by the client with each shipment of samples requiring aqueous and solid volatiles analyses (or as specified in the client's project plan). Additionally, trip blanks may be prepared and analyzed for volatile analysis of air samples, when required by the client. A trip blank may be purchased (certified clean) or is prepared by the laboratory by filling a clean container with pure deionized water that has been purged to remove any volatile compounds. Appropriate preservatives are also added to the container. The trip blank is sent with the bottle order and is intended to reflect the environment that the containers are subjected to throughout shipping and handling and help identify possible sources if contamination is found. The field sampler returns the trip blank in the cooler with the field samples.
Field Blanks [1]	are sometimes used for specific projects by the field samplers. A field blank prepared in the field by filling a clean container with pure reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken. (EPA OSWER)
Equipment Blanks [1]	are also sometimes created in the field for specific projects. An equipment blank is a sample of analyte-free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures. (TNI)
Holding Blanks	also referred to as refrigerator or freezer blanks, are used to monitor the sample storage units for volatile organic compounds during the storage of VOA samples in the laboratory

[1] When known, these field QC samples should not be selected for matrix QC as it does not provide information on the behavior of the target compounds in the field samples. Usually, the client sample ID will provide information to identify the field blanks with labels such as "FB", "EB", or "TB."

Evaluation criteria and corrective action for these controls are defined in the specific standard operating procedure for each analysis.

24.4 Positive Controls

Control samples (e.g., QC indicators) are analyzed with each batch of samples to evaluate data based upon (1) Method Performance (Laboratory Control Sample (LCS) or Blank Spike (BS)), which entails both the preparation and measurement steps; and (2) Matrix Effects (Matrix Spike (MS) or Sample Duplicate (MD, DUP), which evaluates field sampling accuracy, precision, representativeness, interferences, and the effect of the matrix on the method performed. Each regulatory program and each method within those programs specify the control samples that are prepared and/or analyzed with a specific batch.

Note that frequency of control samples vary with specific regulatory, methodology and project specific criteria. Complete details on method control samples are as listed in each analytical SOP.

24.4.1 Method Performance Control - Laboratory Control Sample (LCS)

The LCS measures the accuracy of the method in a blank matrix and assesses method performance independent of potential field sample matrix affects in a laboratory batch.

The LCS is prepared from a clean matrix similar to that of the associated samples that is free from target analytes (for example: Reagent water, Ottawa sand, glass beads, etc.) and is processed along with and under the same conditions as the associated samples. The LCS is spiked with verified known amounts of analytes or is made of a material containing known and verified amounts of analytes, taken through all preparation and analysis steps along with the field samples. Where there is no preparation taken for an analysis (such as in aqueous volatiles), or when all samples and standards undergo the same preparation and analysis process (such as Phosphorus), a calibration verification standard is reported as the LCS. In some instances where there is no practical clean

solid matrix available, aqueous LCS's may be processed for solid matrices; final results may be calculated as mg/kg or ug/kg, assuming 100% solids and a weight equivalent to the aliquot used for the corresponding field samples, to facilitate comparison with the field samples.

Certified pre-made reference material purchased from a NIST/A2LA accredited vendor may also be used for the LCS when the material represents the sample matrix or the analyte is not easily spiked (e.g. solid matrix LCS for metals, TDS, etc.).

The specific frequency of use for LCS during the analytical sequence is defined in the specific standard operating procedure for each analysis. It is generally 1 for each batch of samples; not to exceed 20 environmental samples.

If the mandated or requested test method, or project requirements, do not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample (and Matrix Spike) where applicable (e.g. no spike of pH). However, in cases where the components interfere with accurate assessment (such as simultaneously spiking chlordane, toxaphene and PCBs in Method 608), the test method has an extremely long list of components or components are incompatible, at a minimum, a representative number of the listed components (see below) shall be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses, permit specified analytes and other client requested components. However, the laboratory shall ensure that all reported components are used in the spike mixture within a two-year time period.

- For methods that have 1-10 target analytes, spike all components.
- For methods that include 11-20 target analytes, spike at least 10 or 80%, whichever is greater.
- For methods with more than 20 target analytes, spike at least 16 components.
- Exception: Due to analyte incompatibility in pesticides, Toxaphene and Chlordane are only spiked at client request based on specific project needs.
- Exception: Due to analyte incompatibility between the various PCB Aroclors, Aroclors 1016 and 1260 are used for spiking as they cover the range of all of the Aroclors. Specific Aroclors may be used by request on a project specific basis.

24.5 Sample Matrix Controls

Table 24-3. Sample Matrix Control

Control Type	Details	
Matrix Spikes (MS)	Use	used to assess the effect sample matrix of the spiked sample has on the precision and accuracy of the results generated by the method used;
	Typical Frequency [1]	At a minimum, with each matrix-specific batch of samples processed, an MS is carried through the complete analytical procedure. Unless specified by the client, samples used for spiking are randomly selected and rotated between different client projects. If the mandated or requested test method does not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample and Matrix Spike. Refer to the method SOP for complete details
	Description	essentially a sample fortified with a known amount of the test analyte(s).
Surrogate	Use	Measures method performance to sample matrix (organics only).
	Typical Frequency [1]	Are added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. The recovery of the surrogates is compared to the acceptance limits for the specific method. Poor surrogate recovery may indicate a problem with sample composition and shall be reported, with data qualifiers, to the client whose sample produced poor recovery.
	Description	Are similar to matrix spikes except the analytes are compounds with properties that mimic the analyte of interest and are unlikely to be found in environment samples.
Duplicates[2]	Use	For a measure of analytical precision, with each matrix-specific batch of samples processed, a matrix duplicate (MD or DUP) sample, matrix spike duplicate (MSD), or LCS duplicate (LCSD) is carried through the complete analytical procedure.
	Typical Frequency [1]	Duplicate samples are usually analyzed with methods that do not require matrix spike analysis.
	Description	Performed by analyzing two aliquots of the same field sample independently or an additional LCS.
Internal Standards	Use	Are spiked into all environmental and quality control samples (including the initial calibration standards) to monitor the qualitative aspect of organic and some inorganic analytical measurements.
	Typical Frequency [1]	All organic and ICP methods as required by the analytical method.
	Description	Used to correct for matrix effects and to help troubleshoot variability in analytical response and are assessed after data acquisition. Possible sources of poor internal standard response are sample matrix, poor analytical technique or instrument performance.

[1] See the specific analytical SOP for type and frequency of sample matrix control samples.

[2] LCSD's are normally not performed except when regulatory agencies or client specifications require them. The recoveries for the spiked duplicate samples must meet the same laboratory established recovery limits as the accuracy QC samples. If an LCSD is analyzed both the LCS and LCSD must meet the same recovery criteria and be included in the final report. The precision measurement is reported as "Relative Percent Difference" (RPD). Poor precision between duplicates (except LCS/LCSD) may indicate non-homogeneous matrix or sampling.

24.6 Acceptance Criteria (Control Limits)

As mandated by the test method and regulation, each individual analyte in the LCS, MS, or Surrogate Spike is evaluated against the control limits published in the test method. Where there are no established acceptance criteria, the laboratory calculates in-house control limits with the use of control charts or, in some cases, utilizes client project specific control limits. When this occurs, the regulatory or project limits will supersede the laboratory's in-house limits.

Note: For methods, analytes and matrices with very limited data (e.g., unusual matrices not analyzed often), interim limits are established using available data or by analogy to similar methods or matrices.

Once control limits have been established, they are verified, reviewed, and updated if necessary on an annual basis unless the method requires more frequent updating. Control limits are established per method (as opposed to per instrument) regardless of the number of instruments utilized.

Laboratory generated % Recovery acceptance (control) limits are generally established by taking $\pm$ 3 Standard Deviations (99% confidence level) from the average recovery of a minimum of 20-30 data points (more points are preferred).

- Regardless of the calculated limit, the limit should be no tighter than the Calibration Verification (ICV/CCV). (Unless the analytical method specifies a tighter limit).

- In-house limits cannot be any wider than those mandated in a regulated analytical method. Client or contract required control limits are evaluated against the laboratory's statistically derived control limits to determine if the data quality objectives (DQOs) can be achieved. If laboratory control limits are not consistent with DQOs, then alternatives must be considered, such as method improvements or use of an alternate analytical method.

- The lowest acceptable recovery limit will be 10% (the analyte must be detectable and identifiable). Exception: The lowest acceptable recovery limit for Benzidine will be 5% and the analyte must be detectable and identifiable.

- The maximum acceptable recovery limit will be 185%.

- The maximum acceptable RPD limit will be 35% for waters and 40% for soils. The minimum RPD limit is 10%.

- If either the high or low end of the control limit changes by $\leq$ 5% from previous, the control chart is visually inspected and, using professional judgment, they may be left unchanged if there is no affect on laboratory ability to meet the existing limits.

24.6.1 The lab must be able to generate a current listing of their control limits and track when the updates are performed. In addition, the laboratory must be able to recreate historical control limits. See SOP TA-QA-0600 Quality Control Charting and Establishing Warning and Action Limits.

One example: The QA department generates a Quality Control Limit Summary that contains tables that summarize the precision and accuracy acceptability limits for analyses performed at TestAmerica Seattle. This summary includes an effective date, is updated each time new limits are generated and is located in the LIMS**.** Unless otherwise noted, limits within these tables are laboratory generated. The analysts are instructed to use the current limits in the laboratory (dated and approved by the Technical Manager and QA Manager) and entered into the Laboratory Information Management System (LIMS). The Quality Assurance department maintains an archive of all limits used within the laboratory.

24.6.2 A LCS that is within the acceptance criteria establishes that the analytical system is in control and is used to validate the process. Samples that are analyzed with an LCS with recoveries

outside of the acceptance limits may be determined as out of control and should be reanalyzed if possible. If reanalysis is not possible, then the results for all affected analytes for samples within the same batch must be qualified when reported. The internal corrective action process (see Section 12) is also initiated if an LCS exceeds the acceptance limits. If agreed to by the client, sample results may be qualified and reported without reanalysis if:

- The analyte results are below the reporting limit and the LCS is above the upper control limit.
- If the analytical results are above the relevant regulatory limit and the LCS is below the lower control limit.

Or, for TNI work, there are an allowable number of Marginal Exceedances (ME). (MEs are allowed for DoD/DOE work as long as the analyte is not a chemical of concern):

<11 analytes	0 marginal exceedances are allowed.
11 – 30 Analytes	1 marginal exceedance is allowed
31-50 Analytes	2 marginal exceedances are allowed
51-70 Analytes	3 marginal exceedances are allowed
71-90 Analytes	4 marginal exceedances are allowed
> 90 Analytes	5 marginal exceedances are allowed

- Marginal exceedances are recovery exceedances between 3 SD and 4 SD from the mean recovery limit (TNI).
- Marginal exceedances must be random. If the same analyte exceeds the LCS control limit repeatedly, it is an indication of a systematic problem. The source of the error must be located and corrective action taken. The laboratory has a system to monitor marginal exceedances to ensure that they are random.

Though marginal exceedances may be allowed, the data must still be qualified to indicate it is outside of the normal limits.

24.6.3 If the MS/MSDs do not meet acceptance limits, the MS/MSD and the associated spiked sample is reported with a qualifier for those analytes that do not meet limits. If obvious preparation errors are suspected, or if requested by the client, unacceptable MS/MSDs are reprocessed and reanalyzed to prove matrix interference. A more detailed discussion of acceptance criteria and corrective action can be found in the lab's method SOPs and in Section 12.

24.6.4 If a surrogate standard falls outside the acceptance limits, if there is not obvious chromatographic matrix interference, reanalyze the sample to confirm a possible matrix effect. If the recoveries confirm or there was obvious chromatographic interference, results are reported from the original analysis and a qualifier is added. If the reanalysis meets surrogate recovery criteria, the second run is reported (or both are reported if requested by the client). Under certain circumstances, where all of the samples are from the same location and share similar chromatography, the reanalysis may be performed on a single sample rather than all of the samples and if the surrogate meets the recovery criteria in the reanalysis, all of the affected samples would require reanalysis.

24.7 Additional Procedures to Assure Quality Control

The laboratory has written and approved method SOPs to assure the accuracy of the test method including calibration (see Section 20), use of certified reference materials (see Section 21) and use of PT samples (see Section 15).

A discussion regarding MDLs, Limit of Detection (LOD) and Limit of Quantitation (LOQ) can be found in Section 19.

- Use of formulae to reduce data is discussed in the method SOPs and in Section 20.
- Selection of appropriate reagents and standards is included in Section 9 and 21.
- A discussion on selectivity of the test is included in Section 5.
- Constant and consistent test conditions are discussed in Section 18.
- The laboratories sample acceptance policy is included in Section 23.

SECTION 25. REPORTING RESULTS

25.1 Overview

The results of each test are reported accurately, clearly, unambiguously, and objectively in accordance with State and Federal regulations as well as client requirements. Analytical results are issued in a format that is intended to satisfy customer and laboratory accreditation requirements as well as provide the end user with the information needed to properly evaluate the results. Where there is conflict between client requests and laboratory ethics or regulatory requirements, the laboratory's ethical and legal requirements are paramount, and the laboratory will work with the client during project set up to develop an acceptable solution. Refer to Section 7.

A variety of report formats are available to meet specific needs.

In cases where a client asks for simplified reports, there must be a written request from the client. There still must be enough information that would show any analyses that were out of conformance (QC out of limits) and there should be a reference to a full report that is made available to the client. Review of reported data is included in Section 19.

25.2 Test Reports

Analytical results are reported in a format that is satisfactory to the client and meets all requirements of applicable accrediting authorities and agencies. A variety of report formats are available to meet specific needs. The report is printed on laboratory letterhead, reviewed, and signed by the appropriate project manager or designee. At a minimum, the standard laboratory report shall contain the following information:

25.2.1 A report title (e.g. Analytical Report For Samples) with a "sample results" column header.

25.2.2 Each report cover page printed on company letterhead, which includes the laboratory name, address and telephone number.

25.2.3 A unique identification of the report (e.g. job number) and on each page an identification in order to ensure the page is recognized as part of the report and a clear identification of the end.

Note: Page numbers of report are represented as page # of ##. Where the first number is the page number and the second is the total number of pages.

25.2.4 A copy of the chain of custody (COC).

- Any COCs involved with Subcontracting are included.

25.2.5 The name and address of client and a project name/number, if applicable.

25.2.6 Client project manager or other contact

25.2.7 Description and unambiguous identification of the tested sample(s) including the client identification code.

25.2.8 Date of receipt of sample, date and time of collection, and date(s) of test preparation and performance, and time of preparation or analysis if the required holding time for either activity is less than or equal to 72 hours.

25.2.9 Date reported or date of revision, if applicable.

25.2.10 Method of analysis including method code (EPA, Standard Methods, etc).

25.2.11 Reporting limit.

25.2.12 Method detection limits (if requested)

25.2.13 Definition of Data qualifiers and reporting acronyms (e.g. ND).

25.2.14 Sample results.

25.2.15 QC data consisting of method blank, surrogate, LCS, and MS/MSD recoveries and control limits.

25.2.16 Condition of samples at receipt including temperature. This may be accomplished in a narrative or by attaching sample login sheets (Refer to Sec. 25.2.4 – Item 3 regarding additional addenda).

25.2.17 A statement to the effect that the results relate only to the items tested and the sample as received by the laboratory.

25.2.18 A statement that the report shall not be reproduced except in full, without prior express written approval by the laboratory coordinator.

25.2.19 A signature and title of the person(s) accepting responsibility for the content of the report and date of issue. Signatories are appointed by the Lab Director.

25.2.20 When NELAC accreditation is required, the lab shall certify that the test results meet all requirements of TNI or provide reasons and/or justification if they do not.

25.2.21 Where applicable, a narrative to the report that explains the issue(s) and corrective action(s) taken in the event that a specific accreditation or certification requirement was not met.

25.2.22 When soil samples are analyzed, a specific identification as to whether soils are reported on a “wet weight” or “dry weight” basis.

25.2.23 Appropriate laboratory certification number for the state of origin of the sample, if applicable.

25.2.24 If only part of the report is provided to the client (client requests some results before all of it is complete), it must be clearly indicated on the report (e.g., preliminary). A complete report must be sent once all of the work has been completed.

25.2.25 Any non-TestAmerica subcontracted analysis results are provided as a separate report on the official letterhead of the subcontractor. All TestAmerica subcontracting is clearly identified on the report as to which laboratory performed a specific analysis.

25.2.26 A Certification Summary Report, where required, will document that, unless otherwise noted, all analytes tested and reported by the laboratory were covered by the noted certifications.

Note: Refer to the Corporate SOP on Electronic Reporting and Signature Policy (No. CA-I-P-002) for details on internally applying electronic signatures of approval.

25.3 Reporting Level or Report Type

The laboratory offers four levels of quality control reporting. Each level, in addition to its own specific requirements, contains all the information provided in the preceding level. The packages provide the following information in addition to the information described above:

- Level I is a report with the features described in Section 25.2 above, *excluding 25.2.15 (QC data).*
- Level II is a Level I report plus summary information, including results for the method blank reported to the laboratory MDL (if requested), percent recovery for laboratory control samples and matrix spike samples, and the RPD values for all MSD and sample duplicate analyses.
- Level III contains all the information supplied in Level II, but presented on the CLP-like summary forms, and relevant calibration information. A Level II report is not included, unless specifically requested. No raw data is provided.
- Level IV is the same as Level III with the addition of all raw supporting data.

In addition to the various levels of QC packaging, the laboratory also provides reports in diskette deliverable form. Initial reports may be provided to clients by facsimile. All faxed reports are followed by hardcopy. Procedures used to ensure client confidentiality are outlined in Section 25.6.

25.3.1 Electronic Data Deliverables (EDDs)

EDDs are routinely offered as part of TestAmerica's services in addition to the test report as described in section 25.2. When NELAP accreditation is required and both a test report and EDD are provided to the client, the official version of the test report will be the combined information of the report and the EDD. TestAmerica Seattle offers a variety of EDD formats including Environmental Restoration Information Management System (ERPIMS), Staged Electronic Data Deliverable (SEDD) Environmental Quality Information System (EQuIS), Electronic Deliverable Format (EDF), Excel and custom files.

EDD specifications are submitted to the IT department by the PM for review and undergo the contract review process. Once the facility has committed to providing data in a specific electronic format, the coding of the format may need to be performed. This coding is documented and validated. The validation of the code is retained by the IT staff coding the EDD.

EDDs shall be subject to a review to ensure their accuracy and completeness. If EDD generation is automated, review may be reduced to periodic screening if the laboratory can demonstrate that it can routinely generate that EDD without errors. Any revisions to the EDD format must be reviewed until it is demonstrated that it can routinely be generated without errors. If the EDD can be reproduced accurately and if all subsequent EDDs can be produced error-free, each EDD does not necessarily require a review.

25.4 Supplemental Information for Test

The lab identifies any unacceptable QC analyses or any other unusual circumstances or observations such as environmental conditions and any non-standard conditions that may have affected the quality of a result. This is typically in the form of a footnote or a qualifier and/or a narrative explaining the discrepancy in the front of the report.

Numeric results with values outside of the calibration range, either high or low are qualified as 'estimated'.

Where quality system requirements are not met, a statement of compliance/non-compliance with requirements and/or specifications is required, including identification of test results derived from any sample that did not meet TNI sample acceptance requirements such as improper container, holding time, or temperature.

Where applicable, a statement on the estimated uncertainty of measurements; information on uncertainty is needed when a client's instructions so require.

Opinions and Interpretations - The test report contains objective information, and generally does not contain subjective information such as opinions and interpretations. If such information is required by the client, the Laboratory Director will determine if a response can be prepared. If so, the Laboratory Director will designate the appropriate member of the management team to prepare a response. The response will be fully documented, and reviewed by the Laboratory Director, before release to the client. There may be additional fees charged to the client at this time, as this is a non-routine function of the laboratory.

Note: Review of data deliverable packages for submittal to regulatory authorities requires responses to non-conforming data concerning potential impact on data quality. This necessitates a limited scope of interpretation, and this work is performed by the QA Department. This is the only form of "interpretation" of data that is routinely performed by the laboratory.

When opinions or interpretations are included in the report, the laboratory provides an explanation as to the basis upon which the opinions and interpretations have been made. Opinions and interpretations are clearly noted as such and where applicable, a comment should be added suggesting that the client verify the opinion or interpretation with their regulator.

25.5 Environmental Testing Obtained From Subcontractors

If the laboratory is not able to provide the client the requested analysis, the samples would be subcontracted following the procedures outlined in the Corporate SOP on Subcontracting (SOP No. *CW-L-S-004*).

Data reported from analyses performed by a subcontractor laboratory are clearly identified as such on the analytical report provided to the client. Results from a subcontract laboratory outside of TestAmerica are reported to the client on the subcontract laboratory's original report stationary and the report includes any accompanying documentation.

25.6 Client Confidentiality

In situations involving the transmission of environmental test results by telephone, facsimile or other electronic means, client confidentiality must be maintained.

TestAmerica will not intentionally divulge to any person (other than the Client or any other person designated by the Client in writing) any information regarding the services provided by TestAmerica or any information disclosed to TestAmerica by the Client. Furthermore, information known to be potentially endangering to national security or an entity's proprietary rights will not be released.

Note: This shall not apply to the extent that the information is required to be disclosed by TestAmerica under the compulsion of legal process. TestAmerica will, to the extent feasible, provide reasonable notice to the client before disclosing the information.

Note: Authorized representatives of an accrediting authority are permitted to make copies of any analyses or records relevant to the accreditation process, and copies may be removed from the laboratory for purposes of assessment.

25.6.1 Report deliverable formats are discussed with each new client. If a client requests that reports be faxed or e-mailed, the reports are to meet all requirements of this document, include cover letter.

25.7 Format of Reports

The format of reports is designed to accommodate each type of environmental test carried out and to minimize the possibility of misunderstanding or misuse.

25.8 Amendments to Test Reports

Corrections, additions, or deletions to reports are only made when justification arises through supplemental documentation. Justification is documented using the laboratory's corrective action system (refer to Section 12).

The revised report is retained on the Archive data server, as is the original report. The revised report is stored in the Archive data server under the job number followed by the appropriate revision number. The revised report will have the "Rev" followed by the revision number in the report file name.

When the report is re-issued, a notation of "Revision" with the appropriate number is placed on the cover/signature page of the report or at the top of the narrative page with a brief explanation of reason for the re-issue and a reference back to the last final report generated. For example: Report was revised on 11/3/08 to include toluene in sample NQA1504 per client's request. This final report replaces the final report generated on 10/27/08 at 10:47am.

25.9 Policies on Client Requests for Amendments

25.9.1 Policy on Data Omissions or Reporting Limit Increases

Fundamentally, our policy is simply to not omit previously reported results (including data qualifiers) or to not raise reporting limits and report sample results as ND. This policy has few exceptions. Exceptions are:

- Laboratory error.
- Sample identification is indeterminate (confusion between COC and sample labels).
- An incorrect analysis (not analyte) was requested (e.g., COC lists 8315 but client wanted 8310). A written request for the change is required.
- Incorrect limits reported based on regulatory requirements.
- The requested change has absolutely no possible impact on the interpretation of the analytical results and there is no possibility of the change being interpreted as misrepresentation by anyone inside or outside of our company.

25.9.2 Multiple Reports

TestAmerica does not issue multiple reports for the same work order where there is different information on each report (this does not refer to copies of the same report) unless required to meet regulatory needs and approved by QA.

Appendix 1. Laboratory Floor Plan

Key Areas *

1. Admin/HR
2. QA Offices
3. Project Management
4. Sample Control
5. Metals & Mercury Lab
6. Wet / General Chem
7. Metals Prep
8. Organics Prep
9. GC-MS SVOA
10. GC SVOA
11. GC & GC-MS VOA
12. Sample Disposal
13. GeoTech, Storage, Warehouse
14. Conference Room

Appendix 2. Glossary/Acronyms (EL-V1M2 Sec. 3.1)

Glossary:

Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQC)

Accreditation: The process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory.

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)

Analyst: The designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.

Analytical Uncertainty: A subset of Measurement Uncertainty that includes all laboratory activities performed as part of the analysis. (TNI)

Anomaly: A condition or event, other than a deficiency, that may affect the quality of the data, whether in the laboratory's control or not.

Assessment: The evaluation process used to measure or establish the performance, effectiveness, and conformance of an organization and/or its systems to defined criteria (to the standards and requirements of laboratory accreditation). (TNI)

Audit: A systematic and independent examination of facilities, equipment, personnel, training, procedures, record-keeping, data validation, data management, and reporting aspects of a system to determine whether QA/QC and technical activities are being conducted as planned and whether these activities will effectively achieve quality objectives. (TNI)

Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples. (TNI)

Bias: The systematic or persistent distortion of a measurement process, which causes errors in one direction (i.e., the expected sample measurement is different from the sample's true value). (TNI)

Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)

Calibration: A set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards. (TNI)

1) In calibration of support equipment the values realized by standards are established through the use of reference standards that are traceable to the International System of Units (SI).

2) In calibration according to methods, the values realized by standards are typically established through the use of Reference Materials that are either purchased by the laboratory with a certificate of analysis or purity, or prepared by the laboratory using support equipment that has been calibrated or verified to meet specifications.

Calibration Curve: The mathematical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. (TNI)

Calibration Standard: A substance or reference material used to calibrate an instrument (QAMS)

Certified Reference Material (CRM): A reference material accompanied by a certificate, having a value, measurement uncertainty, and stated metrological traceability chain to a national metrology institute. (TNI)

Chain of Custody (COC) Form: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; the collector; time of collection; preservation; and requested analyses. (TNI)

Compromised Samples: Those samples which are improperly sampled, insufficiently documented (chain of custody and other sample records and/or labels), improperly preserved, collected in improper containers, or exceeding holding times when delivered to a laboratory. Under normal conditions, compromised samples are not analyzed. If emergency situation require analysis, the results must be appropriately qualified.

Confidential Business Information (CBI): Information that an organization designates as having the potential of providing a competitor with inappropriate insight into its management, operation or products. TNI and its representatives agree to safeguarding identified CBI and to maintain all information identified as such in full confidentiality.

Confirmation: Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to Second Column Confirmation; Alternate wavelength; Derivatization; Mass spectral interpretation; Alternative detectors or Additional Cleanup procedures. (TNI)

Conformance: An affirmative indication or judgment that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements. (ANSI/ASQC E4-1994)

Correction: Actions necessary to correct or repair analysis specific non-conformances. The acceptance criteria for method specific QC and protocols as well as the associated corrective actions. The analyst will most frequently be the one to identify the need for this action as a result of calibration checks and QC sample analysis**.** No significant action is taken to change behavior, process or procedure.

Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)

Data Audit: A qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data re of acceptable quality (i.e., that they meet specified acceptance criteria).

Data Reduction: The process of transforming the number of data items by arithmetic or statistical calculations, standard curves, and concentration factors, and collation into a more useable form. (TNI)

Deficiency: An unauthorized deviation from acceptable procedures or practices, or a defect in an item. (ASQC), whether in the laboratory's control or not.

Demonstration of Capability: A procedure to establish the ability of the analyst to generate analytical results of acceptable accuracy and precision. (TNI)

Document Control: The act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly, and controlled to ensure use of the correct version at the location where the prescribed activity if performed. (ASQC)

Duplicate Analyses: The analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA-QAD)

Equipment Blank: Sample of analyte-free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures.

External Standard Calibration: Calibrations for methods that do not utilize internal standards to compensate for changes in instrument conditions.

Field Blank: Blank prepared in the field by filing a clean container with pure de-ionized water and appropriate preservative, if any, for the specific sampling activity being undertaken (EPA OSWER)

Field of Accreditation: Those matrix, technology/method, and analyte combinations for which the accreditation body offers accreditation.

Holding Times: The maximum time that samples may be held prior to analyses and still be considered valid or not compromised. (40 CFR Part 136)

Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical test method. (TNI)

Internal Standard Calibration: Calibrations for methods that utilize internal standards to compensate for changes in instrument conditions.

Instrument Blank: A clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (EPA-QAD)

Instrument Detection Limit (IDL): The minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific instrument. The IDL is associated with the instrumental portion of a specific method only, and sample preparation steps are not considered in its derivation. The IDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is $\pm$ 100%. The IDL represents a range where qualitative detection occurs on a specific instrument. Quantitative results are not produced in this range.

Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample)**:** A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes, taken through all preparation and analysis steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

An LCS shall be prepared at a minimum of 1 per batch of 20 or less samples per matrix type per sample extraction or preparation method except for analytes for which spiking solutions are not available such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. The results of these samples shall be used to determine batch acceptance.

Least Squares Regression (1st Order Curve): The least squares regression is a mathematical calculation of a straight line over two axes. The y axis represents the instrument response (or Response ratio) of a standard or sample and the x axis represents the concentration. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99 for organics and 0.995 for inorganics.

Limit(s) of Detection (LOD) [a.k.a., Method Detection Limit (MDL)]: *The MDL is the minimum measured quantity of a substance that can be reported with 99% confidence that the concentration is distinguishable from method blank results, consistent with 40CFR Part 136 Appendix B, August, 2017*

Limit(s) of Quantitation (LOQ) [a.k.a., Reporting Limit]: The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

(QS) Matrix: The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions shall be used:

Aqueous: Any aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine. Includes surface water, groundwater, effluents, and TCLP or other extracts.

Drinking Water: Any aqueous sample that has been designated as a potable or potential potable water source.

Saline/Estuarine: Any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.

Non-Aqueous Liquid: Any organic liquid with <15% settleable solids.

Biological Tissue: Any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.

Solids: Includes soils, sediments, sludges, and other matrices with >15% settleable solids.

Chemical Waste: A product or by-product of an industrial process that results in a matrix not previously defined.

Air & Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter, or other device. (TNI)

Matrix Spike (spiked sample or fortified sample): A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of sample for which an independent test result of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A replicate matrix spike ~~is~~ prepared and analyzed to obtain a measure of the precision of the recovery for each analyte.

Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

Method Detection Limit: *See Limit of Detection (LOD).*

Negative Control: Measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results.

Non-conformance: An indication, judgment, or state of not having met the requirements of the relevant specifications, contract, or regulation.

Observation: A record of phenomena that (1) may assist in evaluation of the sample data; (2) may be of importance to the project manager and/or the client, and yet not at the time of the observation have any known effect on quality.

Performance Audit: The routine comparison of independently obtained qualitative and quantitative measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory.

Positive Control: Measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects.

Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (TNI)

Preservation: Any conditions under which a sample must be kept in order to maintain chemical and/or biological integrity prior to analysis. (TNI)

Proficiency Testing: A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source. (TNI)

Proficiency Testing Program: The aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results and the collective demographics and results summary of all participating laboratories. (TNI)

Proficiency Test Sample (PT): A sample, the composition of which is unknown to the laboratory and is provided to test whether the laboratory can produce analytical results within specified acceptance criteria. (TNI)

Quality Assurance: An integrated system of management activities involving planning, implementation, assessment, reporting and quality improvement to ensure that a process, item, or service is of the type of quality needed and expected by the client. (TNI)

Quality Assurance [Project] Plan (QAPP): A formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved. (EAP-QAD)

Quality Control: The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality; also the system of activities and checks used to ensure that measurement systems are maintained

within prescribed limits, providing protection against “out of control” conditions and ensuring that the results are of acceptable quality. (TNI)

Quality Control Sample: A sample used to assess the performance of all or a portion of the measurement system. One of any number of samples, such as Certified Reference Materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking, intended to demonstrate that a measurement system or activity is in control. (TNI)

Quality Manual: A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users. (TNI)

Quality System: A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC activities. (TNI)

Raw Data: The documentation generated during sampling and analysis. This documentation includes, but is not limited to, field notes, electronic data, magnetic tapes, untabulated sample results, QC sample results, print outs of chromatograms, instrument outputs, and handwritten records. (TNI)

Record Retention: The systematic collection, indexing and storing of documented information under secure conditions.

Reference Material: Material or substance, one or more properties of which are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (TNI)

Reference Standard: Standard used for the calibration of working measurement standards in a given organization or a given location. (TNI)

Sampling: Activity related to obtaining a representative sample of the object of conformity assessment, according to a procedure.

Second Order Polynomial Curve (Quadratic): The 2^{nd} order curves are a mathematical calculation of a slightly curved line over two axis. The y axis represents the instrument response (or Response ratio) of a standard or sample and the x axis represents the concentration. The 2^{nd} order regression will generate a coefficient of determination (COD or r^2) that is a measure of the "goodness of fit" of the quadratic curvature the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r^2 must be greater than or equal to 0.99.

Selectivity: The ability to analyze, distinguish, and determine a specific analyte or parameter from another component that may be a potential interferent or that may behave similarly to the target analyte or parameter within the measurement system. (TNI)

Sensitivity: The capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. (TNI)

Spike: A known mass of target analyte added to a blank, sample or sub-sample; used to determine recovery efficiency or for other quality control purposes.

Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of standard setting and meets the approval requirements of standard adoption organizations procedures and policies. (TNI)

Standard Operating Procedures (SOPs): A written document which details the method for an operation, analysis, or action, with thoroughly prescribed techniques and steps. SOPs are officially approved as the methods for performing certain routine or repetitive tasks. (TNI)

Storage Blank: A blank matrix stored with field samples of a similar matrix (volatiles only) that measures storage contribution to any source of contamination.

Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

Surrogate compounds must be added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. Poor surrogate recovery may indicate a problem with sample composition and shall be reported to the client whose sample produced poor recovery. (QAMS)

Systems Audit (also Technical Systems Audit): A thorough, systematic, qualitative on-site assessment of the facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a total measurement system. (EPA-QAD)

Technical Manager: A member of the staff of an environmental laboratory who exercises actual day-to-day supervision of laboratory operations for the appropriate fields of accreditation and reporting of results

Technology: A specific arrangement of analytical instruments, detection systems, and/or preparation techniques.

Traceability: The ability to trace the history, application, or location of an entity by means of recorded identifications. In a calibration sense, traceability relates measuring equipment to national or international standards, primary standards, basic physical constants or properties, or reference materials. In a data collection sense, it relates calculations and data generated throughout the project back to the requirements for the quality of the project. (TNI)

Trip Blank: A blank matrix placed in a sealed container at the laboratory that is shipped, held unopened in the field, and returned to the laboratory in the shipping container with the field samples.

Uncertainty: A parameter associated with the result of a measurement that characterizes the dispersion of the value that could reasonably be attributed to the measured value.

Acronyms:

CAR – Corrective Action Report
CCV – Continuing Calibration Verification
CF – Calibration Factor
CFR – Code of Federal Regulations
COC – Chain of Custody
DOC – Demonstration of Capability
DQO – Data Quality Objectives
DUP - Duplicate
EHS – Environment, Health and Safety
EPA – Environmental Protection Agency

GC - Gas Chromatography
GC/MS - Gas Chromatography/Mass Spectrometry
HPLC - High Performance Liquid Chromatography
ICP - Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP/MS – ICP/Mass Spectrometry
ICV – Initial Calibration Verification
IDL – Instrument Detection Limit
IH – Industrial Hygiene
IS – Internal Standard
LCS – Laboratory Control Sample
LCSD – Laboratory Control Sample Duplicate
LIMS – Laboratory Information Management System
LOD – Limit of Detection
LOQ – Limit of Quantitation
LOQV - Limit of Quantitation Check Standard
MDL – Method Detection Limit
MDLV – MDL Verification Check Standard
MRL – Method Reporting Limit
MS – Matrix Spike
MSD – Matrix Spike Duplicate
MSDS - Material Safety Data Sheet
NELAP - National Environmental Laboratory Accreditation Program
PT – Performance Testing
TNI – The NELAC Institute
QAM – Quality Assurance Manual
QA/QC – Quality Assurance / Quality Control
QAPP – Quality Assurance Project Plan
RF – Response Factor
RPD – Relative Percent Difference
RSD – Relative Standard Deviation
SD – Standard Deviation
SOP – Standard Operating Procedure
TAT – Turn-Around-Time
VOA – Volatiles
VOC – Volatile Organic Compound

Appendix 3. Laboratory Certifications, Accreditations, Validations

TestAmerica Seattle maintains accreditations, certifications, and approvals with numerous state and national entities. Programs vary but may include on-site audits, reciprocal agreements with another entity, performance testing evaluations, review of the QA Manual, Standard Operating Procedures, Method Detection Limits, training records, etc. At the time of this QA Manual revision, the laboratory has accreditation/certification/licensing with the following organizations:

Organization	Lab ID Number
DoD ELAP	L2236
ISO 17025	L2236
Alaska	*17-024*
California	2901
Montana	(UST – no number)
Oregon (NELAP)	WA100007
Washington	C553
USDA Soil Permit	P330-17-00039
US Fish & Wildlife	LE058448-0

The certificates and accredited parameter lists are available for each State/Program at www.testamericainc.com under Analytical Services Search – Certifications.

Title: Alkalinity by Titration [Methods 310.1, SM 2320B]

Approvals

Signatures on File	
Stan Palmquist Date Inorganic Department Manager	Manjit Nijjar Date Health & Safety Manager / Coordinator
Manjit Nijjar Date Quality Assurance Assistant For Terri Torres Quality Assurance Manager	Dennis Bean Date Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This method is applicable for the measurement of alkalinity in drinking, surface, and saline waters, and domestic and industrial wastes.

1.1.2 This method is applicable to all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50-mL.

1.1.3 The reporting limit for both methods is 5 mg/L.

1.1.4 Automated titrimetric analysis is equivalent.

1.1.5 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

Samples are titrated with 0.02N sulfuric acid for <1000 mg/L $CaCO_3$ or 0.1N sulfuric acid for > 1000 mg/L $CaCO_3$ to an endpoint of pH 4.5. The end point is determined with a pH meter. Results are reported as mg/L calcium carbonate.

3.0 Definitions

3.1 pH - At a given temperature, the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Because of the ionic interactions in all but very dilute solutions, it is necessary to use the "activity" of the hydrogen ion and not its molar concentration. The approximate equivalent to molarity can be presumed only in very dilute solutions. A logarithmic scale is used for pH in order to express a wide range of hydrogen ion activities. Neutral pH is 7.0 at 25 ^{o}C, while acidic pH's are <7 and basic pH's are >7.

3.2 Alkalinity – A measure of the acid-neutralizing capacity of water.

3.3 Conductivity - A measure of the ability of water to carry an electrical current.

4.0 Interferences

4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity.

4.2 Coatings of oily material or particulate matter can impair electrode response. Gentle wiping or detergent washing, followed by distilled water rinsing can usually remove coatings.

4.3 Samples with high concentrations of salts of weak organic or inorganic acids may have interferences. Alkalinity for samples with high concentrations of mineral acids should be determined using an electrometric endpoint of 3.9, using the ASTM procedure.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum. Cut resistant gloves must be worn when using sharp tools or when washing glassware.

5.1 Specific Safety Concerns or Requirements

5.1.1 None

5.2 Primary Materials Used

There are no materials with a health rating of 3 or 4 used in this method. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

6.1 Method 310.1

- pH meter, Orion SA 720 or equivalent.
- Combination electrode with temperature compensating probe.
- Magnetic stirrer and stir bar.
- Beaker, 50 ml.
- Laboratory balance, minimum 0.001 g accuracy. Check the Balance logbook to determine if the daily calibration check has been completed. If it has not, the analyst must perform this check according to SOP TA-QA-0014.
- Spatula or scoopula.
- Volumetric pipet, 20.0-mL, 3.0-mL
- Buret, 50-mL, 25-mL, and 10-mL, Class A
- Oven, 250 °C
- Desiccator
- Volumetric flask, 1 liter
- Mettler DL70 Autotitrator

7.0 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- Data acquisition/processing system: LIMS system: TALS version 1.0 or higher

8.0 Reagents and Standards

8.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

8.2 Deionized (DI) water.

8.3 0.02N Sulfuric acid solution purchased standardized, Fisher part number, SA226-4.

8.4 0.1 N Sulfuric acid solution purchased standardized, Fisher part number SA220-4.

See certificate of analysis for exact Normality that is used for constant with the auto titrator.

8.5 1000 mg/L Alkalinity Standard, purchased standard, Absolute Standards #54142. 100 gm/L ICV may be diluted from the certified stock standard by a factor of 10. Prepare as needed.

8.6 100 mg/L Spike Standard for LCS and CCV

Stock standard; in a 1000 mL volumetric flask, dissolve 0.1060 g Anhydrous Sodium Carbonate (oven dried at 250 °C for four hours) in 700 mL previously boiled DI water and then bring to 1000 mL with DI water for a 100 mg/L $CaCO_3$ standard. Standard may be stored for up to a week.

8.7 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards/reagents and dispose of them according to SOP TA-EHS-0036.

9.0 Sample Collection, Preservation, Shipment and Storage

9.1 The sample container must be filled completely, sealed and stored between 0-6°C.

9.2 Care must be taken to minimize exposure of the sample to the atmosphere; open the sample immediately before analysis.

9.3 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	HDPE	50 mLs	Cool 0-6°C	14 Days	40 CFR Part 136.3

10.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section.

9.2 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in SOP TA-QA-0620, Quality Control Program.

9.4 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.5 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.6 Batch Definition

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a laboratory control sample (LCS), and duplicate (DUP). As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.7 Method Blank (MB)

Method blanks (MB) are not applicable to this technique.

9.8 Laboratory Control Sample (LCS)

At least one LCS (see Section 7.4) must be processed with each batch. If there isn't sufficient sample for a duplicate sample analysis (9.9), then a LCSD must also be processed. The LCS is used to monitor the accuracy of the analytical process.

Acceptance Criteria: The LCS result must be within 15% of the true value.

Corrective Action: If LCS recoveries are outside established control limits, the analytical system is out of control and corrective action must be taken.

If recoveries are above control limits and carbonate is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.9 Duplicate Sample Analysis

A duplicate pair is required with each analytical batch and must be within 20% RPD. If there isn't sufficient sample for a duplicate sample analysis, then a LCSD (9.8) must also be processed. Note that the control limits only apply to samples with results greater than 5 times the RL. The process of establishing control limits is described in more detail in the QC SOP TA-QA-0620.

Corrective Action: If the RPD is greater than 20 the sample should be reanalyzed if within holding time and sufficient sample is remaining.

9.10 Continuing Calibration Verification (CCV)

A CCV is required after every 10 or fewer samples and after the last sample. Acceptance Criteria: The CCV recovery must be 85-115%. Corrective Action: If the recovery is outside of the acceptance Limits, all samples analyzed since the last successful CCV must be reanalyzed.

9.12 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

11.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of management to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP # TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

11.1 Sample Preparation

The sample must not be filtered, diluted, concentrated, or altered in any way except at the request of the client (this request must be indicated in an NCM).

11.2 Autotitrator Volume Check

11.2.1 Review the calibration label on the titrator to insure that the last volume check conducted on the titrator applies to the current quarter. If not, check the dispensed volume according to the procedures detailed in SOP TA-QA-0016.

11.3 Calibration

11.3.1 Calibrate the **Mettler DL12** autotitrator as follows:

11.3.1.1 The date must be entered into the auto-titrator every day before beginning analysis. Turn on the instrument and when prompted enter the

month, press 'START', enter the day, press 'START', enter the year and press 'START'.

11.3.1.2 The pH probe must be calibrated every day before beginning analysis. Press '3' on the keypad followed by the 'ELEC CALIB' button. Place enough pH 4.0 buffer solution in a sample cup to cover the probe (approx. 30-mL) and when the 'Buffer A' light blinks press 'Start'. When the 'Buffer B' light blinks, replace the pH 4.0 buffer solution with a pH 10.0 buffer solution. When calibration is complete the instrument will print out a calculated slope. This slope must be between –52 and –62 mV/pH to be valid. If the slope is outside of this range, the probe must be recalibrated.

11.3.2 Calibrate the **Mettler DL70** as follows:

11.3.2.1 The date must be entered into the auto-titrator every day before beginning analysis.

11.3.2.2 The pH probe must be calibrated every day before beginning analysis. With about 40 mL of pH buffer solution 4.0 and 10.0 in the first two positions on the autosampler, run User Method 1. When calibration is complete the instrument will print out a calculated slope. This slope must be between –52 and –62 mV/pH to be valid. If the slope is outside of this range, the probe must be recalibrated. Ideally the midpoint should be 7.0 ± 0.1.

11.4 Sample Analysis for the Mettler DL70

11.4.1 Measure 30 mL of sample into sample cup and place cups into autosampler. Note: Autosampler spins clockwise, so samples need to be loaded counter clockwise from the 1st position.

11.4.2 Run User Method 3. Enter sample IDs into the run log.

11.4.3 Open sequence with an ICV, LCS, Sample, DUP. Include a CCV after every 10th samples and at the end of the batch.

11.4.4 A high-level CCV should be used for samples that exceed titration limit using the 0.02 N sulfuric acid and the samples plus the high-level CCV must be re-titrated using 0.1 N sulfuric acid.

11.5 Instrument Maintenance

11.5.1 Volumetric verification of the Mettler DL70 autotitrator must be performed quarterly.

11.5.2 No regular maintenance is required for this instrumentation.

11.5.3 All instrument maintenance must be documented in the instrument maintenance logbook.

11.6 Troubleshooting

11.6.1 Refer to Appendix A, Mettler Troubleshooting Guide.

12.0 Calculations / Data Reduction

12.1 Accuracy

$$\textbf{LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

12.2 Precision (RPD)

Sample Duplicate (SD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

12.3 Concentration

Alkalinity, mg $CaCO_3$/L = $\frac{\text{mL of acid x N of acid x 50,000}}{\text{mL of sample}}$

12.4 Calculate the individual forms of alkalinity as follows:

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
P = ND	ND	ND	T
P < T/2	ND	2P	T - 2P
P = T/2	ND	2P	ND
P > T/2	2P - T	2(T - P)	ND
P = T	T	ND	ND

Where:

T = Total Alkalinity = Alkalinity at pH 4.5
P = Phenolphthalein Alkalinity = Alkalinity at pH 8.3

12.5 Method Detection Limit Study (MDL)

A method detection limit (MDL) study is not performed for this analysis.

12.6 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.7 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 The following waste streams are produced when this method is carried out:

14.1.1 Acidified samples are disposed of into the neutralization tank.

15.0 References / Cross-References

15.1 Methods for the Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method

310.1.

15.2 Standard Methods for Analysis of Water and Wastewater, 19th edition, 1995, Method 2320B.

15.3 Annual book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, 1976.

15.4 Mettler DL 70 Operation Instruction Manual.

16.0 Method Modifications:

None

17.0 Attachments

17.1 Appendix A, Mettler Troubleshooting Guide

18.0 Revision History

- Revision 17.1, dated 30 March 2018
  - Annual review, no changes

- Revision 17, dated 28 March 2017
  - Updated Approvers

- Revision 16, dated 2 January 2016
  - Added allowance for client requests to section 11.1
  - Added mid-point requirement for pH meter, section 11.3.2.2
  - Removed reference and procedures for the Mettler DL12
  - Added requirement for samples exceeding the titration limit using 0.02 N sulfuric acid, section 11.5.3

- Revision 15, dated 2 December 2014
  - Added/Updated Computer Hardware and Software, section 7.0
  - Changed water from ASTM type II to Deionized (DI) water, section 7.2
  - Added Maintenance and Troubleshooting, sections 11.6 and 11.7
  - Added Appendix A

- Revision 14, dated 20 November 2013
  - Added Mettler DL70 as equipment
  - Removed Method Blank (MB) and Continuing Calibration Blank (CCB) from batch QC
  - Clarified that ICV standard is purchased
  - Clarified steps for making LCS/CCV
  - Changed passing slope of pH calibration to match manufactures specifications
  - Added calibration and analytical instructions for Mettler DL70

- Revision 13, dated 25 September 2012
  - Removed portion of calibration section that was about sample analysis and not calibration (coved in sample analysis section).

- Revision 12, dated 10 September 2012
  - Updated section 5.0
  - Updated waste streams, section 14.1.

- Revision 11, dated 16 May 2011
  - Updated method blank acceptance criteria in Section 9.7 for DOD QSM 4.1

compliance (ROMD 00008).
    - Incorporated ROM 00025 in section 9.8 and 9.9
    - Developed sample analysis in section 10.4

- Revision 10, dated 16 April 2010
    - Updated reporting limit, section 1.1.3
    - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
    - Added removal of expired standards Section 7.6.
    - Added requirement for daily balance check, Section 6.1.
    - Added criteria for extra QC, Section 9.2.
    - Added instruction to verify the last volume check performed. Section 10.2

- Revision 9, dated 1 December 2008
    - Integration for TestAmerica and STL operations.
    - Removal of reference and procedures related to MCAWW Method 310.2.

Appendix A, Mettler Troubleshooting Guide

9. Error messages and malfunctions

9.1 Error messages of the titrator

The titrator sends you messages regarding errors that you can rectify yourself. Four such messages draw your attention to this section:

1. **EEPROM inserted wrongly** (EEPROM = user data memory)

   For some reason or other, you have inserted the user data memory in which the installation data are stored into the second IC socket (see Section 11.1.8: ***Illustration IC socket (2)***).

   Measure: – Switch off the titrator and disconnect from power supply.
   – Insert the user data memory into the first IC socket.

2. **Faulty data deleted**

   a. The titrator has saved only parts of a method if, e.g. during storage of this method the power failed. It deletes this method completely. It is also possible that several methods have been deleted.

   Measure: – Confirm the message with **RUN**.
   – Check whether your methods have been deleted and reenter if necessary.

   b. The titrator has saved only parts of parameters of a resource if, e.g. during storage of these parameters the power failed. It deletes the entire list of this resource (e.g. all titrants or all sensors).

   Measure: – Confirm the message with **RUN**.
   The titrator now loads the standard list of the resource, e.g. all titrants stored in the titrator on delivery.
   – Check what list has been changed:
   If the user data memory is too small, the titrator stores only the titrants for which it has space.
   If the memory is full, the titrator does not store any titrant. In this case, you must delete other installation data or one of your methods to create memory space.
   – Then switch the titrator off and on again.
   – Check that all resources are again present.

   If you are frequently shown the error message, you should contact METTLER service.

3. Storage not possible

a. The titrator can **not** assign the titer, auxiliary value or the calibration parameters to the appropriate resources as their list is missing (titrant, sensors or auxiliary values).

Measure: – Confirm the message with **RUN**.
– Check whether the list of the resource has been deleted.
– Switch the titrator off then on again: The titrator reloads the standard list of the corresponding resource, e.g. all the titrants stored in the titrator on delivery.
If the user data memory is too small, the titrator stores only the titrants for which it has space.
If the memory is full, the titrator does not store any titrant. In this case, you must delete other installation data or one of your methods to create memory space.
– Then switch the titrator off and on again.
– Check that all resources are again present.

b. The titrator cannot, for example, save data if the user data memory is full. This is possible

- for auxiliary reagents you want to add in INSTALLATION,
- for a method you create in EDITOR,
- for sample data you want to enter in the method list for methods in ANALYSIS,
- for "permanently" saving a modification of a currently running method,
- for "permanently" saving the evaluation criteria of the Titration function of a currently running method (parameter: "Stop for reevaluation").

Measure: – Confirm the message with **RUN**.
– Delete method or installation data, or insert a second user data memory.

c. The titrator is controlled by a computer and is performing a **learn method**. The EQP or EP parameters of the Titration function are **not saved** by the titrator.

Measure: – Confirm the message with **RUN**.
– Always perform a learn method with a method stored in the titrator!

If you are frequently shown the error message, you should contact METTLER service.

4. Memory faulty

Parts of the user data memory are faulty.

Measure: – Call METTLER service to have the memory changed.

In the meantime, you can continue working with the titrator.

9.2 Other errors and malfunctions

The following is a listing of faults and malfunctions which are not reported by the titrator and should help you rectify many of the possible malfunctions yourself thereby reducing your dependency on the METTLER service.

Note: Before you call METTLER service, please print out the system information, which provides details of the equipment configuration of the titrator, and inform the service of these:

press [—↑] + [! ₀] : The information will be printed out.

Fault	Possible cause	Corrective measure
No display on titrator	Instrument not connected to power Fuse defective	Plug in instrument Check fuse and replace if necessary
A few dots of the display are missing		Call METTLER service
The display does not match the key pressed		Call METTLER service
Stirrer will not stir	Sensors can block stirrer at the titration stand	Check placement of sensors
Units attached to the outputs are inoperative	Auxiliary instrument defective	Check instrument at another auxiliary output Call METTLER service
Transfer error to attached peripheral	Peripheral faulty	Check attached units for proper functioning
Unit (printer, balance, terminal) at serial interface does not respond	Unit not switched on Wrong installation data Wrong configuration (switch settings)	Switch on unit Installation data and configuration must match (see Section 1.8)

Fault	Possible cause	Corrective measure
Burette does not move to zero position when instrument switched on		Check burette drive at another station
	Burette drive faulty	Call METTLER service
Wrong potential or pH values	Electrode defective	Check electrode (see electrode sheet) Check installation data Use new electrode
No dispensing, titrant discharged from stopcock or piston	Burette tip blocked	Clean burette tip
	Follower cam at burette stopcock installed wrongly	Insert follower cam correctly (see Section 11.1.2.3)

Title: Cyanide, Automated Colorimetric [Methods EPA 335.4, SW 9010B/9013/9012A, SM 4500 CN-E, G, and I]

Approvals

Signatures on File

Stan Palmquist — Date
Inorganic Department Manager

Manjit Nijjar — Date
Health & Safety Manager / Coordinator

Manjit Nijjar — Date
Quality Assurance Assistant
For Terri Torres
Quality Assurance Manager

Dennis Bean — Date
Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This procedure is for the determination of:

Analyte	CAS Number
Total Cyanide	57-12-5
Cyanide amenable to chlorination	10-87-7
Weak acid dissociable cyanide	10-71-9

1.1.2 This procedure is applicable to drinking, surface and saline water, domestic and industrial wastes, soil, and other non-aqueous matrices.

1.1.3 This procedure detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine total cyanide, cyanide amenable to chlorination and weak and dissociable cyanides described in SW-9010B/9012A, EPA 335.4, and Standard Methods 4500CN.

1.1.4 This procedure describes the reduced volume version of the methods and uses the same reagents and molar ratio to meet the quality control and performance requirement stated in the method.

1.1.6 Dynamic Range

The approximate working range extends from 0.05 mg/L to 1 mg/L for water samples and 1 mg/kg to 20 mg/kg for solid samples. Samples with higher concentrations are analyzed with dilution.

2.0 Summary of Method

2.1 **Total cyanide** – Cyanide, as hydrocyanic acid (HCN) is released from samples by means of reflux-distillation under acidic condition and absorbed in a scrubber containing sodium hydroxide (NaOH) solution. The cyanide concentration in the scrubber solution is determined using an automated analyzer. The cyanide is converted to cyanogen chloride by reactions with Chloramine-T that subsequently reacts with pyridine and barbituric acid to give a red-colored complex. The color intensity which is proportionate to the cyanide concentration is measured at 570 nm.

2.2 **Cyanide amenable to chlorination** – A portion of the sample is alkaline chlorinated (pH > 11) to decompose the cyanide. Cyanide levels in the chlorinated samples are then determined by the procedure outlined for total cyanide in this SOP. Cyanides amenable to chlorination are then calculated by difference.

2.3 **Weak acid dissociable cyanide** – Hydrogen cyanide (HCN) is liberated from a slightly acidified (pH 4.5 to 6.0) sample under the prescribed distillation conditions. The method does not recover cyanides from tight complexes that would not be amenable to oxidation by chlorine. The acetate buffer contains zinc salts to precipitate iron cyanide as a further assurance of the selectivity of the procedure. The cyanide is trapped in a scrubber and analyzed by automated colorimetry as described in total cyanide.

3.0 Definitions

3.1 **Cyanide:** The term "cyanide" refers to all of the CN groups in cyanide compounds that can be determined as the cyanide ion, CN- by the various chemical methods. These compounds include both simple and complex cyanides.

3.2 **Dissociable cyanide:** The degree of dissociation of the various metallo-cyanide complexes at equilibrium, which may not be attained for a long time, increases with decreased concentration and decreased pH, and is inversely related to their stability, which varies greatly by compound. For example, the zinc and cadmium cyanide complexes are easily dissociated, whereas the iron and cobalt cyanides are very stable. Due to the differences in toxicity and treatment abilities among these complexes, environmental regulations specify chemical methods that can distinguish at least broad categories of these complexes.

4.0 Interferences

4.1 Oxidizing agents such as chlorine will destroy cyanide. 3% H_2O_2 and Ascorbic acid are used to remove chlorine interferences. Sodium arsenite may also be used.

4.2 Some unidentified organic compounds may oxidize or form decomposition products during chlorination, giving higher results for cyanide after chlorination than before chlorination; this gives a negative value for cyanide amenable to chlorination. Examples include samples from petroleum refineries, the steel industry, and pulp from paper processing. The weak acid dissociable method should be used for these samples.

4.3 Samples that contain sulfide compounds may produce hydrogen sulfide during the distillation and interfere with color development. This is treated by adding an excess of bismuth nitrate to the sample prior to distillation, which removes sulfur by precipitation as bismuth sulfide

4.4 Chlorine added to the sample for amenable cyanide must be completely destroyed before distillation. Otherwise, it may distill over and destroy the non-amenable cyanide. Chlorine present in samples from chlorinated sources will also destroy cyanide and must be destroyed before distillation.

4.5 Nitrate and/or nitrite may react with organic compounds during distillation to form cyanide. Sulfamic acid is added to remove the nitrate and/or nitrite interference.

4.6 Samples containing surfactants may foam excessively during distillation.

4.7 For cyanide amenable to chlorination, the extent to which some metal-cyanide complexes are destroyed by chlorination depends on the amount of chlorine present and the time allowed for reaction.

4.8 High carbonate concentrations may react violently when sulfuric acid is added to the samples during distillation.

4.9 Aldehydes, glucose, and other sugars may convert cyanide to cyanohydrin during distillation.

4.10 Amino acids may distill with the cyanide and interfere with the analysis.

4.11 Fatty acids may interfere by forming soaps in the absorption solution.

4.12 Thiocyanate greater than 10 mg/L may interfere.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve

hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Potassium cyanide and sodium cyanide will give off Hydrogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, and dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Potassium Hydroxide	Corrosive Poison Reactive	2 mg/m3 - ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting and diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness and swelling. Greater exposures cause severe burns with possible blindness.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm - ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat and upper respiratory tract and in severe cases, pulmonary edema, circulatory failure and death. Can cause redness, pain and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric acid	Corrosive Poison Irritant	1mg/m3 TWA	Inhalation symptoms may include irritation of the nose and throat, and labored breathing. Swallowing can cause severe burns of the mouth, throat, and stomach, leading to death. Can cause sore throat, vomiting, and diarrhea. Skin contact can cause redness, pain, and severe burn. Eye contact can cause blurred vision, redness, pain and severe tissue burns.
Calcium hypochlorite	Strong oxidizer	None listed	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting.
Glacial acetic acid	Corrosive Poison Flammable Irritant	10 ppm TWA	Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Swallowing can cause severe injury leading to death. Skin contact may include redness, pain, and skin burns. Eye contact may cause severe eye damage followed by loss of sight.
Sulfamic acid	Corrosive Irritant	None listed	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting.
Chloramine-T	Irritant	None listed	May cause irritation to the mucous membranes and upper respiratory tract, skin and eyes.
Barbituric acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as a potential health hazard; do not ingest.
Bismuth Nitrate	Oxidizer	None	May cause irritation to the respiratory tract, skin and eyes.
Silver Nitrate	Corrosive Poison Oxidizer	0.01 mg/m3 (TWA) for silver metal dust and fume as Ag	Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns, and eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3 All distillations are to be performed with adequate ventilation.

5.4 Exposure to chemicals must be maintained as low as reasonable achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and

prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit. For cyanide amenable to chlorination, the chlorination step will also be performed in a fume hood.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Seattle associate. The situation must be reported immediately to a laboratory supervisor and the Health and Safety Officer.

6.0 Equipment and Supplies

6.1 Instrumentation

- Astoria 2 RFA
- Analytical balance, 0.0001 gram accuracy. Check the Balance logbook to determine if the daily calibration check has been completed. If it has not, the analyst must perform this check according to SOP TA-QA-0014.
- Lachat Micro-Distillation apparatus and associated consumables.

6.2 Software

- TestAmerica LIMS (TALS), current version.
- FAS PACII, ver 2.1.2.36 or higher

6.3 Supplies

- Disposable auto-sampler vials or culture tubes for samples.
- Eppendorf pipettes, various sizes.
- Volumetric flasks, class A, various sizes.
- Volumetric pipettes, class A, various sizes.
- Miscellaneous laboratory apparatus, such as balances, and glassware.

7.0 Reagents and Standards

7.1 All Standards purchased from vendors are NIST traceable. Reagents used in the lab for standard preparation must meet ACS specifications. Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Cyanide Calibration Stock Standard, 1,000 mg/L:

This standard is purchased commercially. Alternatively, it can be made as described here: Dissolve 2.51 g of dried (103°C) potassium cyanide and 2 g potassium hydroxide in DI Water and dilute to 1,000 mL.

7.3 Cyanide Calibration Stock Standard, 100 mg/l:

This standard is purchased commercially. Alternatively, it can be made as described here: Dissolve .251 g of dried (103°C) potassium cyanide and 2 g potassium hydroxide in DI Water and dilute to 1,000 mL.

7.4 Calibration Standards

7.3.1 Initial Calibration Standards:

Dilute the 100.0 mg/L cyanide working standard (7.3) with 1% (0.25N) sodium hydroxide as follows:

Standard Level	Stock Std	Aliquot (mL)	Final Volume (mL)	Concentration (mg/L)
C1	None	0	100	0.00 (Blank)
C2	100 mg/l	0.05	100	0.05
C3	100 mg/l	0.10	100	0.10
C4	100 mg/L	0.20	100	0.20
C5	100 mg/L	0.30	100	0.30
C6	100 mg/L	0.50	100	0.50
C7	100 mg/L	0.70	100	0.70
C8	100 mg/l	1.0	100	1.0

Calculate the exact concentration for each calibration curve standard by dividing the exact working cyanide standard concentration by the dilution factors shown above if stock concentration is different from 1.0 mg = 1.0 ml.

7.5 Continuing Calibration Verification Standards (CCV):

A high level calibration verification standard is prepared from the cyanide stock described in section 7.2 as follows: (A low-level standard check must be distilled and run each day of use)

Standard Level	Working Standard	Aliquot (mL)	Final Volume (mL)	Concentration (mg/L)
CCV	100 mg/L	0.50	100	0.500

7.6 Second-Source Standards:

Second-Source, Initial Calibration Verification (ICV) Stock Standard, 1,000 mg/L:

The second-source standard is obtained from a different source than the calibration standards. This standard is purchased from Ultra Scientific.

Standard Level	Working Standard	Aliquot (mL)	Final Volume (mL)	Concentration (mg/L)
ICV	1,000 mg/L	0.1	200	0.5

7.7 Pyridine-Barbituric Acid Solution:

In a hood, place 15 g barbituric acid in a 1000 mL volumetric flask and add about 100 mL deionized water. Add 75 mL pyridine and mix. Carefully add 15 mL concentrated hydrochloric acid and mix. Dilute to volume with deionized water and store in an amber bottle. Expires 1 year from preparation.

7.8 Phosphate Buffer Solution:

Dissolve 138 g sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$) in 6 mL of Brij 35 solution with deionized water and dilute to 1000 mL. Expires 1 year from preparation.

7.9 Chloramine-T:

Dissolve 2.0 g Chloramine-T in deionized water and dilute to 500 mL.

7.10 Sodium Hydroxide, 10N:

Dissolve 400 g sodium hydroxide in deionized water. Cool to room temperature, dilute to 1000 mL, and mix well. Store in a plastic bottle. Solution is also commercially available.

7.11 Sodium Hydroxide Dilution Solution, 1% wt/wt (0.25N):

Add 25-mL of 10N NaOH and dilute to 1000 mL. Store in a plastic bottle. Solution is commercially available

7.12 Sulfuric acid, concentrated (36N)

7.13 Sulfuric acid, 0.02 N:

In a 2000 mL volumetric flask, carefully add 1 mL concentrated sulfuric acid to approximately 1900 mL deionized water. Dilute to final volume of 2000 mL with deionized water and mix. Solution is also commercially available.

7.14 Calcium Hypochlorite solution, 5%:

Dissolve 5 g calcium hypochlorite in 100 mL deionized water. Store in an amber bottle. Solution is also available commercially.

7.15 Magnesium chloride solution:

Dissolve 510 g magnesium chloride 6-hydrate in deionized water and dilute to 1000 ml. This reagent is available commercially.

7.16 Acetate buffer:

Dissolve 410 g sodium acetate trihydrate in approximately 450 mL deionized water. Adjust the pH to 4.5 with glacial acetic acid and dilute to final volume of 500 mL with deionized water. Expires 1 year from preparation.

7.17 Zinc Acetate solution:

Dissolve 100 g zinc acetate monohydrate in a 1 liter volumetric flask with approximately 500 mL deionized water. Dilute to final volume of l000 mL with deionized water. Expires 1 year from preparation.

7.18 Methyl Red Indicator solution:

Dissolve 0.1 g methyl red in 100 mL deionized water. Expires 1 year from preparation. Solution is also commercially available.

7.19 Acetic acid, 10%:

Carefully add 100 mL glacial acetic acid to about 500 mL deionized water, mix, and dilute to 1000 mL. Expires 1 year from preparation.

7.20 1% Ascorbic acid solution. Dissolve 10g of Ascorbic Acid to 1 L deionized water. Also available commercially.

7.21 pH test strips.

7.22 Lead acetate test paper.

7.23 Potassium iodide-starch test paper.

7.24 Bismuth nitrate, 0.062 M:

Dissolve 30 g of bismuth nitrate, Bi(NO3)3·5H20, in 100 mL of deionized water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved and dilute to 1 liter with deionized water. Expires 1 year from preparation. (Treatment for sulfide interference).

7.25 Sulfamic Acid, 10% wt/wt:

Dissolve 10 g sulfamic acid in 100mL of deionized water. Mix well. Expires 1 year from preparation. (Treatment for NO2/NO3 interference).

7.26 Brij-35 Start-Up Solution:

Concentrated Brij-35 is a buffer solution obtained from the equipment vendor. The start-up solution is prepared by diluting 1 mL of the Brij-35 concentrate to 500 mL with reagent water.

7.27 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards/reagents and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters[1]	HDPE, Glass	250 mLs	NaOH, pH > 12; Cool 0-6°C	14 Days	40 CFR Part 136.3
Soils	Glass	4 ounce	Cool 0-6°C	14 Days	N/A

[1] Add 1.2 g of ascorbic acid per liter of sample if residual chlorine is present.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. The process of establishing control limits, and the use of control charts are described more completely in TA-QA-0620, Quality Control Program. Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.3 Sample QC: The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< RL Limit or < 5% of sample concentration For DoD, BP Lamp; < ½ RL

Quality Controls	Frequency	Control Limit
Laboratory Control Sample(s) (LCS and/or LCSD)[1] (can also be used as the High Distilled Standard)	1 in 20 or fewer samples	Statistical Limits [4], but no more than 80-120% recovery and 90-110% recovery for method 335.4.
Matrix Spike (MS)[2]	1 in 10 or fewer samples	Statistical Limits [4],but no more than 75-125% recovery.
MS Duplicate (MSD)[2] (Waters only)	1 in 10 or fewer samples	Statistical Limits [4],but no more than 75-125% recovery. ≤ 20% RPD.
Sample Duplicate (Solid only)	1 in 20 or fewer samples	≤ 20% RPD
High Distilled Standard (LCS) (0.5 mg/L)	1 in 20 or fewer samples	±10% of true value
Low Distilled Standard (0.1 mg/L)	1 in 20 or fewer samples	± 10% of true value

[1] LCS Duplicate (LCSD) is performed when the High and Low Distilled Standards are not required (High and Low Distilled standards are required for methods 9010B/9012A and 9013/9012A).
[2] Sample selection for MS/MSD is random, unless specifically requested by a client.
[3] Analytical and QC samples (MB, LCS, MS/MSD)
[4] Statistical control limits are updated annually and are updated into LIMS.

9.4 Method Blank (MB):

Add 6 mL of 1% (0.25N) NaOH into a sampler tube.

Corrective Action: The corrective action for method blank failures is redistillation and reanalysis of all samples in the batch. If there is insufficient sample for reanalysis, a Nonconformance Memo must be prepared and the client contacted by the laboratory Project Manager.

9.5 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD):

Spike 0.03 mL of 100 ppm stock (described below) to 6 mL of 1% (0.25N) NaOH.

Corrective Action: If the LCS fails, redistill and reanalyze all samples in the batch. If reanalysis is not possible, a Nonconformance Memo must be prepared and the client contacted by the laboratory Project Manager. See SOP, Quality Assurance Program, TA-QA-0620 for additional guidance.

9.6 Amenable Laboratory Control Sample (LCS_A):

Spike 0.025 mL of the 1000 mg/L stock standard (7.2) into a specimen cup filled with 50 mL 1% (0.25N) NaOH. This LCS is run through the chlorination/de-chlorination process. Section 10.1.5

Corrective Action: If there is any measureable cyanide in the treated spike, then the chlorination step was not complete enough, and the analysis should be repeated. This spike is not part of the batch QC that is reported in the LIMS system and to the client.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD):

Measure 6 mL of sample and spike the aliquot with 0.03 mL of the 100 mg/L cyanide standard (7.2). The matrix spike and matrix spike duplicate are prepared in the same manner. Both the matrix spike and matrix spike duplicate are taken through the distillation and analysis process.

Corrective Action: If MS/MSD recoveries exceed LIMS historical limits for total cyanide. Consult your Supervisor, a Technical Specialist, QA Manager, or if contractually required, the client before proceeding. Because MS/MSD results may not have a direct bearing on other samples in the batch, the appropriate corrective action is generally governed by specific project requirements. At a minimum, QC failures will be noted as anomaly and discussed in the final report.

9.8 Low Distilled Standard, 0.1 mg/L:

For samples analyzed under methods 9010B/9012A or 9013/9012A, a low level distillation standard is to monitor the efficiency of the distillation process.

Corrective Action: Distilled standard failure results in redistillation and reanalysis of all associated samples. One possible exception is the situation in which recoveries are greater than 110% and cyanide was not detected in the samples. In that case, a Nonconformance Memo should be prepared and the failure noted in the report together with the sample results without taking other corrective action.

9.9 Sample Duplicate (DUP) Analysis:

A duplicate is required with each soil analytical batch processed under 9012A/9013 and must be 20% RPD.

Corrective Action: If the RPD is greater than 20% the sample should be reanalyzed if within holding time and if sufficient sample is remaining.

9.10 Instrument QC

9.10.1 Initial Calibration Verification (ICV):

Immediately after the initial calibration, the calibration is verified using a second-source, initial calibration verification (ICV, see preparation in Section 7.6) standard and an initial calibration blank (ICB, 1% NaOH). The measured result for the ICV must be within 10% of the expected value, and the ICB must be less than the reporting limit.

Corrective Action: If these criteria are not met, check the accuracy of the standards and recalibrate.

9.10.2 Continuing Calibration Verification (CCV):

A blank CCB (0.25N NaOH) and standard check CCV (see preparation in Section 7.5) are required after every 10 or fewer samples and at the end of the run. Standard checks (CCV) must be within 10% of the expected value. Blanks must be less than the reporting limit. For samples associated with LaMP, blanks must be ½ the RL or lower.

Corrective Action: If either continuing calibration check fails, all samples since the last successful calibration check must be reanalyzed.

9.11 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of management to accommodate variations in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.1 Sample Preparation

NOTE: The distillation procedure using the Lachet Micro Distillation block is described in Attachment 3.

Section 10.1.5: Cyanide Amenable To Chlorination

Section 10.1.6: Total Cyanide

Section 10.1.7: Weak Acid Dissociable

10.1.1 Check aqueous samples for sulfide prior to distillation using lead acetate paper. Moisten the paper with 2 or 3 drops of acetate buffer, and then place 1 drop of sample on the paper. A dark color indicates a positive test for sulfide. Record the result as "positive" or "negative" on the bench sheet.

10.1.2 If the samples test positive using lead acetate paper, treat 75 mL of the stabilized sample (pH > 12) with bismuth nitrate solution. Blue bismuth sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper and from the filtrate, measure the sample aliquot to be used for analysis. Avoid a large excess of bismuth and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

10.1.3 Soil Sample Leach prior to Distillation

10.1.3.1 Check the Balance logbook to determine if the daily calibration check has been completed. If it has not, the analyst must perform this check according to SOP TA-QA-0014.

10.1.3.2 Use 5.0 g of sample and 1 mL of 10N sodium hydroxide plus spike volume as required for QC sample and add DI water to a total volume of 100 mL. Cover with lid and shake for 24 hours and allow to settle. Use a 50-mL aliquot for amenable cyanide and a 6-mL aliquot for total cyanide determinations.

10.1.4 Cyanide Amenable To Chlorination Sample Preparation

10.1.4.1 Two sample aliquots are required for the determination of cyanide amenable to chlorination. The first aliquot is distilled for total cyanide (see Section 10.1.6), the second aliquot is chlorinated under an alkaline

condition prior to distillation and is used to determine cyanide not amenable to chlorination.

10.1.4.2 The samples are pH checked when they are received in Sample Receiving. If the pH is not correct, it is corrected in Sample Receiving and verified prior to chlorination in the lab.

10.1.4.3 Measure the sample aliquots to be chlorinated (including a MB and LCS) into 250 mL specimen cups. For water samples, use 50 mL of sample. For soil samples, use 50 mL of sample as prepared in section 10.1.4.

Note: The chlorination process must be performed in a fume hood.

10.1.4.4 If Needed, adjust the pH of the samples in the cups to between 11 and 12 with the 10 N Sodium hydroxide solution.

10.1.4.5 Test the samples with KI-Starch paper and add calcium hypochlorite drop-wise to sample while mixing until a positive test is obtained. A positive test is indicated by a blue or black color on the paper.

10.1.4.6 Maintain the excess chlorine level in the sample for 1 hour while keeping the pH of the samples between 11 and 12 with constant mixing (use a magnetic stirrer). Add calcium hypochlorite and sodium hydroxide as necessary.

10.1.4.7 After 1 hour, add 2-3 mL of 3% hydrogen peroxide or a small amount of 1% ascorbic acid until a negative test is obtained with KI-Starch paper.

10.1.4.8 Pipette 6 mL aliquots from the cups into the micro distillation cups.

10.1.4.9 After preparing the sample as described in attachment 3, proceed to section 10.1.6 for the distillation process.

10.1.5 Total Cyanide Sample Preparation

10.1.5.1 The samples are pH checked when they are received in Sample Receiving. If the pH is not correct, it is corrected in Sample Receiving and verified prior to analysis in the lab.

10.1.5.2 Check aqueous samples for oxidizing agents such as chlorine. Place one drop of sample on a strip of potassium iodide (KI)-starch test paper previously wetted with acetate buffer. A blue color indicates the need for treatment. Record the result as “positive” or “negative” on the benchsheet. If a positive test is obtained, add H_2O_2 or ascorbic acid until a drop of sample produces no color on the indicator paper.

10.1.5.3 Measure sample aliquots into the distillation cups as follows:

- For water samples use 6 mL of sample.
- For solid samples use 6 mL of sample as prepared in section 10.1.3.

10.1.5.4 After preparing the sample as described in attachment 3, proceed to Section 10.4 for colorimetric analysis of the distillates.

10.1.6 Weak Acid Dissociable Cyanide Sample Preparation

10.1.6.1 The samples are pH checked when they are received in Sample Receiving. If the pH is not correct, it is corrected in Sample Receiving and verified prior to analysis in the lab.

10.1.6.2 Measure sample aliquots into the distillation flasks as follows:

- For water samples use 6 mL of sample.
- For solid samples use 6 mL of sample as prepared in section 10.1.3.

10.1.6.3 After preparing the sample as described in attachment 3, proceed to Section 10.4 for colorimetric analysis of the distillates.

10.2 Instrument Set-Up

10.2.1 Instrument Operating Conditions

10.2.1.1 Instrument operating parameters are defined in the instrument's maintenance logbook.

10.3 Initial Calibration

10.3.1 Calibration is performed daily or each time the instrument is set up using the standards shown in Section 7.4. A minimum of six standards and a blank are required for the calibration.

10.3.2 The calibration function is calculated by least-squares linear regression, and the correlation coefficient must be > 0.995 and the absolute value of the intercept must be significantly lower than the value for the reporting limit. For more information about calibration curves, see corporate SOP CA-Q-S-005.

Corrective Action: If the correlation coefficient is < 0.995 or the absolute value of the intercept is too large, locate and correct the problem and re-calibrate the instrument.

10.3.3 Initial Calibration Checks: Immediately after the initial calibration, the calibration is verified using a second-source, initial calibration verification (ICV, see preparation in Section 7.6) standard and an initial calibration blank (ICB, 0.25N NaOH). The measured result for the ICV must be within 10% of the expected value, and the ICB must be less than the reporting limit. The absolute response of the daily ICV or the initial "SYNC" sample is evaluated and tracked in the logbook.

Corrective Action: If these criteria are not met, check the accuracy of the standards and recalibrate.

10.3.4 Continuing Calibration Checks: A blank CCB (0.25N NaOH) and standard check CCV (see preparation in Section 7.5) are required after every 10 or fewer samples and at the end of the run. Standard checks (CCV) must be within 10% of the expected value. Blanks must be less than the reporting limit.

Corrective Action: If either continuing calibration check fails, all samples since the last successful calibration check must be reanalyzed.

Calibration Controls	Sequence	Control Limit
Calibration Standards	6-point (minimum) linearity	≥0.995 correlation coefficient
Initial Cal. Verification (ICV)	Immediately after the calibration	± 10% of the expected value
Initial Cal. Blank (ICB)	Immediately after the calibration	Less than the reporting limit
Cont. Cal. Verif. (CCV)	Prior to / after every 10 injections	± 10% of the expected value
Cont. Cal. Blank (CCB)	Prior to / after every 10 injections	Less than the reporting limit

10.4 Sample Analysis

10.4.1 Following instrument set up and calibration, the sample distillates are analyzed in exactly the same manner as the calibration standards. A routine run sequence may look like:

Cal 0.00 ppm
Cal 0.05 ppm
Cal 0.1 ppm
Cal 0.2 ppm
Cal 0.3 ppm
Cal 0.5 ppm
Cal 0.7 ppm
Cal 1.0 ppm

Second-source ICV 1.0 ppm
ICB
CCV
CCB
Baseline
Low concentration distilled standard
Method blank
LCS
LCSD
6 samples (may include duplicated and/or MS/MSD)
Baseline
CCV
CCB
Baseline
10 samples (may include MS/SD)
Baseline
CCV
CCB
Baseline
Additional cycles of 10 samples with CCV/CCB
Closing CCV
Closing CCB

10.5 RFA System Maintenance

10.5.1 All instrument maintenance must be documented in the instrument maintenance logbook.

- The logbook must include the instrument name, serial number for each major component (e.g., RFA, autosampler) and the date of start-up.
- When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service".
- Routine Maintenance (which includes, but is not limited to daily, weekly, and semiannual maintenance) is completed periodically and does not necessary indicate the instrument is out of control is noted in the logbook with the notation "RM".
- For non-routine maintenance or repairs, logbook entries must include a description of the problem and what actions were taken to address the problem.
- When non-routine maintenance or repairs are complete, the instruments return to control is noted in the logbook with the notation "RTC".
- All method settings must be recorded in the maintenance log book.

10.5.2 Check the condition of all pump tubing before running a particular chemistry. Worn pump tubing is the most common cause of poor instrument performance, and should be checked first in any troubleshooting operation.

10.5.3 Keep the instrument and the surrounding area clean. Wipe up spills immediately, and dispose of the waste bottle contents frequently.

10.5.4 At a frequency of every two to four weeks, or whenever instrument performance is poor, flush all of the reagent lines with Chemwash solution.

10.5.5 For long-term care and troubleshooting, consult the Astoria 2 Operations Manual. If further support is needed, contact Astoria Pacific for technical support.

11.0 Calculations / Data Reduction

11.1 Calibration Curves

See corporate SOP CA-Q-S-005, Calibration Curves

11.2 Accuracy

$$\textbf{ICV / CCV, LCS/ HDS, LDS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\textbf{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.3 Precision (RPD)

$$\textbf{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.4 Total Cyanide Calculation:

All routine calculations for total cyanide are performed by the instrument data system, provided dilutions and other information have been correctly entered.

11.5 Cyanide Amenable to Chlorination:

Amenable Cyanide = Total CN Unchlorinated Result – Treated Result

If the chlorinated aliquot shows more cyanide than the unchlorinated aliquot, a corrective action and/or a discussion in the final report is required. Iron-cyanides can cause this to occur. Weak acid dissociable cyanide would be a better method for these types of samples.

11.6 Reporting Final Results:

Final results are routinely reported in mg/L for aqueous samples and in mg/kg for solid samples. Results can also be reported as ug/L or ug/kg if there are special project instructions requiring it.

Note: Unless special instructions indicate otherwise, samples less than the reporting limit are reported as ND.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TC-QSM-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities:

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method:

14.1.1 Acidic Waste Stream: the cyanide and reagent waste generated from the analysis is collected in a 5 gallon satellite waste container marked "Hazardous Waste" under the bench top in wet chemistry. When the container is full, it is removed to the 90 day waste pad in the waste warehouse and sent out for incineration.

14.1.2 Expired Chemicals are collected in the expired chemical satellite storage shelf located inside the waste room door. Store chemicals by their hazard class, incompatible chemical must be kept separate. The chemicals are then lab packed and sent out for incineration. Sulfuric Acid and Sodium Hydroxide may be neutralized in the neutralization tank.

Class 8 Corrosives Acid
Hydrochloric Acid
Sulfamic Acid
Barbituric Acid
Chloramine -T
Glacial acetic acid

Class 8 Corrosives Base
Potassium Hydroxide

Class 5.1 Oxidizers
Calcium Hypochlorite
Bismuth Nitrate
Silver Nitrate

Class 3 Flammable
Pyridine

Class 6.1 Toxic
Potassium cyanide

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Methods 9010B, 9013, and 9012A.

15.2 EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983, Methods 335.1, 335.3 and 335.4

15.3 Methods 4500 CN- B, C, E, G, and I, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 335.1	Cyanide amenable to chlorination is sometimes referred to as “Free Cyanide.” The weak acid dissociable method also determines “Free Cyanide” and it is important to distinguish between the two due to the different sample preparation required.
3	SW 9012A	Calibration is verified with an independently prepared check standard (ICV) with every analytical run and a CCV is run after every 10 samples, instead of for every 15 samples.

Item	Method	Modification
4	SM 4500 and SW 9012A	There are differences among the referenced methods concerning the sodium hydroxide concentration in working standards: Standard Method 4500-CN E states in Section 4a that working standards are made using a solution containing 1.6 grams per liter of water, which is equal to 0.04 N; Method 9012A states in Section 7.4.1 that calibration standards are prepared using 50 mL of 1.25N sodium hydroxide and diluting to 250 ml, which produces a 0.25N sodium hydroxide concentration. To be sure that the standards are stable, the working standards in this SOP are prepared in 0.25N NaOH.

17.0 Attachments

Attachment 1: Example Instrument Sequence
Attachment 2: QC Summary Table
Attachment 3: Micro Distillation Instructions
Attachment 4: Astoria-Pacific Instrument Manual

18.0 Revision History

- Revision 16.1, dated 13 March 2018
  - Updated approvers

- Revision 16, dated 28 March 2017
  - Removed requirement to prepare calcium hypochlorite solution monthly, section 7.14
  - Clarified when MSD is required and when Sample Duplicate is required, section 9.3
  - Updated Crystal ascorbic acid to 1% ascorbic acid, sections 7.20 and 10.1.4.7
  - Added option of using “SYNC” sample for daily response to section 10.3.3

- Revision 15, dated 2 January, 2016
  - Removed Midi-distillation apparatus and vacuum pump, section 6.1
  - Added low-level standard check, section 7.5
  - Updated ICV concentration, section 7.6
  - Removed boiling chips, section 7.24
  - Updated High and Low standard concentrations, section 9.3
  - Removed reference to midi-distillation unit and updated sample volumes and spike amounts for sections 9.1 to 9.5
  - Updated compound used to remove sulfide from sample, section 10.1.2
  - Updated sample volumes and remove procedures for midi-distillation, sections 10.1.6 to 10.1.7
  - Removed modification dealing with midi-distillation, section 16.0
  - Removed Attachment 3, Midi-distillation manual

- Revision 14, dated 28 November, 2014
  - Added Calibration Stock Standard, 100 mg/l, section 7.3
  - Removed reference to low-level CCV, section 7.4
  - Updated concentration and amounts of ICV used, section 7.6.1
  - Added description of treatment purpose to sections 7.24 and 7.25
  - Removed lead carbonate as this is not used, section 7.26
  - Added more detail to the note section of sample preparation, section 10.1
  - Updated how pH is verified, sections 10.1.5.2, 10.1.6.1 and 10.1.7.1
  - Removed note under section 10.3.2
  - Updated Attachment 1

- Revision 13, dated 24 May, 2013
  - Updated calibration Dynamic Range in section 1.1.6
  - Updated frequency of Matrix Spike and Matrix Spike Duplicate in section 9.3
  - Updated waste streams, section 14.1

- Revision 12, dated 6 August 2012
  - Updated calibration and calibration verification standards in sections 7.3.1, 7.4 and 7.6.1.
  - Updated sequence example, section 10.4.1
  - Updated waste streams, section 14.1
  - Updated Attachments 1 and 4

- Revision 11, dated 16 May 2011
  - Updated water and soil RLs in section 1.1.6.
  - Specified software requirements in section 6.2
  - Incorporated ROMD 00025 in section 9.2
  - Added chlorinated LCS (for amenable CN) in section 9.3
  - Revised CCV criteria in Sections 9.7.2 and 10.3.4 to match criteria in Attachment 2 (ROMD 00011).
  - Incorporated ROMD 00021 in sections 10.1.6.13 and 10.1.7.10.
  - Incorporated ROMD 00020 in sections 10.2.1.1. and 10.5.1
  - Incorporated ROMD 00022 in section 10.3.2.
  - Incorporated ROMD 00033 in section 10.3.3.

- Revision 10, dated 16 April 2010
  - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
  - Added removal of expired standards Section 7.19.
  - Added CCV and blank criteria for LaMP samples Section 9.6.2
  - Added criteria for extra QC, Section 9.7.
  - Added balance check instructions, section 10.1.4
  - Added instrument maintenance section, section 10.5
  - Added QC Summary, Table 2

- Revision 9, dated 7 August 2009
  - Added Attachment 2. QC Summary Table to include updated requirements in the DoD QSM v4.1.

- Revision 8, dated 23 September 2008
  - Updated initial calibration standards, continuing calibration standards, and initial

calibration verification standard information.
  - Included Manual for Midi-Distillation Apparatus as Attachment 2
  - Included Astoria-Pacific Instrument Manual as Attachment 3

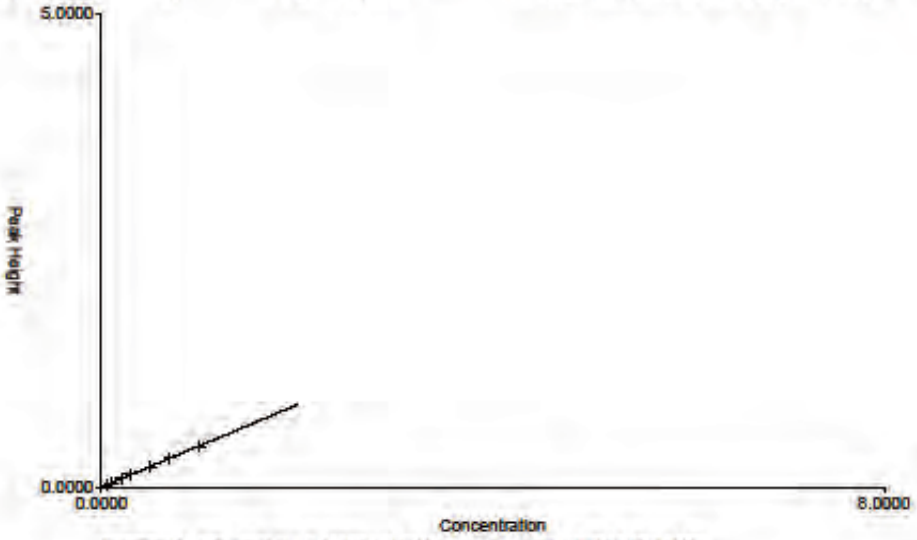
- Revision 7, dated 12 March 2008
  - Integration for TestAmerica and STL operations.
  - This revision is a complete rewrite and an expansion of scope.
  - This SOP is the combination of SOPs 0106.6, 0149.8, 0150.8, and 0151.1.

Attachment 1 Example Instrument Sequence

Run Name: 112014-cn
Configuration: CyanideB
Run date: 11/20/2014

Instrument ID: Astoria Analyzer (Flow2)

	Position	Identifier	Comment	Date	Time	Cyanide Cor Ht	Cyanide mg/l
1	SR:1	SYNC	1163742	11/20/2014	9:48:57	0.4346	0.9965
2	SR:2	CO	NaOH	11/20/2014	9:50:42	0.0005	-0.0047
3	SR:2	W	NaOH	11/20/2014	9:52:42	0.0000	-0.0058
4	SR:2	C1	NaOH	11/20/2014	9:54:42	0.0005	-0.0046
5	SR:3	C2	0.05-1323446	11/20/2014	9:56:42	0.0217	0.0441
6	SR:4	C3	0.10-1323451	11/20/2014	9:58:42	0.0444	0.0965
7	SR:5	C4	0.20 1341964	11/20/2014	10:00:4	0.0945	0.2122
8	SR:6	C5	0.30 1344618	11/20/2014	10:02:4	0.1361	0.3080
9	SR:7	C6	0.50 1341965	11/20/2014	10:04:4	0.2141	0.4879
10	SR:8	C7	0.70 1344619	11/20/2014	10:06:4	0.3118	0.7132
11	SR:9	C8	1.00 1341966	11/20/2014	10:08:4	0.4329	0.9926



Segment 1: Equation: y = 0.4336x + 0.002527
Correlation: 0.9996
X Range = 0.0000 to 2.0000
Y Range = 0.0000 to 7.2000

	Position	Identifier	Comment	Date	Time	Cyanide Cor Ht	Cyanide mg/l
12	SR:2	w		11/20/2014	10:10:4	0.0006	-0.0045
13	SR:2	W		11/20/2014	10:12:4	0.0000	-0.0058
14	SR:10	ICV	0.50 1344621	11/20/2014	10:14:4	0.2239	0.5105
15	SR:11	ICB		11/20/2014	10:16:4	-0.0002	-0.0063

	Position	Identifier	Comment	Date	Time	Cyanide Cor Ht	Cyanide mg/l
16	SR:7	CCV	0.50 1341365	11/20/2014	10:18:4	0.2202	0.5020
17	SR:11	CCB		11/20/2014	10:20:4	-0.0009	-0.0079
18	1:1	MB		11/20/2014	10:22:4	0.0006	-0.0044
19	1:2	0.10		11/20/2014	10:24:4	0.0443	0.0962
20	1:3	LCS		11/20/2014	10:26:4	0.2120	0.4832
21	1:4	LCSD		11/20/2014	10:28:4	0.2147	0.4894
22	1:5	321-1		11/20/2014	10:30:4	0.0117	0.0211
23	1:6	321-1d		11/20/2014	10:32:4	0.0133	0.0249
24	1:7	321-1ms		11/20/2014	10:34:4	0.1009	0.2269
25	1:8	321-1msd		11/20/2014	10:36:4	0.1042	0.2345
26	1:9	a		11/20/2014	10:38:4	0.1979	0.4505
27	1:10	b		11/20/2014	10:40:4	0.2004	0.4563
28	SR:7	CCV	0.50 1341365	11/20/2014	10:42:4	0.2119	0.4829
29	SR:11	CCB		11/20/2014	10:44:4	-0.0003	-0.0065
30	0	AutoWash		11/20/2014	10:46:4	0.0000	-0.0058

Attachment 2 QC Summary Table

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Four-point Initial Calibration **For DoD:** Six points are required.	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV fails.	r ≥ 0.995 and RSD between multiple exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
Distilled Standard	Once per multipoint calibration.	Results must be with ± 10% of true value.	Terminate analysis; Correct the problem; Recalibrate.
ICV	Beginning of every analytical run.	Results must be with ± 10% of true value.	Terminate analysis; Correct the problem; Recalibrate.
CCV	After the ICV, after every 10 samples and at the end of the run.	Results must be with ± 10% of true value.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
ICB	Beginning of every analytical run, immediately following the initial CCV.	The result must be within ± RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCB	Immediately following each CCV (except for the CCV following the ICV).	The result must be within ± RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
Method Blank (MB)	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. **For DoD and BP Lamp:** ≤ ½ RL. Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis.	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.10 for additional requirements.
Laboratory Control	One per sample	LCS must be within 80	Terminate analysis;

Sample (LCS)	preparation batch of up to 20 samples.	- 120% recovery or in-house control limits. 90 - 110% for Method 335.4 Samples for which the contaminant is < RL and the LCS results are > UCL may not require redistillation or reanalysis	Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike (MS)	10% of field samples preparation batch of up to 20 samples.	75 – 125% recovery or tighter in-house control limits. **For DoD:** LCS control limits.	In the absence of client specific requirements, flag the data.
Matrix Spike Dup (MSD)	10% of field samples preparation batch of up to 20 samples.	75 – 125% recovery or tighter in-house control limits. **For DoD:** LCS control limits.	In the absence of client specific requirements, flag the data.
Sample Duplicate (DUP)	One per sample preparation batch of up to 20 samples for DoD projects.	RPD ≤ 20%	In the absence of client specific requirements, flag the data.

Attachment 3
Micro Distillation Instructions

1. Set the controller to 120°C. Allow the heater block to warm up. This will take about 40 minutes

2. With the M end up; put the required number of collector tubes into the collector tube rack. When using the pre-filled collector tubes, re-seal the foil pack if there are any left.

3. Put the required number of sample tubes into the rack; up to 21 for one block. Place 6.0 ml of sample into each sample tube with an automatic pipette.

4. For the MS/MSD and LCS/LCSD, add 0.03 mL of 100 ppm stock (described below) to 6 mL of sample.

5. If needed for sulfur interference, add 0.3 ml of bismuth nitrate (Do not add to WAD cyanide samples or QC - see section immediately below) and if you add bismuth nitrate then add 0.3 ml of sulfamic acid to each sample

    - WAD Cyanide Prep. Add 1 drop of methyl red indicator. Add 0.75ml of WAD releasing agent (see below). If the solution is not pink, add 10% acetic acid drop-wise until a pink color persists. Continue on from section 7.

        - WAD releasing agent: Mix 950g DI water, 70.97g Sodium Acetate Trihydrate, 10.0 g Zinc Acetate Dihydrate, and 52.5 Glacial Acetic Acid

6. Then add 0.75 ml of 7.11 M sulfuric/0.79 M magnesium chloride into the sample tube and immediately push the D end of the collector tube over the open end of the sample tube.

7. Place the assembly in the press, putting the sample tube through the hole in the white base. Press the collector tube onto the sample tube. The pressing motion should be a smooth constant pressure, which is just enough to slide the sample tube into the collector tube.

8. Place the assembled unit into the heating block and set the timer for 30 minutes.

9. When the 30 minutes is up, put on the heat resistant gloves. Remove the first tube from the block and immediately pull off the sample tube. You must remove the sample within 4 seconds or suck-back may occur. After all the sample tubes have been removed, let the collector tube cool for at least 10 minutes.

10. For each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Slowly roll the distillate around in the tube to gather all droplets clinging to the tube walls into the bulk of the distillate. Return the collector tube to the rack with the D end up.

11. Break the collector tube in half by pulling the D end off and discarding it.

12. In the remaining M end of the collector tube, dilute the sample to 6 ml with DI water using a graduated cylinder. This results in the original sample volume, but now in 0.25 M NaOH.

13. Determine the amount of cyanide on the RFA just as you would when you get samples off of the midi distillation unit.

Releasing agent:

200 ml of 7.11 M Sulfuric acid/0.79 M Magnesium chloride recipe.

1. In the hood, place a 500 ml Erlenmeyer on a stir plate.
2. Weight out 32.2 g magnesium chloride hexahydrate and 110.8 grams of DI water. Stir until all of the magnesium chloride is dissolved in the water.
3. Slowly add 139 g of concentrated sulfuric acid
4. Continue to mix until cool the transfer to a 500 ml brown bottle.

Spiking solution:

Cyanide Calibration Stock Standard, 100 mg/l:

This standard is purchased commercially. Alternatively, it can be made as described here: Dissolve .251 g of dried (103°C) potassium cyanide and 2 g potassium hydroxide in water and dilute to 1,000 mL.

1. In a 100 ml volumetric flask add 10 ml of 1000-ppm cyanide This gives you a 100 ppm Cyanide spiking solution
2. When spiking the sample tubes, add 0.03mls of the 100ppm spiking solution to the MS, MSD, LCS, and LCSD. This will give you a concentration of 0.5 ppm in the 6 ml sample.

User filled NaOH solution:

1. 0.95 M NaOH 38grams of NaOH to 1 liter of DI water.
2. If you use the user fill tubes, add 1.59mls of .95 M NaOH to each digestion tube

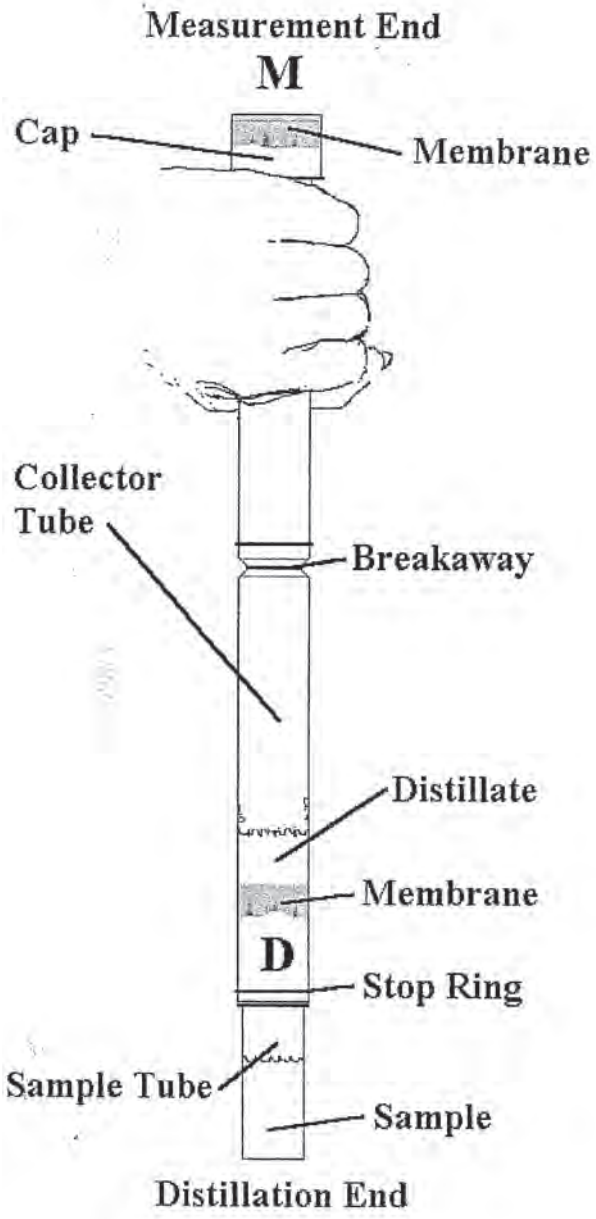


Figure 2 Collector Tube

Attachment 4

Astoria-Pacific Instrument Manual

Astoria® Analyzer

CYANIDE
A111

A. Scope and Application

This method is used for the determination of cyanide in water and wastewater. The EPA range of this method is 5 to 500 µg/L. However, this method is also applicable to other ranges.

B. Summary of Method

Samples containing cyanide are manually distilled into a solution of sodium hydroxide. The liberated hydrogen cyanide is converted to cyanogen chloride by reaction with chloramine-T at a pH less than 8. The cyanogen chloride then reacts with pyridine-barbituric acid reagent to form a red colored complex. The complex is measured at 570 nm.[1]

C. Interferences

Interferences are eliminated or reduced by distillation prior to determination. Samples containing sulfides should be treated to remove the sulfide as outlined in "Sample Handling and Preservation" or distilled by the procedure for samples containing sulfide. Refer to the cited references for manual distillation procedures.[1]

D. Sample Handling and Preservation

Add 2 ml of 10 N sodium hydroxide per liter of sample to achieve a pH greater than 12 and cool to 2 - 8°C. If residual chlorine is present, add 1.2 g of ascorbic acid to each liter of sample. The maximum holding time for samples without any sulfide present is 14 days.[3]

If sulfide is present, the holding time is 24 hours. Samples may be tested for sulfide with lead acetate paper before adding sodium hydroxide and the sulfide removed by the addition of cadmium nitrate powder. Filter the sample immediately, then add 2 ml of 10 N NaOH per liter of sample. The samples may be held for 14 days following the removal of the sulfide.[3]

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E. Raw Materials Required

NOTE:	**Chemicals should be of ACS grade or equivalent.**

Barbituric Acid $C_4H_4N_2O_3$ (FW 128.09)
Brij®-35 30% w/v (API p/n 90-0710-04)
Chloramine-T Trihydrate $C_7H_7SO_2NNaCl \cdot 3H_2O$ (FW 281.70)
Deionized Water (ASTM Type I or Type II)
Hydrochloric Acid, concentrated HCl (FW 36.47)
Potassium Cyanide KCN (FW 65.12)
Potassium Hydroxide KOH (FW 56.11)
Pyridine C_5H_5N (FW 79.10)
Sodium Hydroxide NaOH (FW 40.00)
Sodium Phosphate, Monobasic Monohydrate $NaH_2PO_4 \cdot H_2O$ (FW 137.99)

F. Reagent Preparation

1. Phosphate Buffer (500 ml)

Sodium Phosphate, Monobasic Monohydrate ..... 69.0 g
$NaH_2PO_4 \cdot H_2O$ (FW 137.99)
Deionized Water
Brij-35, 30% w/v ..... 3.0 ml

Dissolve 69.0 g of sodium phosphate monobasic monohydrate in approximately 400 ml of deionized water contained in a 500 ml volumetric flask. Dilute the solution to the mark. Add 3.0 ml of Brij-35, and mix the solution well. Filter to 0.45 µm.

2. Chloramine-T (500 ml)

Chloramine-T Trihydrate ..... 2.0 g
$C_7H_7SO_2NNaCl \cdot 3H_2O$ (FW 281.70)
Deionized Water

Dissolve 2.0 g of chloramine-T trihydrate in approximately 400 ml of deionized water contained in a 500 ml volumetric flask. Dilute the solution to the mark with deionized water and mix it well. Filter to 0.45 µm.

Cyanide A111

Add 100 ml of 10 N sodium hydroxide to approximately 800 ml of deionized water contained in a 1 L volumetric flask. Dilute the solution to the mark with deionized water and mix it well.

6. Sampler Wash Solution

Deionized Water

See Operating Note #12 for distilled samples.

7. Startup/Shutdown Solution (1 L)

Deionized Water ..... 1 L
Brij-35 ..... 3.0 ml

Add 3.0 ml of Brij-35 to 1 L of deionized water. Mix well.

G. Calibrants

Specific Stock and Working Calibrant preparation instructions can be found on the back of the flow diagram. Be sure to use the flow diagram that covers the concentration range you wish to analyze.

Working calibrants may be prepared to cover alternate ranges by adding the appropriate volumes of stock or intermediate calibrant *and appropriate volume(s) of sodium hydroxide (to match final sodium hydroxide concentration in samples / distillates)* to 100 ml volumetric flasks that contain approximately 80 ml of sampler wash solution. Dilute the solution(s) to 100 ml with sampler wash solution and mix well.

The following formula can be used to calculate the amount of stock (or intermediate) calibrant to be used.

$$C_1V_1 = C_2V_2$$

Where:

C_1 = desired concentration (in mg/L) of working calibrant to be prepared

V_1 = final volume (in ml) of working calibrant to be prepared (generally 100 ml)

C_2 = concentration (in mg/L) of stock (or intermediate) calibrant

V_2 = volume (in ml) of stock (or intermediate) calibrant to be used

Rearranging the equation to solve for V_2 yields:

$$V_2 = \frac{C_1V_1}{C_2}$$

I. Operating Notes

1. Operate the system under a ventilation hood or in a well ventilated area.

CAUTION: Cyanogen chloride is a toxic gas. Use care in operating the system.

2. Add sodium hydroxide to the waste container to ensure that the wastes do not become acidic and evolve hydrogen cyanide gas.
3. For a discussion of determination of the various forms of cyanide, refer to Standard Methods.[6]
4. Use narrow neck containers for the pyridine reagent and the waste. Cover with foil or parafilm to reduce odor.
5. A syringe filter with a polypropylene membrane and a glass fiber prefilter, such as the Gelman GHP Acrodisc GF (part number 4559), is an effective way to filter the pyridine barbituric acid. Other filtering methods may be used, but use caution to avoid filter types not tolerant to pyridine. Filter to 0.45 μm.
6. If a periodic air bubble going through the flowcell is causing interference in the baseline of the analysis, verify that the pump tube of the debubbler prior to the flowcell is in good working order.
7. The sample pump tube should be cut within ¼" of the shoulders to reduce carryover.
8. A common cause of low sensitivity and noise in the baseline is debris in the flowcell. Particulate matter from the reagents can become lodged in the flowcell restricting the amount of light that is passed through the flowcell. Flushing the flowcell with approximately 10 ml of startup solution with a syringe will help dislodge any debris in the flowcell. Following proper filtration procedures for the reagents will reduce the frequency of this occurring.
9. If bubbles are sticking in a debubbler, cleaning the debubbler will allow bubbles to escape smoothly out the debubble line. Bubbles sticking in the debubbler can cause a loss in the overall precision of the peak height. To clean, soak the debubbler for 20 – 30 minutes in a mixture of 20-30% Contrad®NF (API p/n 80-0007-04) and hot tap water. Rinse thoroughly.
10. If the flowrate of the sample pump tube is ≤ 226 μl/minute (a blk/blk pump tube), a helper line must be added when the cartridge is run alone. See Section 9 of the Astoria Analyzer Operation Manual for information on how to add a helper line.

NOTE: If the sample line is debubbled, a helper line is not necessary.

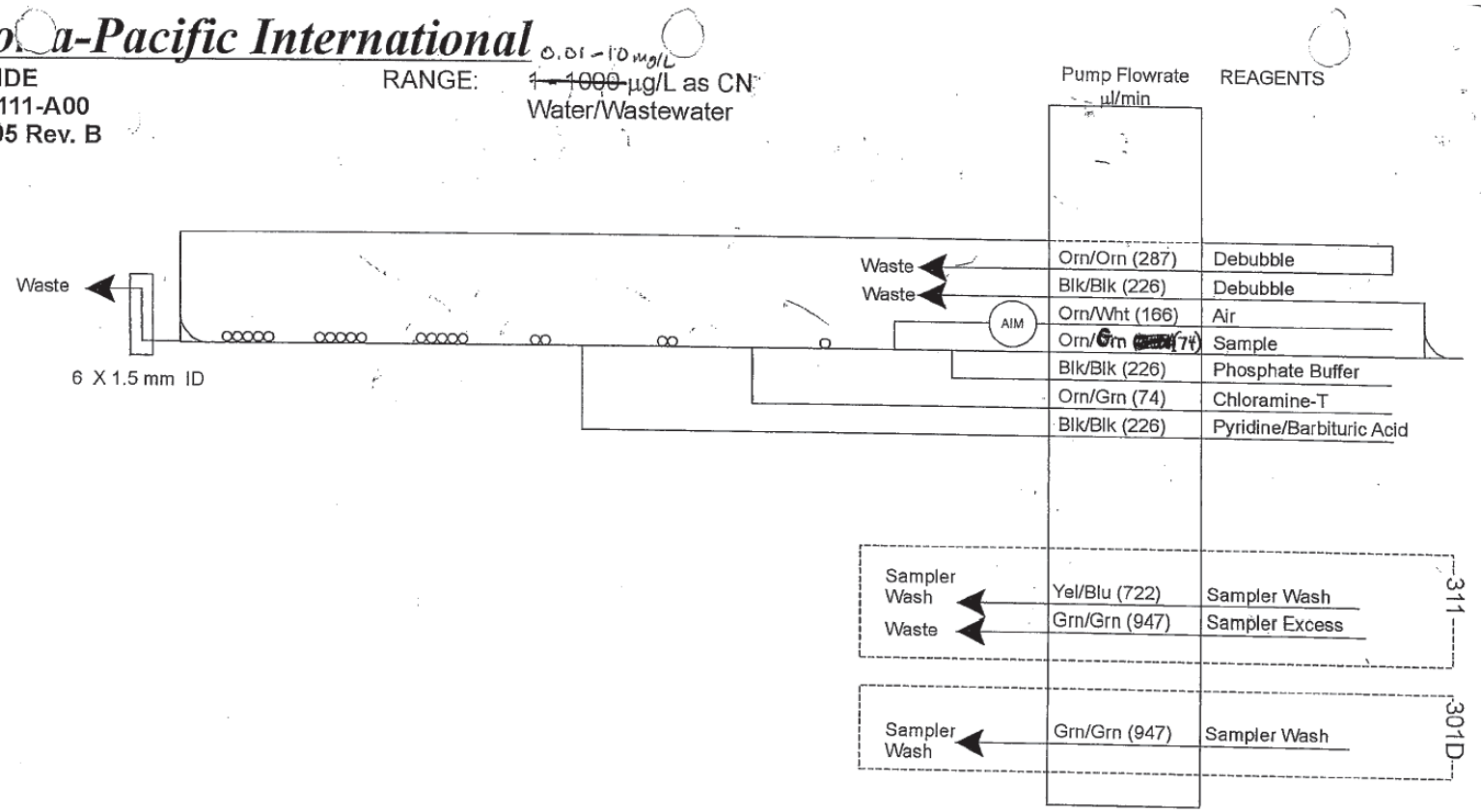
11. Cover all reagents and other solutions to avoid interference due to dust and other particulates. This will also help prevent contamination of the solutions from absorbance of analytes in the air.

Astoria-Pacific International

0.01 - 10 mg/L

CYANIDE
200-A111-A00
07/2005 Rev. B

RANGE: ~~1 - 1000~~ µg/L as CN
Water/Wastewater



DETECTOR PARAMETERS

Interference Filter:	570 nm
Neutral Density Filter:	90 ~~none or 30~~
Smoothing: Poly	~~0~~ 30
Smoothing: MAF	30

SAMPLER PARAMETERS

Analysis Rate:	~~55/hr~~ 36/hr
Sample Time:	~~30 s~~ 20s
Wash Time:	~~35 s~~ 80s
Pecking:	ON
Pump Speed:	42

CLEANING SOLUTIONS
CHEMWASH (API p/n 80-0005-250)

STARTUP/SHUTDOWN SOLUTION
Deionized Water with Brij®-35 (1-2 ml/L) (API p/n 90-0710-04)

CURVE PARAMETERS

mg/L	Curve 1	~~1.0 - 100 µg/L~~	~~1st Order~~	0.01 - 0.5 1st order
mg/L	Curve 2	~~100 - 1,000 µg/L~~	~~1st Order~~	0.5 - 10 2nd order

Symbol Key, Copyright Information

o = 5 turns

6 X 1.5 Flowcell (API p/n 315-0106-00)

Debubbler (API p/n 303-0122-00 or 303-0103-00)

Brij®-35 is a registered trademark of ICI Americas, Wilmington, DE

Title: Hexavalent Chromium [Methods SM 3500 Cr-B and 7196A]

Approvals

Signatures on File

Stan Palmquist — Date
Inorganic Department Manager

Manjit Nijjar — Date
Health & Safety Manager / Coordinator

Manjit Nijjar — Date
Quality Assurance Assistant
For Terri Torres
Quality Assurance Manager

Dennis Bean — Date
Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This method describes the measurement of hexavalent chromium in aqueous samples. Samples that cannot be analyzed by this procedure should be analyzed by the current version of SOP TA-IP-0179.

1.1.2 The reporting limit for this procedure is 0.012 mg/L.

1.1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

Hexavalent chromium in filtered aqueous samples is complexed and analyzed spectrophotometrically at 540 nm.

3.0 Definitions

The quality control terms used in this procedure are consistent with SW-846 terminology. Definitions are provided in the glossary of the TestAmerica Seattle Quality Assurance Manual (QAM).

4.0 Interferences

4.1 Sample turbidity may interfere with observations of color.

4.2 The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with the reagent but the intensities are much lower than that for chromium at the specified pH. Concentrations as high as 200 mg Mo/L or 200 mg Hg/L can be tolerated. Vanadium interferes strongly but concentrations up to 10 times that of chromium will not cause problems.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M^3 TWA as CrO_3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
Acetone	Flammable Irritant Poison	TWA 1000 ppm	Inhalation: coughing, dizziness, dullness, and headache unconsciousness. Ingestion: abdominal pain, nausea and vomiting. Aspiration into lungs can produce severe lung damage and is a medical emergency Skin: redness, pain, drying. Eyes: stinging, tearing, redness and pain.
Diphenylcarbazide (1,5 DPC) (2-0-0)	Irritant		Causes irritation to skin, eyes, mucous membranes, upper respiratory tract.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Spectrophotometer, for use at 540 nm, with a light path of 5 cm.

6.2 Software

- TestAmerica LIMS (TALS), current version.

6.3 Supplies

- Graduated cylinders, 100ml, 50ml.
- Automatic pipets, disposable tips, various volumes.
- Filtration apparatus, 0.45 um filters.
- Specimen cups.
- pH meter, Accumet Basic or equivalent.

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Concentrated Sulfuric acid, Purchased from Mallinckrodt, P/N 5557-46.

7.3 Sulfuric acid, H_2SO_4, 1:1. This solution will generate a lot of heat. Work in a hood and with secondary containment. Add approximately 250 ml of DI water to a 500 ml volumetric flask. Place the flask of DI water in a container of ice and chill the water for several minutes. **SLOWLY** add 250mls of concentrated H2SO4 while keeping the flask in the ice bath. Mix the cold acid/water solution and allow it to come to room temperature before bring it to final volume with DI water.

7.4 Deionized water. DI water

7.5 Diphenylcarbazide solution: dissolve 250 mg 1,5-diphenylcarbazide in 50-mL acetone or purchased equivalent. Store in a brown bottle. Solution expires one week after preparation or as assigned by the manufacturer if purchaced. Dispose of solution if at any time it becomes colored (brownish).

7.6 Chromium Calibration Stock Standard, 100 ppm: dissolve 28.28 mg $K_2Cr_20_7$ in water and dilute to 100-mL. An alternate equivalent source at similar concentrations may be purchased from a certified vendor.

7.7 2.0 ppm intermediate standard is prepared by diluting 1ml of the stock standard (7.7) to 50ml with deionized water.

7.8 Working Calibration Standards are prepared by using a 2.0 ppm intermediate standard and serially diluted into pH 1.0 adjusted deionized water as follows:

7.9 *Add two drops of 1:1 H_2SO_4 to each standard, method blank, and check standards.*

Volume of 2 ppm intermediate standard (ml)	Final Volume (mL)	Final Concentration (mg/L)
0.25	50	0.010
0.50	50	0.020
2.5	50	0.1
5.0	50	0.2
10.0	50	0.4

NOTE: To prevent possible slight losses of chromium during digestion or other analytical operations, treat chromium standards by the same procedures as the sample

7.10 Secondary source stock chromium check standard, 100 ppm: 28.28 mg K2Cr207 (from a different source than the primary calibration stock prepared in section 7.8) in water and dilute to a final volume of 100 mL. An alternate equivalent source at similar concentrations may be purchased from a certified vendor.

7.11 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples submitted for hexavalent chromium should be analyzed within 24 hours of collection.

8.2 Sample may be filtered and preserved in the field.

8.3 Sample container, please check preservation requirements for SM 20/21Ed or SW-846. preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	HDPE	50 mL	Cool 0-6°C	24 Hours	40 CFR Part 136.3

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section.

9.2 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in SOP TA-QA-0620, Quality Control Program.

9.4 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.5 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.6 Batch Definition

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a laboratory control sample (LCS), duplicate(s) (DUP), and matrix spike (MS) when adequate sample volume is received. As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.7 Method Blank (MB)

One method blank (MB) must be processed with each batch. The MB consists of reagent water that is carried through the entire analytical procedure, including preparation and analysis. Develop color as for samples, transfer a suitable portion of each colored solution to a 5 cm absorption cell, and measure absorbance at 540 nm. As reference, use distilled water. Correct absorbance readings of standards by subtracting absorbance of a reagent blank carried through the method.

Acceptance Criteria: The MB should not contain hexavalent chromium at or above the reporting limit (RL) for non-DoD jobs and less than one-half the RL for DoD jobs.

Corrective Action: If the analyte level in the MB exceeds the above requirement for the test, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data must be taken in consultation with the client and must be addressed in the project

narrative.

If the analyte concentration is greater than the reporting limit (RL) in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

If all samples associated with a blank greater than the RL are greater than 10 times the blank value, the samples may be reported with an NCM to qualify the high blank value.

9.8 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)

At least one LCS must be processed with each batch by adding 100 uL of stock standard (section 7.8) to 50 mL of deionized water for a target concentration of 0.20 mg/L. The LCS is used to monitor the accuracy of the analytical process. *Add two drops of 1:1 H2SO4 to each standard, method blank, and check standards.*

Acceptance Criteria: The LCS result must be within 10% of the true value and 20 % Relative Percent Difference (RPD) for SM3500 Cr-B and non-DoD 7196A jobs. The LCS result must be within 90-111% recovery and 20% RPD for DoD 7196A jobs.

Corrective Action: If LCS recoveries are outside established control limits, the analytical system is out of control and corrective action must be taken.

If recoveries are above control limits and *hexachrome* is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

In other circumstances, the entire batch must be re-prepared and reanalyzed.

NOTE: An LCSD must be prepared and evaluated when adequate sample volume for a duplicate is not provided.

9.9 Duplicate Sample Analysis

A duplicate is required with each ten samples in an analytical batch and must be within 20% RPD. Note that the control limits only apply to samples with results greater than 5 times the RL. The process of establishing control limits is described in more detail in the QC SOP TA-QA-0620.

Corrective Action: If the RPD is greater than 20 the sample should be reanalyzed if within holding time and sufficient sample is remaining.

9.10 Matrix Spike (MS)

An MS is prepared by taking a second aliquot of a selected sample and spiking it by adding 100 uL of stock standard (section 7.8). The spike concentration is the same level as the LCS.

Acceptance Criteria: The MS result must be within 30% of the true value for SM3500 Cr-B and non-DoD 7196A jobs and within 90-111% for DoD 7196A jobs.

Corrective Action: If the MS result does not meet the acceptance criteria and all other quality control criteria have been met, then matrix interference is suspected. If the LCS is within QC limits, the batch does not need to be reanalyzed, but the data should be flagged appropriately.

9.11 Initial Calibration Verification (ICV)

9.1 Analyze a second-source ICV standard (Section 7.11) immediately after the initial calibration (ICAL). 100 uL of stock standard (section 7.11) to 50 mL of deionized water for a target concentration of 0.20 mg/L. *Add two drops of 1:1 H_2SO_4 to each standard, method blank, and check standards.*

Acceptance Criteria: The recovery must be within the 90-110% range.

Corrective Action: If it is outside the acceptance limits, check the equipment and standards, and then recalibrate.

9.12 Continuing Calibration Verification (CCV)

Analyze the CCV standard, which is prepared from the same source and at the same concentration as the midrange calibration standard (Section 7.8), after every ten samples and at the end of the analytical sequence.

Acceptance Criteria: The recovery must be within the 90-110% range.

Corrective Action: If routine corrective action fails to produce a second consecutive (immediate) CCV within acceptance limits, then two consecutive successful CCVs need to be performed or the instrument should be recalibrated and all samples tested since the last successful CCV reanalyzed.

9.13 Initial and Continuing Calibration Blank

System cleanliness is checked at the beginning (with an initial calibration blank or ICB), and after every ten samples and at the end of the analytical sequence using a continuing calibration blank (CCB). *Add two drops of 1:1 H_2SO_4 to each standard, method blank, and check standards.*

Acceptance Criteria: Results must be less than the reporting limit for non-DoD jobs and less than one-half the RL for DoD jobs.

Corrective Action: If the blank is greater than the above requirement, check for carry-over from high level samples, clean the system, recalibrate, and rerun all samples analyzed since the last successful CCB.

Note: ICV/CCVs need to be followed by ICB/CCBs. ICV/CCVs cannot be preceded by a ICB/CCB unless a blank is analyzed before each sample in the bracket.

9.14 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of management to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP # TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

10.1 Sample Preparation

10.1.1 Filter 50 mLs of standards, sample(s), blank, blank spikes (*LCS)*, duplicate(s), and matrix spike(s) through 0.45 um filter paper the sample into disposable specimen cups.

10.1.2 pH adjust a minimum of 50 mL (150 ml if it is the QC sample) aliquot of sample to a pH of 1.0 +/- 0.3 with *1:1 H2SO4*. Do not add more than 1% of total volume of acid, i.e. do not add more than 0.5 ml of acid to a 50ml sample volume. If sample will require more than 1% of acid to pH adjust use a higher concentrated acid.

10.1.3 *Add two drops of 1:1 H_2SO_4 to all QC standards, method blank, and check standards.*

10.1.4 Spike the blank and sample chosen for matrix spike analysis by adding 100 uL of stock standard (section 7.8) to a 50 mL portion of un-filtered (MS) sample and pH1 DI water (LCS).

10.1.5 Split the samples, matrix spike samples, and standards into two equal volumes of 50 mL each.

10.1.6 Add 1.0 mL diphenylcarbazide solution to one portion of the samples, MB, LCS, MS, DUP, and standards, mix, and let stand 5 to 10 minutes for full color development.

10.2 Calibration and Sample Analysis

10.2.1 Calibrations should be done every six months or as needed following failing CCV or instrument maintenance.

10.2.2 Warm up the Spectronic 20 Genesys for approximately 5 minutes and set to 540 nm. Record the instrument ID on the batch sheet.

10.2.3 Analyze calibration standards and ICV/ICB as prepared in sections 7.10 and 7.4. Rinse and fill the 5 cm cuvette with the reacted pH 1 DI water and zero the instrument. Record the absorbance on the spreadsheet.

10.2.2.1 Repeat 10.10.2 with each calibration standard with out zeroing the instrument.

10.2.3 For details regarding calibration models, refer to corporate SOP CA-Q-S-005. The calibration curve must have a linear correlation coefficient ≥ 0.995, and each of the individual calibration points must be ± 50% of the actual value. See attached spread sheet.

10.2.4 Rinse and fill the 5 cm cuvette with non-reacted sample and record the absorbance in the background field of the spread sheet.

10.2.5 Rinse and fill the 5 cm cuvette with the corresponding reacted sample.

10.2.6 Record absorbance; determine micrograms chromium present by reference to the calibration curve.

10.3 Routine Instrument Maintenance

10.3.1 Replace the light bulb whenever the light source fails (after approximately 1,000 hours of use) following the procedure outlined in the operator's manual.

10.3.2 Clean the optical lens semiannually following the procedure outlined in the operator's manual.

10.3.3 Perform and document wavelength checks annually following the procedure outlined in the operator's manual.

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., autosampler) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, etc as may be the case).

11.0 Calculations / Data Reduction

11.1 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.2 Precision (RPD)

Sample Duplicate (DUP) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Concentration

$$\text{mg/L} = \frac{\text{ug Cr (in 102 mL final volume)} \times 100}{\text{(sample volume, mL)(mL portion from 100 mL digested sample)}}$$

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Acidic waste generated by the analysis. The fluid produced during analysis is poured into the Acid Waste Drum which is sent out for waste water treatment.

14.1.2 Sample aliquots and standards. Laboratory sample aliquots and standards are disposed of the in the high metals waste drum located in the waste warehouse. This waste stream is sent out for waste water treatment.

14.1.3 Expired Chemicals. Potassium Dichromate is placed in the satellite storage area in the bin marked "Hazardous Waste, Oxidizers, 5.1." At or before the satellite waste reaches 55 gallons it is lab packed and sent out for incineration. Diphenylcarbazide is placed in the satellite storage area in the bin marked "Hazardous Waste, Non Regulated Toxic, 9." At or before the satellite waste reaches 55 gallons it is lab packed and sent out for incineration.

15.0 References / Cross-References

15.1 Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998, Method 3500 Cr-B.

15.2 EPA Method 7196A, "Chromium, Hexavalent (Colorimetric)", SW-846, Rev.1, July 1992.

16.0 Method Modifications:

None

17.0 Attachments

Attachment 1: Example Hexchrom Bench Sheet.

18.0 Revision History

- Revision 17, dated 28 March 2018
  - Updated approvers
  - Updated reagents and standards
  - Updated batch definitions
  - Updated procedure for clarifications, section 10.1
- Revision 16, dated 18 October 2016
  - Adjusted RL, section 1.1.2
  - Removed reference to SM 3500 Cr-D throughout
  - Added Diphenylcarbazide (1,5 DPC) (2-0-0) to section 5.2
  - Added DoD QC requirements in sections 9.7, 9.8 and 9.10
  - Updated QC limits in sections 9.8, 9.9 and 9.10

  - Clarified Duplicate frequency in section 9.9
  - Added Acidic waste, section 14.1.1

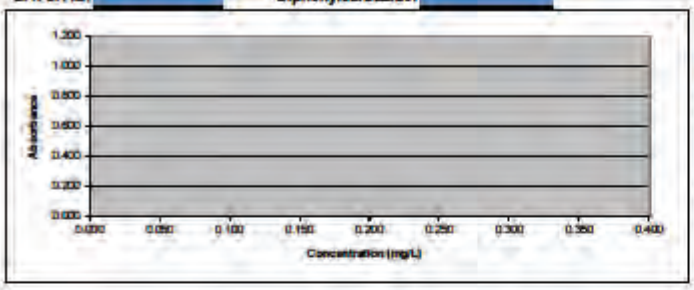
- Revision 15, dated 5 November 2015
  - Adjusted RL, section 1.1.2
  - Removed balance (not used), section 6.1
  - Reworded section 7.6 for clarification
  - Added purchased reagent to section 7.7
  - Removed lowest working calibration standard, section 7.10
  - Updated 10.2.3 to corporate requirements
  - Added SW-846 7196A method reference, section 15.3
  - Updated attachment 1
- Revision 14, dated 22 May 2014
  - Added section 10.2.1 outlining calibration frequency criteria
  - Changed Calibration Time on Attachment 1 to Calibration Date
- Revision 13, dated 15 November 2013
  - Updated cited methods in SOP title
- Revision 12, dated 13 March 2013
  - Updated primary materials used in section 5.2
  - Updated waste streams in section 14.1
- Revision 11, dated 5 March 2012
  - Added software, section 6.2
  - Fixed formatting and numbering, sections 10 and above
  - Updated equipment specified in section 10.2
  - Updated waste streams in section 14.1
- Revision 10, dated 4 February 2011
  - Incorporated ROMD 00025, Section 9.8
  - Incorporated ROMD 00022, Section 10.10.3
  - Updated sections 7, 9 and 10 to address findings in MA0008.
- Revision 9, dated 16 April 2010
  - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
  - Updated calibration standards, section 7.6
  - Added removal of expired standards Section 7.8
  - Added ICV/CCV/Blank requirement, Section 9.13.
  - Added criteria for additional QC, Section 9.14.
  - Updated instrument maintenance documentation requirements, section 10.11
  - Integration for TestAmerica Bothell and TestAmerica Tacoma operations.
- Revision 8, dated 16 December 2008
  - Integration for TestAmerica and STL operations.

Attachment 1. Example Hexchrom Bench Sheet

HEXAVALENT CHROMIUM SPECTROPHOTOMETER LOG
SW-846 7196A, SM 3500-Cr B/D ***SOP TA-WC-0175***

Instrument ID:

ANALYST:
DATE:
BATCH ID:
ICV Standard:
LCS / CCV Standard:
Diphenylcarbazide:
1:1 H_2SO_4:



CALIBRATION DATE:			
Standard ID	Concentration (mg/L)	Absorbance λ = 540 nm	Read Back Recovery
Calibration Zero	0.000		
Standard #A	0.010		#VALUE!
Standard #B	0.020		#VALUE!
Standard #C	0.100		#VALUE!
Standard #D	0.200		#VALUE!
Standard #E	0.400		#VALUE!
correlation coefficient	r =	#DIV/0!	

Final Volume = 50 mL, note in comments if different

ANALYSIS TIME	#	SAMPLE I.D.	Abs. W/O color rgt.	Abs. W color rgt.	Corrected Abs.	DILUTION FACTOR	SAMPLE VOLUME (mL)	Result (mg/L)	COMMENTS/OBSERVATIONS	
		ICV			0	1	50	#VALUE!	Result = 0.200 ± 0.020	#VALUE!
		ICB			0	1	50	#VALUE!	Result ≤ 0.010	
		MB			0	1	50	#VALUE!	Result ≤ 0.010	
		LCS			0	1	50	#VALUE!	Result = 0.200 ± 0.020	#VALUE!
	1				0	1	50	#VALUE!		
		DU	0.000		0	1	50	#VALUE!		
		MS 0.10 mL of LCS Standard	0.000		0	1	50	#VALUE!		
	2				0	1	50	#VALUE!		
	3				0	1	50	#VALUE!		
	4				0	1	50	#VALUE!		
	5				0	1	50	#VALUE!		
	6				0	1	50	#VALUE!		
	7				0	1	50	#VALUE!		
	8				0	1	50	#VALUE!		
	9				0	1	50	#VALUE!		
	10				0	1	50	#VALUE!		
		CCV			0	1	50	#VALUE!	Result = 0.200 ± 0.020	#VALUE!
		CCB			0	1	50	#VALUE!	Result ≤ 0.010	
	11				0	1	50	#VALUE!		
	12				0	1	50	#VALUE!		
	13				0	1	50	#VALUE!		
	14				0	1	50	#VALUE!		
	15				0	1	50	#VALUE!		
	16				0	1	50	#VALUE!		
	17				0	1	50	#VALUE!		
	18				0	1	50	#VALUE!		
	19				0	1	50	#VALUE!		
	20				0	1	50	#VALUE!		
		CCV			0	1	50	#VALUE!	Result = 0.200 ± 0.020	#VALUE!
		CCB			0	1	50	#VALUE!	Result ≤ 0.010	

Title: Determination of Low-Level Volatile Organics in Ambient / Indoor Whole Air Samples Using GC/MS-Scan Mode

[Methods EPA TO-14A and EPA TO-15]

Approvals (Signature/Date):

Koroush Vaziri Department Manager 11/19/17 Date	Joe Schairer Health & Safety Manager / Coordinator 11/17/17 Date
Lisa Stafford Quality Assurance Manager 11/16/2017 Date	Crystal Pollock Laboratory Director 11.21.17

1. SCOPE AND APPLICATION

1.1. This standard operating procedure (SOP) is applicable to the analysis of low-level volatile organic compounds (VOCs), having molecular weight in the general range of 40-200 g/mol and vapor pressure greater than 0.10 Torr at 25°C and 760 mm Hg in ambient air, by gas chromatography/mass spectroscopy (GC/MS) technique. This SOP is based on the EPA TO-14A/TO-15 method specifications and is applicable to various air matrices that include ambient air and indoor air.

1.2. Target analytes and reporting limits with this SOP are listed in Attachment 1. Reporting limits will be proportionately higher for samples that require dilution.

1.3. On occasion, clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the laboratory's Quality Assurance Manual (WS-QAM) in the section that discusses Service to the Client

1.4. When undertaking projects for Department of Defense (DoD) and/or the Department of Energy (DOE) the relevant criteria in QA Policy WS-PQA-021 "Federal Program Requirements" must be checked and incorporated.

2. SUMMARY OF METHOD

2.1. An air sample and internal standards (IS) are metered by a mass flow controller onto a cryogenically cooled trap (using either a Microscale Purge and Trap or a Cold Trap Dehydration technique described in Section 11). The trap is heated and the contents are transferred to a Tenax trap to remove water. The Tenax trap is heated and the analytes are transferred to a cryofocusing module. The cryofocuser is heated to transfer the analytes to the gas chromatographic column for separation and detection by a mass spectrometer operated in the Scan Mode.

3. DEFINITIONS

3.1. Note that "must" and "shall" in this SOP denote required activities.

3.2. Air Sample Bag: Commonly referred to as FlexFilm or Tedlar bag, in 1.0-L or 3.0-L volumes, that is constructed of proprietary material (e.g., SKC or ESS).

Note: Use of air sample bags as sample collection media constitutes a modification to the method (see Section 17.5) that is defined in the final report.

3.3. Part per billion volume to volume (ppbv or ppb v/v): Concentration expressed as part of gaseous (vapor) volume of pure target compound contained in a billion part of gaseous volume of sample.

Note: This reporting unit is NOT equivalent to the common ppb unit used in soil or water analysis.

3.4. Particulate Filter: A cylindrical stainless steel fitting containing a fritted metal disc, which is connected to the valve of a passivated canister or to the vacuum flow regulator (VFR), to prevent particulate matter from entering and damaging the passivated canister or VFR.

3.5. Passivated canister: Commonly referred to as SUMMA canister, SilcoCan, or T.O.-Can in 1.0-L, 1.8-L, 6-L, 15-L, or 33-L volumes.

3.5.1. SUMMA canister: A spherical stainless steel container, of which the interior has been specially treated by a process (SUMMA passivation), that renders all surfaces inert to VOCs.

3.5.2. SilcoCan: A sampling canister manufactured by Restek Corporation using the Restek Silcosteel® process to coat the interior of the canister with fused silica, rendering it inactive to most VOCs.

3.5.3. T.O.-Can: A spherical stainless steel container (which is the equivalent of a SUMMA canister) that is manufactured by Restek using a proprietary electropolishing process and is extensively cleaned using an ultrasonic method that ensures a high-quality, passivated surface that maintains the stability of VOCs during storage.

3.6. Standard molar volume = 24.45 L/mol at standard conditions (i.e., room temperature of 25°C and standard pressure of 1 atmosphere).

3.7. Standard pressure = 1.0 atmosphere or 14.6 pounds per square inch absolute (psia) or 0 inches of mercury or 0 pound per square inch gauge (psig), based on laboratory elevation and average barometric pressure.

Note: Full vacuum (0 psia) = -30 inches of mercury vacuum

3.8. QC section: Surrogates: Organic compounds which are similar to the target analytes in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Although not required by the method, each client and QC sample is spiked with surrogate standards via the analytical trap. Surrogates are used to monitor method performance with each sample. Surrogates are only reported to the client by request.

3.9. Vacuum Flow Regulator: A device which, when connected to a passivated canister, regulates the flow of sample into the passivated canister so that a timed, representative sample can be obtained (also called a composite sample), as opposed to an unregulated, instantaneous sample (grab sample).

3.10. Vacuum/Pressure Gauge: Device used to measure the vacuum or pressure in a passivated canister. Units of measure range from -30 to 0 inches of mercury (for vacuum) to 0 to 30 psig (for positive pressure). All pressure units are converted to psia (psig + 14.7 = psia).

3.11. Further definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

4. INTERFERENCES

4.1. Gas regulators are cleaned by the manufacturer using Freon 113, a target analyte in this SOP. Before using Ultra High Purity Nitrogen (UHP N2), hydrocarbon-free air, IS mix, or target compound standard mix cylinders, each regulator should be purged with the appropriate gas.

4.2. Contamination may occur in the sampling system if passivated canisters are not properly cleaned prior to use. Passivated canisters shall not be used for the collection of samples until a batch blank analysis indicates that no target compounds are present above the RL, or a level previously agreed upon between the laboratory and the client. When more stringent canister cleaning acceptance criteria are warranted based on project-specific or regulatory requirements, and then the more stringent criteria must be used. Further information regarding the cleaning and certification of passivated canisters may be found in TestAmerica SOP WS-QA-0032. All other sampling equipment including pumps, flow controllers, and filters must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

4.2.1. Passivated canisters may be batch-certified or individually-certified, depending on client request.

4.2.2. Passivated canisters will be certified-clean down to the MDL of the target analytes of interest if sample results need to be evaluated down to those limits. However, the laboratory must be provided advanced notification of the requirement.

4.2.2.1. Common laboratory contaminants like Acetone and Methylene chloride may be present above the MDL. In this instance, client approval must be received prior to sending out these passivated canisters.

4.3. Carry-over may occur when samples with high levels of contaminants are analyzed. The sample immediately following a high-level sample shall be re-analyzed if carry-over is suspected.

4.4. Air sample bags may contain low levels of target analytes.

4.5. Only compounds having both similar mass spectrum and GC retention time (RT) would be expected to interfere in the method. This situation most commonly occurs with structural isomers.

4.6. Large concentrations of water, Methane, or Carbon dioxide may limit the size of the sample aliquot that can be effectively cryo-trapped. This may elevate the RLs for samples of this type.

4.7. Matrix interferences may be caused by non-target contaminants that are present in the sample. The extent of matrix interference will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the West Sacramento Addendum to the Corporate EH&S Manual (WS-PEHS-002) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toed, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Pressurized gas equipment is used in this procedure. Be sure all valves and gauges are operating properly and that no equipment is over-pressurized. After changing cylinders, check all gas line connectors for leaks, with soapy water. Release of high pressure gas can cause rapid suffocation.

5.1.2. This analysis may require transfer of the sample from an air sample bag to a canister (Section 11.2). Because of the flexible nature of the air sample bag, insertion of the syringe needle into the bag may cause the septa to flex or the shaft of the syringe needle may flex within the septa. This may allow sample to escape along the shaft of the needle. All samples being manually removed from an air sample bag and transferred into a canister must be handled inside a fume hood with chemical protective gloves, lab coat, and safety glasses.

5.1.3. When pressurizing canisters or changing cylinders, face shield must be worn over safety glasses.

5.1.3.1. Passivated canisters should never be pressurized over 40 psig.

5.1.4. Pressurized gas cylinders must be securely retained. The use of a face shield is required when changing regulators.

5.1.5. Air sample bags should not be pressurized, as seam splitting will result.

5.1.6. The preparation of standards and reagents will be performed in a fume hood with the sash set at the level indicated on the side of the hood.

5.1.7. Both the GC and the MS contain elevated temperature zones. These zones must be cooled prior to an analyst or technician working on the instrument.

5.1.7.1. Temperature-appropriate gloves must be worn when working with hot or cold items.

5.1.8. Latex and vinyl gloves provide no protection against organic solvents. Nitrile or similar gloves must be used.

5.1.9. The effluents from the sample splitters for the GC and the roughing pumps for the MS must be vented to a fume hood or at a minimum, must pass through a charcoal filter.

5.1.10. The MS is under deep vacuum and must be brought to atmospheric pressure before working on the source.

5.1.11. Due to high voltage risk, power to the GC and/or MS must be turned off or disconnected before work can be done on the instrument.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Helium	Simple Asphyxiant	NA – Keep oxygen levels at 19.5%	Oxygen Deficient atmosphere may cause headaches, ringing in ears, dizziness, drowsiness, unconsciousness, nausea, vomiting and depression of all the senses.
Liquid Nitrogen	Simple Asphyxiant Cryogenic liquid	NA – Keep oxygen levels at 19.5%	Oxygen Deficient atmosphere may cause headaches, ringing in ears, dizziness, drowsiness, unconsciousness, nausea, vomiting and depression of all the senses. Contact with skin may cause frostbite-changes in skin color to white or grayish-yellow.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. Gas chromatograph – capable of sub-ambient temperature programming and electronic pressure control (Hewlett Packard 6890 or equivalent).

6.1.2. Mass-selective detector – equipped with computer and appropriate software (Hewlett Packard 5973/5975 or equivalent with Chemstation data acquisition software).

6.1.3. Sample concentrator – equipped with a cryogenic trap and appropriate systems for the control of moisture (Entech 7100 or equivalent).

6.1.4. Chrom version 2.1 data processing software.

6.2. Supplies

6.2.1. Chromatographic grade stainless steel or nickel tubing and stainless steel plumbing fittings.

6.2.2. Chromatographic column – Rtx-Volatiles, 0.32 mm ID, 1.5 µm df, 60 m length, methyl polysilicate liquid phase (Restek Corporation or equivalent).

6.2.3. Transducer and process meter capable of measuring 0 psia to 50 psia, for preparing standards (Ashcroft Digital Vacuum/Pressure Gauge or equivalent).

6.2.3.1. The process meter must be calibrated quarterly, at a minimum, against the master gauge.

6.2.4. Pressure regulators for carrier gas and standards – 2-stage, stainless steel diaphragm (single stage acceptable for standards).

6.2.5. Stainless steel vacuum/pressure gauge capable of measuring from -30 inches of mercury to 40 psig (Span Instruments or equivalent).

6.2.6. Air sample bags and passivated canisters used for the preparation of standards and the dilution of samples.

6.2.7. Screen can for preparation of method blanks. This is a cleaned canister certified to be free of analytes at levels greater than or equal to the MDL or levels specified by client or program requirements, whichever is appropriate to the samples being analyzed.

6.2.8. Gas-tight syringes of various sizes (Hamilton or equivalent).

7. REAGENTS AND STANDARDS

All reagents must be ACS reagent grade or better unless otherwise specified.

7.1. Reagents

7.1.1. UHP N_2 – used for Method Blanks and preparing dilutions of samples and standards

7.1.2. UHP Helium – used as the gas chromatograph carrier gas

7.1.3. Pressurized air source for Entech 7100 heater gas

7.1.4. Liquid N_2

7.1.5. Distilled or NanoPure water

7.2. Standards

7.2.1. Gas calibration stock standards containing the target compounds, at a nominal concentration of 1 part per million volume/volume (ppmv or ppm v/v), are purchased from NIST-approved vendors or prepared from neat in passivated canisters. Suppliers are required to provide certification of the analyte concentrations.

7.2.2. IS and surrogate stock standard mix (see Attachments 5 and 6, respectively), at a concentration of 300 ppbv, are purchased from NIST-approved vendors. Suppliers are required to provide certification of the analyte concentrations.

7.2.2.1. The surrogate mix is also used to tune the mass spectrometer.

7.3. Standard Preparation

Static dilutions and other standard preparation activities are performed in accordance with TestAmerica SOP WS-QA-0017.

7.3.1. Static dilutions of the stock standard gas mixtures are made in 6- or 15-L passivated canisters to create working standards. A high precision vacuum gauge is flushed with UHP N_2 and attached to the top valve of a clean, evacuated passivated canister, and the absolute pressure is recorded.

7.3.1.1. Distilled or NanoPure water (50 µL) is added to calibration standards prior to mixing.

7.3.1.2. The IS mix does not contain water.

7.3.2. Depending on the concentration of each stock standard gas mixture, a particular pressure of each is added to the passivated canister to achieve the

desired concentration in the working standard.

7.3.2.1. As an example, the daily working standard, at a nominal concentration of 10 ppbv, is created by adding 5.0 psia of the 100 ppbv standard mix and adding UHP N_2 to the passivated canister to achieve a final pressure of 50 psia.

7.3.2.2. Care should be taken to flush each regulator and transfer line with standard prior to transfer to the passivated canister.

7.3.3. Detailed preparation of each standard is recorded in the Laboratory Information Management System (LIMS) reagent module.

7.3.4. Other preparation techniques may be used to obtain the desired standard concentration, provided these techniques do not compromise the integrity of the standards used, and that the details of the preparation are properly documented in the LIMS.

7.3.5. Working standards are valid for a period of 30 days, after which fresh standards are prepared.

7.4. Expiration dates for source standards and reagents are based on vendor specification. If no vendor expiration date is assigned, the laboratory assigns an expiration date of two years from the date of receipt. Refer to TestAmerica SOP WS-QA-0017 for further information on standards and expiration dates. Expiration dates must be documented on the gas cylinders.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample container, preservation techniques, and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Passivated Canister	2000 mL	None	30 days	EPA/625/R-96/010b, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Passivated Canister	2000 mL	None	30 days	Advisory – Active Soil Gas Investigations, April, 2012 (DTSC, LARWQCB, and SFRWQCB)
Air Sample Bag	500 mL	None	72 hours	N/A

8.2. Passivated canisters used for sample collection must be certified clean (< RL or program specific limit). Canisters are cleaned in accordance with TestAmerica SOP WS-QA-0032. Filters (e.g., 7-micron or 2-micron) should be placed on the inlet of the canister to protect the valve from particulates.

8.3. Samples should be shipped at room temperature, in packaging suitable to prevent puncture and exposure to light.

8.4. If air sample bags are to be shipped by aircraft, they should be filled about 75% full to allow for expansion during shipment.

8.5. The pressure of a passivated canister should be recorded before and after sample collection in the field to help detect canister leakage and document proper sampling.

8.6. Samples are stored at room temperature.

8.7. Samples should be protected from extreme temperatures.

9. QUALITY CONTROL

9.1. Batch

A batch is defined as a set of up to 20 client samples of the same matrix processed using the same procedures and the same lot(s) of reagents within the same time period. A batch must contain a Laboratory Control Sample (LCS) and a Method Blank, but they do not count towards the maximum 20 samples in a batch.

9.1.1. In some cases, an LCS Duplicate may be required by a client or program to provide batch precision. In that instance, the acceptance criteria and corrective actions appropriate for the LCS are applied.

9.1.2. Rerun of the same client sample is counted as part of the 20 in a batch (i.e., a client sample analyzed twice in the same batch must be counted as two client samples).

9.1.3. Field quality control (QC) samples (e.g., trip blanks, equipment blanks, and field duplicates) count as client samples; therefore, they add to the batch

count.

9.1.4. Laboratory QC samples, including duplicates and clean canister blanks (screen cans), do not add to the batch count.

9.1.5. The batch must be analyzed sequentially using the same instrument and instrument configuration within the same calibration event. That is, the same calibration curve, calibration factors, or response factors must be in effect throughout the analysis.

9.1.6. Refer to the laboratory's QC Program document (WS-PQA-003) for further details of the batch definition.

9.2. Laboratory Control Sample– For each batch, an LCS must be analyzed. The LCS is analyzed after the calibration standards and before the Method Blank and client samples. The LCS is spiked with the target analytes in Attachment 1, from which a sub-set may be reported..

9.2.1. Refer to the QC Program document (WS-PQA-003) for details on the requirements for LCS composition.

9.2.2. If any analyte is outside established recovery and precision control limits, or any surrogate is outside the established recovery control limits, the system is out of control and corrective action must occur. Corrective action typically includes reanalysis of the batch.

9.2.3. If the batch is not reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. Acceptable reasons for not reanalyzing include evaluation of sporadic marginal exceedances (ME), or an elevated recovery (indicating a high bias) with samples non-detect for the failing analyte. Refer to the QC program document (WS-PQA-003) for more details regarding evaluation and acceptance of out of control LCS data.

9.2.3.1. Refer to WS-PQA-021 for details of corrective actions applicable for sample batches analyzed under the DoD/DOE QSM.

9.2.4. Exceedance outside the ME limits require corrective action, regardless of whether the associated result is positive or ND. See Section 9.2.6.

9.2.4.1. For failures that exceeded the ME at the high end, the ND analyte may be flagged and reported only if the program or project-specific requirements allow.

9.2.4.2. For all other ND results that failed the ME requirements, the client must approve to flag and report the data since the nonconformance does not meet the NELAC or TNI Standard.

9.2.5. All data reported with out of control LCS values will be flagged by the LIMS. Analysts shall also file a nonconformance memo (NCM) within the LIMS detailing why the data is reported, and any corrective actions performed.

9.2.6. Corrective actions to occur before batch reanalysis:

9.2.6.1. Evaluate the analytical run for errors and anomalies. Re-analyze the LCS.

9.2.6.2. Consult the troubleshooting guidelines in Section 11.8. Evaluate the instrument status and perform maintenance.

9.2.6.3. Re-analyze the continuing calibration verification (CCV) standard and LCS, or recalibrate.

9.2.7. Current LCS control limits are stored in the LIMS. Control and ME limits are subject to change based on periodic evaluation of LCS control charts by Quality Assurance personnel, in accordance with the procedures detailed in policy WS-PQA-003.

9.3. Method Blank

9.3.1. For each batch, an acceptable Method Blank must be analyzed. The Method Blank is analyzed after the calibration standards and LCS and prior to client samples. The Method Blank is a 6-L screen can (Section 6.2.7) humidified with 50 µL of Distilled or NanoPure water and then pressurized to 40 psia with UHP N_2.

9.3.2. If a method blank is requested to be analyzed using an air sample bag similar to which samples are collected the client is required to submit a bag for that purpose. The laboratory does not maintain an inventory of air sample bags, therefore, Method blanks in bags is by client request only.

9.3.3. The Method Blank must <u>not</u> contain any analyte of interest ≥ RL (or ≥1/2 RL, as dictated by the QSM or project-specific requirements), except common laboratory contaminants, (Section 9.3.2). Otherwise, the Method Blank is further evaluated and corrective actions must be performed, as stated below. See troubleshooting guidelines in Section 11.8.

9.3.3.1. Re-analyze the Method Blank once to determine if an error or an anomaly occurred during sample analysis. If the re-analysis is acceptable, then the Method Blank can be considered in control.

9.3.3.2. If there are no results greater than the RL in the samples or if the results in the samples are greater than 10X the Method Blank level, the data may be reported with qualifiers. In this case, the elevated

Method Blank result is not believed to impact data quality. The anomaly must be reported in an NCM.

9.3.3.3. If there are results greater than the RL in the samples and if these results are less than 10X the Method Blank level, the samples must be re-analyzed.

9.3.3.3.1. If re-analysis is not possible due to limited sample volume or other constraints, the Method Blank is reported and all associated samples are flagged. The client must be consulted. The anomaly must be reported in an NCM. The laboratory Project Manager (PM) must record the client's decision in the NCM.

9.3.4. If the analyte detected in the Method Blank is a common laboratory contaminant (Methylene chloride, Acetone, and 2-Butanone), the data may be reported with qualifiers if the concentration of the analyte is less than 5X times the RL. Otherwise, corrective actions, as stated in Section 9.3.1, must be performed. The anomaly must be reported in an NCM.

9.3.5. If surrogates are a project-specific requirement, then the Method Blank must have acceptable surrogate recoveries. If surrogate recoveries are unacceptable, the data must be evaluated to determine if the Method Blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-analysis of the Method Blank and affected samples must be performed.

9.4. Surrogate Standards.

Surrogates are not a method requirement. The laboratory routinely adds surrogates to all QC and client samples via the analytical trap and will report these results only if defined in a project/contract or at client's request. The surrogate compounds used in this SOP are listed in Attachment 6.

Surrogate recoveries in QC and client samples may be assessed to ensure that recoveries are within laboratory control limits. If any surrogate is outside these limits and if surrogates are a project-specific requirement, the following corrective actions must be performed:

- Check all calculations for error.
- Ensure that instrument performance is acceptable. See troubleshooting guidelines in Section 11.8.
- Re-analyze the QC/client sample.

9.4.1. It is only necessary to re-analyze a client sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst has reason

to believe that the repeated out of control results are due to problems other than matrix effect.

9.4.2. If re-analysis is not possible due to limited sample volume or other constraints, the surrogates are reported with a flag. The client must be consulted. The anomaly must be reported in an NCM. The nature of the matrix interference must be noted in the NCM. The PM must record the client's decision in the NCM.

9.4.3. Current surrogate control limits are stored in the LIMS and are subject to change based on periodic evaluation of surrogate control charts by Quality Assurance personnel, in accordance with the procedures detailed in policy WS-PQA-003.

9.5. Internal standard (IS)

IS compounds are added to each calibration standard, LCS, Method Blank, and client sample via the analytical trap. IS compounds are monitored for each shift by comparing the IS areas and retention times in each client and QC sample against those of the associated CCV standard. The IS compounds used in this SOP are listed in Attachment 5.

9.5.1. IS evaluation criteria for the initial calibration (ICAL) may be found in Section 10.3.8.

9.5.2. For all other QC and client samples, IS areas are considered acceptable if they fall between 60% and 140% (for TO-15) or –50% and 200% (for TO-14A Low-level) of the CCV IS areas. The RTs are considered acceptable if they fall within ±20 seconds (±0.33 minutes) of the IS RT of the associated CCV.

9.5.3. Any QC or client sample exceeding the acceptance criteria above must be re-analyzed. If the IS fails upon re-analysis, the failure must be documented in an NCM. All corrective actions performed must also be documented in the NCM.

9.6. Sample Duplicate Analysis

9.6.1. A client sample duplicate is analyzed and reported with the batch when requested by the client.

9.6.2. The acceptance criteria for the duplicate analysis is an RPD $\leq$ 25 for target analytes detected >5X the RL. No criteria are established for duplicate results <5X the RL.

9.7. Calibration standards and other QC samples (e.g., BFB, LCS, Method Blank, etc.) may not be analyzed more than twice without documented corrective action. If the initial

run fails acceptance criteria, re-inject the calibration standard or QC sample. If second run passes, analysis may proceed. Otherwise, conduct instrument maintenance or perform corrective action. Completely document failure, corrective action performed, and return to control in the Instrument Maintenance Logbook. Section 11.8 lists troubleshooting guidelines.

9.7.1. Refer to WS-PQA-021 for corrective actions specific to QSM programs.

10. CALIBRATION

For details of the calculations used to generate the regression equations, and how to use the factors generated by these equations, refer to the policy CA-Q-P-003, "Calibration Curves and the Selection of Calibration Points".

10.1. Initial/Daily Tuning of the Instrument

10.1.1. After a successful autotune per manufacturer's recommendations, each instrument is manually tuned using perfluorotributylamine (PFTBA) so that mass-to-charge ratio (m/z) 69 is 100%, m/z 131 is approximately 34%, and m/z 219 is approximately 36%. The width and axis parameters are set using the routines in the software. This initial tune should remain stable for extended periods of time, and retuning with PFTBA should not be necessary every day.

10.1.2. At the beginning of each 24-hour shift, prior to any analytical runs, it must be verified that the GC/MS system meets acceptable tune performance criteria. This is done through the analysis of 50 ng of 4-bromofluorobenzene (BFB); the acceptance criteria are listed in Attachment 3 (for TO-14A) or in Attachment 4 (for TO-15).

10.1.2.1. Using the BFB method in the cryotrap software, the IS mixture volume required is 50 ng of BFB on column (currently 24 mL of 300 ppbv standard).

10.1.2.2. An alternate way to load 50ng BFB is to use 50mL of a 20ppbv IS/SURR mix and 20mL of a 3000ppbv IS/SURR mix.

10.1.2.3. The mass spectrum of BFB must be acquired using the peak apex and the scans immediately before and after the apex and averaged. A background subtraction is applied using a scan prior to the elution of BFB.

10.1.3. If any of the key ions fail the ion abundance criteria listed in the attachments, the system is considered out of tune and any subsequent sample/standard analysis shall be considered unacceptable. The BFB must be re-analyzed and re-evaluated. If the BFB continues to fail, the GC/MS system must be

evaluated. See troubleshooting guidelines in Section 11.8.

10.1.3.1. Adjustments to the mass axis calibration, the electron multiplier voltage, or other tune parameters may be required. All parameter changes must be recorded in the Instrument Maintenance Logbook.

10.1.4. BFB tunes may be analyzed more frequently depending on documented client requirements.

10.2. Initial Calibration

10.2.1. Instruments are calibrated at initial setup and as needed thereafter, and at least annually.

10.2.2. An ICAL curve consisting of a minimum of five points is analyzed to determine the linear working range of the analytical system for each compound. An average response factor (RF), or sometimes called the relative response factor (RRF), and the percent relative standard deviation (%RSD) are calculated for each target analyte using the equations in Section 12.5.

10.2.3. The ICAL is considered acceptable if the calculated %RSD for the RF (or RRF) for each analyte not listed in Section 10.2.4 is <30, with at most two exceptions up to a limit of 40%.

10.2.3.1. ICALs associated with DoD/DOE QSM samples are considered acceptable if the calculated RSD for the RF or RRF for each requested analyte is < 30%, with no exceptions.

10.2.4. Any four of the following analytes, which are not listed as target analytes in the published methods and are considered poor performers, may have a %RSD limit up to 55:

1,1,2-Trichloro-1,2,2-trifluoroethane	Dichlorodifluoromethane
1,2,3-Trichlorobenzene	Naphthalene
2-Hexanone	Propene
Acetone	Tetrahydrofuran
alpha-Methylstyrene	

10.2.5. Linear calibration using least squares regression may be used with the appropriate number of calibration points. Details regarding its use and the calculations involved may be found in policy CA-Q-P-003. The analyst must read and understand the topics regarding Forcing Through Zero and Curve Weighting.

10.2.5.1. The coefficient of determination for a line fit must be greater than or equal to 0.990

10.2.5.2. The absolute value of the intercept (printed on the calibration curve plot in Chrom) should be less than ½ the reporting limit (-RL ≤ intercept ≤ +RL). If the intercept is outside the limits, any values below the reporting limit must be evaluated to ensure that false positives or false negatives are not being reported.

10.2.6. If the ICAL acceptance criteria are not met, corrective action (documented in the Instrument Maintenance Logbook) must be performed and a new ICAL generated. See troubleshooting guidelines in Section 11.8.

10.2.7. The nominal concentrations of the ICAL standards are typically 0.20, 0.30, 0.40, 0.80, 2.0, 4.0, 8.0, 20, and 40 ppbv, but these may vary depending on the certified mix used to prepare the standards or the volume trapped. The low standard must be at or below the RL. The standards are analyzed by preparing stock standards at the required concentration or by varying the trapped volume of the working standards from the default volume of 250 mL. For example, the 0.20, 0.40, and 0.80 ppbv standards are analyzed by trapping 62.5, 125, and 250 mL, respectively, of a 0.80 ppbv working standard.

10.2.7.1. At times, the default volume may be changed, depending on required instrument sensitivity for a project.

10.2.8. Internal Standards in the ICAL

10.2.8.1. The IS response at each calibration level must fall between 60% and 140% (for TO-15) or –50% and 200% (for TO-14A) of the IS response in the mid-point calibration standard. The mid-point standard is normally 8ppbv.

10.2.8.2. The RT shift for each of the IS at each calibration level must be within ±20 seconds (0.33 minutes) of the RT of the IS in the mid-point calibration standard.

10.2.8.3. Any calibration level exceeding the above acceptance criteria must be re-analyzed.

10.2.9. The analyst may elect to drop points from the calibration curve to improve subsequent quantitation, in accordance with Policy CA-Q-P-003, Calibration Curves and the Selection of Calibration Points.

10.3. Essential components for ICAL evaluation

10.3.1. The signal-to-noise (S/N) in the low point of the ICAL must be ≥ 2.5:1 for the compound to be considered valid at that level. Evaluate the EICP for the S/N determination.

10.3.2. Qualitative compound identification criteria must be met for all calibration levels; (primary and secondary ions >10% must be present in each standard level. Consult the technical director or QA for clarification.

10.3.3. Check retention times for isomers to ensure correct peak assignment.

10.3.4. Check co-eluting peaks for the proper reference spectrum.

10.3.5. The 're-fit' or 'read-back' for each point of the calibration curve is evaluated for the % error. The guideline is ≤ 20% for each level of the curve. This can be observed in the calibration summary in Chrom for each compound.

10.4. Initial Calibration Verification (ICV)

10.4.1. Each new ICAL must be verified using a second-source standard.

10.4.2. Since the regulatory agencies have not provided guidance on second-source verification, the ICV is considered acceptable if the %Recovery for each analyte not listed in Section 10.4.3 is 70–130%, with at most two exceptions up to a limit of 60–140%.

10.4.2.1. ICVs associated with DoD/DOE QSM samples are considered acceptable if the calculated result for requested analyte is with ± 30% of the true value, with no exceptions.

10.4.3. Any four of the following analytes, which are not listed as target analytes in the published methods and are considered poor performers, may have a %Recovery of 45–155:

1,1,2-Trichloro-1,2,2-trifluoroethane	Dichlorodifluoromethane
1,2,3-Trichlorobenzene	Naphthalene
2-Hexanone	Propene
Acetone	Tetrahydrofuran
alpha-Methylstyrene	

10.4.4. For samples analyzed in the same batch where the ICAL and ICV were analyzed, every time an allowed exception to the 70–130% Recovery ICV criteria is used, the sample results (whether J-value, ND, or positive) for the affected analyte must be flagged and explained in an NCM.

10.4.5. If the ICV acceptance criteria are not met, the following corrective actions must be performed. See troubleshooting guidelines in Section 11.8.

10.4.5.1. Rerun the second-source check standard.

10.4.5.2. Re-prepare or acquire a new standard.

10.4.5.3. Evaluate instrument conditions.

10.4.5.4. Regenerate a new ICAL.

10.4.6. Due to the limited availability of second-source manufacturers for the air standard mixes and some neat compounds, the following options may be considered as second-source:

10.4.6.1. Different certified lot from the same manufacturer.

10.4.6.2. Same certified lot from the same manufacturer but the stock standard used for the second-source is prepared by an analyst other than the one who prepared the stock standard used for the ICAL. This option is only allowed if the program or project-specific requirements allow.

10.5. Continuing Calibration Verification

10.5.1. Unless the QC batch follows a new ICAL and an ICV, for every 24 hours of operation, a CCV standard is analyzed to verify the ICAL average RF. The %D of the CCV RF from the ICAL average RF is calculated for each target analyte using the equation in Section 12.5.4.

10.5.1.1. CCVs associated with DoD/DOE QSM samples are analyzed daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.

10.5.2. The CCV is considered acceptable if the %D for each analyte not listed in Section 10.5.3 is ±30.

10.5.2.1. CCVs associated with DoD/DOE QSM samples are considered acceptable if the calculated result for requested analyte is with ± 30% of the true value, with no exceptions.

10.5.3. Any four of the following analytes, which are not listed as target analytes in the published methods and are considered poor performers, may have a %D ±55:

1,1,2-Trichloro-1,2,2-trifluoroethane	Dichlorodifluoromethane
1,2,3-Trichlorobenzene	Naphthalene
2-Hexanone	Propene
Acetone	Tetrahydrofuran
alpha-Methylstyrene	

10.5.4. Any time an allowed exception to the ±30%D CCV criteria is used, the sample results (whether J-value, ND, or positive) for the affected analyte must be flagged and explained in an NCM.

10.5.5. The following NELAC requirements (NELAC Quality Systems, June 5, 2003, 5.5.5.10e, page 217 of 324) and TNI Standard EL-V1M4-2009, Quality Systems for Chemical Testing, Section 1.7.2e, page 92) apply when the CCV acceptance criteria are not met.

10.5.5.1. If routine corrective action procedures fail to produce a second consecutive (immediate) CCV within acceptance criteria, then either the laboratory has to demonstrate acceptable performance after corrective action with two consecutive CCVs, or a new ICAL must be generated.

10.5.5.2. When the acceptance criteria for an analyte in the CCV are exceeded high (i.e., high bias), and the analyte was ND in the associated samples, the ND analyte may be reported with a flag. An NCM must be generated and the high bias discussed in the case narrative of the final report.

10.5.5.3. When the acceptance criteria for an analyte in the CCV are exceeded high (i.e., high bias), and the analyte was detected at a positive hit in the sample, the sample must be re-analyzed after a passing CCV or after a new ICAL has been established, evaluated, and accepted.

10.5.5.4. When the acceptance criteria for an analyte in the CCV are exceeded low (i.e., low bias), sample results may be reported if they exceed a maximum regulatory limit/decision level (if known). Otherwise, the affected samples must be re-analyzed after a passing CCV or after a new ICAL has been established, evaluated, and accepted. An NCM must be generated and the low bias discussed in the case narrative of the final report.

10.5.6. CCVs may be analyzed more frequently depending on documented client requirements.

10.5.7. CCVs must be monitored on a routine basis using the control chart program (refer to SOP WS-QA-0035) to evaluate the data for trends. The frequency is dependent on the frequency of the analysis. In the LIMS control chart module, select the CCV chart. Once the chart has been evaluated, click “Save Log” to save the chart evaluation in the LIMS.

10.6. Calibration standards and other QC samples (e.g., BFB, LCS, Method Blank, etc.) may not be analyzed more than twice without documented corrective action. If the initial run fails acceptance criteria, re-inject the calibration standard or QC sample. If second run passes, analysis may proceed. Otherwise, conduct instrument maintenance or perform corrective action. Completely document failure, corrective action performed,

and return to control in the Instrument Maintenance Logbook. Section 11.9 lists troubleshooting guidelines.

11. PROCEDURE

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file.

Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Sample Preparation – Air Bag Samples

11.2.1. For air sample bag samples, the air sample bag is checked for damage and is analyzed as received.

11.2.2. Air sample bags are analyzed directly from the bag or transferred to an evacuated can within 72 hours of sampling.

11.2.2.1. If the entire bag is transferred to a can, the bag needle valve septum is pierced with a needle attached to a 1-L or a 6-L evacuated can, and the entire contents transferred.

11.2.2.2. If only a portion of the bag is to be transferred, a measured aliquot of the bag is transferred via a clean syringe through a septum attached to the top of a 1-L or a 6-L humidified can.

11.2.3. After transfer, the can is then pressurized to a positive pressure and the pressure is recorded.

11.3. Sample Preparation – Canister Samples

11.3.1. For passivated canister samples, the initial pressure is checked by attaching the process meter line connector to the passivated canister. The process meter line connector must be rinsed before use, with the pressurization gas (UHP N_2 or UHP He, if requested) by physically holding it against the gas outlet and flushing for 10 seconds, as this avoids possible carry-over concerns from high concentration samples. With the process meter line connector attached, the passivated canister valve is opened briefly and the pressure is recorded. If the pressure is less than 6 psig, the passivated canister is pressurized to 10 psig

with the pressurization gas. The initial and final pressure must be recorded in the Canister Pressurization Logbook (see Attachment 10) and in the individual Canister Field Data Record.

11.3.1.1. Samples received above ambient pressure (14.6 psia) do not require pressurization unless additional volume is needed to perform multiple analyses. If samples are received below ambient pressure, UHP N_2 should be added. The default final pressure is 24 to 26 psia, however, the final pressure should be above ambient but not more than three times the initial pressure.

11.3.2. When the passivated canister vacuum/pressure is increased, a dilution factor (DF) is calculated and is applied to results. The calculation is provided in Section 12.5.5.

11.3.3. Passivated canisters received as trip blanks (without sample collected) are pressurized to 24-26 psia. These samples are considered to have a DF =1.0.

11.4. Sample Screening

Samples are screened to check for contamination before analysis or if suspected to contain significant contamination, using a GC/MS. Screening is performed to determine a proper dilution or the optimum volume of sample for the calibrated range, and to prevent overloading the analytical instrument. The screening instrument is generally calibrated at a single-point for common analytes of interest. The sample screen data are stored in TALS within the Chrom module.

11.5. Tuning

Refer to section 10.2 for details regarding instrument tuning.

11.6. Calibration

11.6.1. Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration must be documented.

11.6.2. Refer to Sections 10.3 through 10.5 for details regarding instrument calibration.

11.7. Sample Analysis

11.7.1. The calibration standards and the sample QC are analyzed in the same manner as client samples. After the calibration standards are analyzed and evaluated

(Sections 10.3 through 10.5), the LCS is analyzed and evaluated (Section 9.2), and then the Method Blank is analyzed and evaluated (see Section 9.3), all prior to client sample analysis.

11.7.2. Each passivated canister is attached to the autosampler and recorded in the instrument sequence. A sequence is created in the GC/MS software to prepare the instrument for data acquisition. The sequence information controls the GC/MS method, data file creation, sample parameters, and report output. A second sequence must be created in the autosampler control software to control the sampling process such as line position, sample volume, trap temperatures, flow rates, and times. The sequence is verified by another analyst. This analyst verifies the autosampler sequence, port position, chem. station sequence, and Chrom worklist. The analyst annotates in the instrument maintenance log if the sequence has been verified.

11.7.3. The valves are opened on all passivated canisters and the autosampler and GC/MS sequences are started.

11.7.4. The pressure DF must be compensated for by trapping more than the default volume. For example, a sample received at 12.0 psia and pressurized to 24.6 psia has a pressure DF of 2.05. If the default volume is 250 mL, then 510 mL should be trapped. The recorded volume is rounded to three significant figures.

11.7.5. A sample that requires only a small dilution can be analyzed by trapping a volume less than the standard volume. The minimum volumes that can be trapped are 10 mL for an Entech 7200 and 20 mL for an Entech 7100. The maximum volume that can be trapped is three times the default volume. Larger dilutions may require analysis using different methodology.

11.7.6. Sample dilutions may also be performed by transferring an aliquot of the sample (originally from either an air sample bag or a passivated canister) into an air sample bag and filling it up to volume or by removing an appropriate amount of the original pressurized sample from a passivated canister and then re-pressurizing to approximately 24 to 26 psia or no more than 3x the initial pressure with UHP N_2. Serial dilutions can be performed, as necessary.

11.7.6.1. Air sample bag dilutions can be used for reporting analytes that exceeded calibration range in the original analysis, but not as a reportable analysis for all other analytes due to the low-level contamination inherent in the air sample bag.

11.7.6.2. When air sample bag dilutions are performed, the syringe used for transferring sample must be fitted with a valve (e.g., Luer-Lok)

that allows the syringe contents to be isolated from the room air during transfer between containers.

11.7.7. For routine analysis, either the Microscale Purge and Trap or the Cold Trap Dehydration technique is used.

11.7.7.1. For Microscale Purge and Trap technique, the autosampler will follow the sequence of events below (parameters may be modified based on instrument performance):

11.7.7.1.1. Glass Bead trap (Module 1) is cooled to -150°C

11.7.7.1.2. Internal standard is trapped

11.7.7.1.3. Sample is trapped

11.7.7.1.4. Tenax trap (Module 2) is cooled to -15°C and the Glass Bead trap is heated to 10°C. Any remaining sample is transferred to Module 2 by passing UHP Helium through Module 1. Conditions may vary based on instrument performance. This step is designed to remove water from the sample.

11.7.7.1.5. When GC is ready, the cryofocuser (Module 3) is cooled to –170°C. Module 2 is heated to 200°C. The sample is transferred to Module 3.

11.7.7.1.6. Module 3 is heated and the GC/MS column flow is routed through Module 3 to inject the sample and begin the run.

11.7.7.1.7. The system is pre-flushed with the next sample and the system is baked to limit carry-over.

11.7.7.2. For Cold Trap Dehydration technique, the autosampler will follow the sequence of events below (parameters may be modified based on instrument performance):

11.7.7.2.1. Blank (empty) trap (Module 1) is cooled to -40°C and the Tenax trap (Module 2) is cooled to -40°C.

11.7.7.2.2. Internal standard is trapped.

11.7.7.2.3. Sample is trapped.

11.7.7.2.4. Blank trap is heated to 10°C. Any remaining sample is transferred to Module 2 by passing UHP Helium through Module 1. Conditions may vary based on

instrument performance. This step is designed to remove water from the sample.

11.7.7.2.5. When GC is ready, the cryofocuser (Module 3) is cooled to –155°C. Module 2 is heated to 200°C. The sample is transferred to Module 3.

11.7.7.2.6. Module 3 is heated and the GC/MS column flow is routed through Module 3 to inject the sample and begin the run.

11.7.7.2.7. The system is pre-flushed with the next sample and the system is baked to limit carry-over.

11.7.8. Upon completion of the analytical sequence, the Entech software generates a QA/QC report that records data from the sampling event (i.e. actual volume trapped, temperature at the time of trapping, sample pressure, etc.).

11.8. Troubleshooting Guidelines

11.8.1. Many problems encountered during analysis are due to low standard pressures or carrier/detector gas supply issues. Always confirm that adequate pressure remains in the standards and that the instrument gas supplies are sufficient before working on the instrument hardware.

11.8.2. Low response – typically caused by leaking sample lines or valves or contaminated/dirty sources. Instrument software can perform automated leak checks of the system. Specific components can be checked by isolating the component in question from the system (disconnect and cap or plug the ends) and then performing a leak test using a pressure gauge and passivated canister at positive pressure. Leaking components will not hold pressure when the passivated canister is closed. Low internal standard areas may be caused by degradation of the MS performance and increasing the electron multiplier (EM) voltage may solve this concern.

11.8.3. Baseline noise – check for supply gas contamination and leaking fittings. Carrier gas filters may need to be changed, including the pencil filters inside the GC. Sample carry-over or contamination may also be an issue and baking the system while flushing sample lines will remove most carry-over. A dirty source or leaking MS may also cause issues. The use of automated leak check routines in the MS software can indicate if a leak is present. Source-cleaning should be performed according to the manufacturer's instructions.

11.8.4. Tune issues – if an instrument will not pass tune the first step is to perform a mass axis calibration and peak-width adjustment. If the failure is due to ratios of ions with large differences, the tune parameters should be adjusted to

achieve the desired ratios. The final corrective action is to clean the source according to the manufacturer's instructions.

11.8.5. Instrument issues – if data loss or error messages are encountered, consult the instrument troubleshooting guidance found in the operator's manual. The manual is in the help section of the GC software.

11.9. Maintenance or Repair of Analytical Instruments or Support Equipment

11.9.1. When analytical instruments or support equipment require repair or maintenance, they shall be taken out of operation or otherwise isolated, and tagged as 'out-of-service' until such a time as the repairs or maintenance have been made and the instrument or support equipment can be demonstrated as operational by calibration and/or verification or other tests to demonstrate acceptable performance. Details on the tag-out procedures to be followed may be found in the section of the QAM that discusses Equipment and Calibrations.

11.9.2. A new ICAL must be generated following major maintenance such as changing the column, cleaning or repairing the source, replacing filaments, changing electronics, replacing the multiplier or changing the concentrator.

11.9.3. Minor maintenance includes cleaning the injector port, replacing filters, changing the pump oil, autotuning, switching filaments (instrument contains two filaments under vacuum), replacing the syringe or injector tower, changing/refilling the calibration vial, changing seals and o-rings, ballasting pump, replacing fuses, replacing roughing pumps or transfer lines.

11.9.4. Schedule for routine maintenance of analytical instruments may be found in Attachment 9.

11.9.5. All maintenance or repair must be documented in the Instrument Maintenance Logbook.

12. CALCULATIONS/DATA REDUCTION

12.1. Qualitative Analyses

Two criteria must be satisfied to verify positive identification:

12.1.1. Elution of sample component at the same GC relative or absolute RT as those of the standard component.

12.1.1.1. The sample component relative retention time (RRT) must compare within ±0.06 RRT units of the RRT of the standard component.

12.1.1.2. As an option, RT must compare within 0.33 minutes of the standard component absolute RT. For reference, the RT standard must be run within the same 24-hour shift as the sample.

12.1.2. Correspondence of the sample component and the standard component mass spectra.

12.1.2.1. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

12.1.2.2. The relative intensities of ions must agree within ±30% between the standard reference and sample spectra. For example, for ions with ratio of 50% in the reference spectra, the corresponding sample ratio must be between 20 and 80%.

12.1.2.3. Standard reference mass spectra must be obtained on each individual GC/MS system.

12.1.3. If an analyte cannot be verified by all of the criteria in the above sections, but in the technical judgment of the analyst the identification is correct, then the analyte may be reported

12.1.3.1. Technical judgment may be based on whether a compound is present when co-elution occurs and a determination is made based on retention time and mass spectrum.

12.1.3.2. The difference in the spectra and the reason for the decision to report results must be explained in an NCM.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analysis being conducted. The following sections identify the guidelines for making tentative identification:

12.2.1.1. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

12.2.1.2. Relative intensities of the major ions should agree within ±30%.

12.2.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.2.1.6. Only peaks having a total ion current greater than 10% of the nearest eluting IS total ion current will be evaluated for reporting.

12.2.2. TICs will be given general names consisting of major functional groups and number of carbon atoms unless an RT reference is available.

12.2.3. When TICs are requested to be reported using specific compound names, the following procedure must be followed:

12.2.3.1. Choose characterized ions of the specific compounds from the mass spectrum.

12.2.3.2. Search ions from expected RT range or entire RT range if the RT of the specific compound is unknown or uncertain.

12.2.4. Semi-quantitative results will be calculated for TICs using total ion current areas and assuming an RRF = 1.0.

12.2.5. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the analyst assign a tentative identification.

12.3. Quantitative Analysis

12.3.1. When an analyte has been identified, the quantification of that analyte will be based on the integrated abundance from the extracted ion current profile (EICP) of the primary characteristic ion. Quantitation will take place using the IS technique.

12.3.2. A sample must be analyzed and reported at a dilution if one or more target analytes have an on-column amount above the upper calibration level. Dilutions are acceptable if at least one of the following criteria are met:

12.3.2.1. Any target analyte in the diluted sample is at or above the mid-point calibration standard (e.g., 8 ppbv on-column if 8 ppbv is the mid-point).

12.3.2.2. The peak height of any non-target analyte in the diluted sample exceeds the largest peak height of the highest calibration standard.

12.3.2.3. A heavy hydrocarbon matrix in the diluted sample raises the baseline two times that of the relative IS.

12.3.3. Analyte quantitation must be performed from the ICAL response and not from the CCV response. Test results must be qualified in reports when analyte quantitation is based on the CCV at client's request. This request must also be documented in an NCM and reported in the case narrative of the final report.

12.4. All manual or re-integration of chromatograms must be documented in accordance with TestAmerica Corporate SOP CA-Q-S-002. Documentation includes, at a minimum, before and after copies of the chromatograms with a reference to the reason for re-integration, dated, and initialed. All manual integrations must undergo a secondary-level review.

12.5. Calculations

12.5.1. Calculation for RPD

$$RPD = \frac{Value\ A - Value\ B}{Average\ of\ Values} X\ 100$$

12.5.2. Calculation for RRF

$$RRF = \frac{Area\ cpd\ in\ Std.}{Area\ I.S.} X \frac{Conc.\ I.S.}{Conc.\ cpd\ in\ Std.}$$

The area of the primary quantitation ion is used in the calculation.

I.S. = Internal Standard

12.5.3. Calculation for %RSD

$$\%RSD = \frac{Std.\ Dev.\ of\ RRFs}{Mean\ of\ RRFs} X 100$$

12.5.4. Calculation for %D

$$\%D = \frac{Average\ RRF\ from\ ICAL - RRF\ CCV.}{Average\ RRF\ from\ ICAL} X 100$$

12.5.5. Calculation for pressure DF

$$DF = \frac{Y_a}{X_a}$$

Where:

X_a = absolute canister pressure before dilution (initial pressure)

Y_a = absolute canister pressure after dilution (final pressure)

12.5.6. Calculation for Determining the Concentration of Compounds
The data system automatically quantitates the sample results based on a standard sample size of 250 mL. The default result units are in ppbv. If a sample size other than 250 mL was used or a canister sample was pressurized, the result must be adjusted as shown below:

$$Final\ result\ \ ppbv = raw\ result\ ppbv\ X\ \frac{250\ mL}{sample\ vol\ injected}\ X\ \frac{final\ psia}{initial\ psia}$$

Where:

$$raw result\ ppbv = \frac{Area\ \ cpd\ \ in\ \ sample}{Area\ \ I.S. in\ \ sample}\ X\ \frac{Conc. I.S.}{RRF\ \ \ ICAL.}$$

Note: The area of the primary quantitation ion is used in the calculation.
I.S. = Internal Standard

12.5.7. Calculation for Percent Recovery (%Rec)

$$\%\ \mathrm{Re}\,c = \frac{Amount\ cpd.\ recovered}{Amount\ cpd.\ spiked}\ X\ 100$$

12.5.8. Standard reporting units are ppbv (also ppb v/v). If results are to be reported in ng/L or ug/m^3, use the following equation:

$$result\ ppbv\ X\ \frac{Molecular\ weight\ \ of\ \ cpd}{24.45} = results\ ng/L\ \ or\ \ ug/m^3$$

Note: 24.45 is the molar volume of ideal gas in liters at 25°C and 1 atmosphere.

12.6. Estimates of uncertainty are based upon LCS historical control limits, and are provided on request only.

12.7. "J" values (results below the RL but above the MDL) are reported on request only.

12.8. No conversion of the analytical results to standard conditions is made.

12.9. The number of significant figures to be used when reporting sample and QC results are defined in QA Policy WS-PQA-004.

12.10. Technical Data Review

Technical data review is performed in accordance with Policy WS-PQA-012, and is documented utilizing review checklists. Examples of appropriate review checklists are found in Attachments 7 and 8.

12.10.1. One aspect of technical review is to ensure that the test instructions are clear, and that all project-specific requirements have been understood and followed. If directions to the analyst are not clear, the analyst must consult the Department Manager or the appropriate PM, who must clarify the instructions.

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

13.2. Method Detection Limit

The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOP SAC-QA-0006. MDLs are available in the Quality Assurance Department.

13.3. Initial Demonstration

The laboratory must make an initial demonstration of capability for each individual method. This requires analysis of QC check samples containing all of the standard analytes for the method. It may be necessary to use more than one QC check mix to cover all analytes of interest.

13.3.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be less than or equivalent to the LCS samples.

13.3.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these to the laboratory generated QC Limits.

13.4. If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

14. POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must

abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Expired standards will be part of the Lab Pack waste stream. They will be identified as expired, stored under the manufacturer's recommended conditions, and then packed for disposal as outlined in SOP WS-EHS-0001.

15.1.1. Gas standards in non-returnable, non-refillable cylinders, such as Scotty® Transportables, are slowly vented in the fume hood when empty. They are then turned over to the hazardous materials specialist, who ensures that they are damaged (e.g., a hole is drilled into the cylinders) so they cannot be reused. The damaged cylinders are then either recycled or scrapped.

15.1.2. Gas standards in returnable, refillable cylinders are returned to the manufacturer.

15.2. Air sample bags are slashed in a hood and then placed into an orange high VOA lab trash can. When the can is full or at the end of the day, tie the plastic bag liner shut and put the lab trash into the appropriate steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. EPA/625/R-96/010b, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd edition, January 1999

16.1.1. Compendium Method TO-14A, Determination of Volatile Organic Compounds (VOCs) in Ambient Air using Specially Prepared Canisters With Subsequent Analysis Gas Chromatographic Analysis

16.1.2. Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)

16.2. TestAmerica Sacramento QAM, current revision

16.3. TestAmerica Sacramento SOP WS-QA-0032, Cleaning, Certification, and Preparation of Sampling Equipment, current revision

16.4. TestAmerica Corporate Environmental Health and Safety Manual CW-E-M-001, current revision

16.5. Advisory – Active Soil Gas Investigations, April 2012 (CAEPA, DTSC, LARWQCB, and SFRWQCB)

16.6. EPA/600/R-04/003, 2003 NELAC Standard, June 5, 2003

16.7. The NELAC Institute (TNI) Standard 2009, Volume 1, Management and Technical Requirements for Laboratories Performing Environmental Analysis

16.8. TestAmerica Sacramento SOP WS-PQA-003, Quality Control Program, current revision

16.9. TestAmerica Corporate SOP CA-Q-P-003, Calibration Curves and Selection of Calibration Points, current revision.

16.10. TestAmerica Corporate SOP CA-Q-S-002, Acceptable Manual Integration Practices, current revision

16.11. TestAmerica Sacramento Policy WS-PQA-004, Rounding and Significant Figures, current revision

16.12. TestAmerica Corporate SOP CA-Q-S-006, Detection Limits, current revision

16.13. TestAmerica Sacramento SOP WS-EHS-0001, Sample and Chemical Waste Characterization, Collection, Storage and Disposal, current revision

17. METHOD MODIFICATIONS

17.1. Method TO-15 describes the use of zero air when making standards. TestAmerica Sacramento uses UHP nitrogen in the standards preparation.

17.2. UHP Nitrogen is used for dilution/pressurization purposes.

17.3. Method TO-15 describes canisters leak check being performed using pressure. TestAmerica performs the canisters leak check using vacuum unless specified by the project.

17.4. Method TO-15 presents criteria for evaluating canister cleanliness as less than 0.2 ppbv of any target VOC. TestAmerica Sacramento works with clients to ensure that the canisters meet their data quality objectives, by providing canisters evaluated to the reporting limit or method detection limit as required by their program.

17.5. Method TO-14A describes an inlet system that uses a vacuum to pull the sample through the trap. TestAmerica Sacramento optionally uses the pressure of the sample canister to drive the sample through the trap.

17.6. Method TO-14A describes the use of a Nafion dryer to remove excess moisture from air matrices. TestAmerica Sacramento does not use a Nafion dryer since polar compounds may be lost during this removal step.

17.7. Method TO-14A describes the BFB tune check to be a gas sample introduced via a sample loop. TestAmerica Sacramento traps and analyzes BFB using the same analytical technique used with samples.

17.8. Methods TO-14A and TO-15 describe the use of passivated steel canisters for sampling and analysis. No mention is made of the use of air sample bags. TestAmerica Sacramento analyzes samples in air sample bags for VOCs using the same procedures described herein. A modification to the method is noted in the NCM submitted with the final report.

17.9. Methods TO-14A and TO-15 indicate that in order for the ICAL to be acceptable, all compounds must have a %RSD <30 (with allowance for two that could be up to 40% in TO-15). For routine analysis, for those analytes not listed in the published methods and are considered poor performers, TestAmerica Sacramento accepts the ICAL if up to four of these analytes have a %RSD ≤ 55. See Section 10.3.4. This modification accounts for analytical issues that arise from poor performing analytes.

17.10. For the continuing calibration criteria, Method TO-14A states that the RPD of each RF (in the CCV) from the mean RF of the ICAL curve should be <30%; for Method TO-15, the %D for each target compound must compare to the ICAL at ±30%. For routine analysis, for those analytes not listed in the published methods and are considered poor performers, TestAmerica Sacramento accepts the CCV if up to four of these analytes have a %D ±55. See Section 10.6.3. This modification accounts for analytical issues that arise for poor performing analytes.

17.11. Method TO-15 recommends maintaining control charts of the %D values for CCV standards. Due to limitations of the LIMS control chart module, these control charts are maintained using the % recovery values for the CCVs. This modification still permits monitoring for adverse trends.

17.12. Surrogates are not required by the methods. This SOP adds surrogates to every QC and client sample to help monitor for matrix effects and method performance. These compounds are included in the initial calibration at a single concentration for each calibration point. However, surrogates are not reported unless requested.

17.13. Method TO-15 states that the scan time must give 10 scans per peak, not to exceed 1 second per scan. The GC/MS software is set for a sampling rate of 3, which

corresponds to approximately 2 to 3 scans per second, depending on the instrument. See the GC/MS operator's manual or "help" on the software for more information about the sampling rate.

17.14. The transfer of sample from Tedlar bags to canisters is supported by the conclusions of an EPA poster titled LOSS/GAIN OF VOCS FROM TEDLAR BAGS AND OTHER SAMPLING EQUIPMENT, by C. Loss Paul as presented at the Presented at The 17th Annual Association for Environmental Health and Sciences Meeting, San Diego, CA, March 21 - 22, 2007. According to the synopsis,

> Soil gas samples are collected to evaluate human health risk from vapor intrusion into homes and other buildings. In order to meet risk assessment goals, the analytical reporting limit for many compounds of concern are down to part per billion ranges. The appropriate sampling tubing, sample containers and leak check compounds should be selected in order to ensure data quality objectives. Mechanisms which can impact sample integrity include adsorption of volatile organic compounds (VOCs) onto the sampling media and diffusion of VOCs through the sampling media which may result in artificially low values, and desorption of compounds from the sampling media into the sample which may results in artificially high values. A literature search was conducted to compile published results of impacts on soil gas samples from sampling equipment (i.e., tubing) and containers (i.e., Tedlar® bags). The literature search revealed that the recommended holding time for samples stored in Tedlar® bags not exceed 48 hours. A laboratory study was conducted to evaluate the holding times for certain VOCs in 1 L Tedlar® bags stored at two different temperatures. VOCs used in this experiment include 1,1,1-trichloroethane (1,1,1-TCA), trichloroethylene (TCE), benzene, and toluene that were combined in a gas mixture with nitrogen. Bags were filled with the gas mixture and then stored for different times and temperatures. Two incubators were set at two temperatures, C to simulate field temperatures and the bags were stored from 8°C and 25°C 15 hours to 2 weeks. Results of this study show that 1,1,1-TCA, TCE, and benzene can be stored up to one week without significant impact on concentrations. Results for toluene are less conclusive. However, soil gas samples collected in Tedlar® bags should be analyzed as quickly as practical or samples can be transferred to another container with longer holding times (i.e., Summa canister).

18. ATTACHMENTS

18.1. Attachment 1: Standard Analytes, Reporting Limits, and Characteristic Ions

18.2. Attachment 2: BFB GC Operating Conditions, EPA TO-15

18.3. Attachment 3: BFB Acceptance Criteria, EPA TO-14A

18.4. Attachment 4: BFB Acceptance Criteria, EPA TO-15

18.5. Attachment 5: Internal Standards

18.6. Attachment 6: Surrogate Standards

18.7. Attachment 7: Example GC/MS Initial Calibration Curve Review Checklist

18.8. Attachment 8: Example GC/MS Technical Data Review Checklist

18.9. Attachment 9: Schedule for Routine Maintenance of Analytical Instrument

18.10. Attachment 10: Canister Pressurization Logbook (Example Page)

18.11. Attachment 11: GRO Analysis

19. REVISION HISTORY

The revision history prior to 2014 has been removed. It is available for review in previous revisions of this SOP.

19.1. WS-MSA-0015, Revision 1.7, Effective 11/21/2017

19.1.1. Updated references to DoD to be DoD/DOE or QSM, as appropriate

19.1.2. Inserted Section 9.2.3.1, “Refer to WS-PQA-021 for details of corrective actions applicable for sample batches analyzed under the DoD/DOE QSM.”

19.1.3. Inserted Section 10.2.3.1, “ICALs associated with DoD/DOE QSM samples are considered acceptable if the calculated RSD for the RF or RRF for each requested analyte is < 30%, with no exceptions.”

19.1.4. Inserted Section 10.4.2.1, ICVs associated with DoD/DOE QSM samples are considered acceptable if the calculated result for requested analyte is with ± 30% of the true value, with no exceptions.”

19.1.5. Inserted Section 10.5.2.1, CCVs associated with DoD/DOE QSM samples are considered acceptable if the calculated result for requested analyte is with ± 30% of the true value, with no exceptions.”

19.1.6. Inserted Section 10.5.1.1, “CCVs associated with DoD/DOE QSM samples are analyzed daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.”

19.1.7. Attachment 11, Inserted Section 10.9.1.1, “CCVs associated with DoD/DOE QSM samples are analyzed daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.”

19.1.8. Editorial Revisions

19.2. WS-MSA-0015, Revision 1.6, Effective 07/31/2015

19.2.1. Changed Copyright Information statement on Title page.

19.2.2. Table A3 –Changed gasoline calibration standard 1 from 200 ppb v/v to 100 ppb v/v.

19.2.3. Editorial changes.

19.3. WS-MSA-0015, Revision 1.5, Effective 04/03/2015

19.3.1. Changed Section 10.1.2.1 from “28mL of 250pbv” to “24mL of 300ppbv”.

19.3.2. Changed Section 10.1.2.2 from: An alternative way to load 50ng BFB is to use 100ml of a 10ppbv IS/SURR mix and 24mL of a 250 IS/SURR” to “An alternate way to load 50ng BFB is to use 50mL of a 20ppbv IS/SURR mix and 20mL of a 3000ppbv IS/SURR mix.”

19.3.3. Editorial changes

19.4. WS-MSA-0015, Revision 1.4 Effective 03/06/2015

19.4.1. Added Section 7.3.5 to read, “Working standards are valid for a period of 30 days, after which fresh standards are prepared.”

19.4.2. Added Section 10.5.7 to read, “CCVs must be monitored on a routine basis using the control chart program (refer to SOP WS-QA-0035) to evaluate the data for trends. The frequency is dependent on the frequency of the analysis. In the LIMS control chart module, select the CCV chart. Once the chart has been evaluated, click “Save Log” to save the chart evaluation in the LIMS.”

19.4.3. Inserted Section 17.4 to read, “Method TO-15 presents criteria for evaluating canister cleanliness as less than 0.2 ppbv of any target VOC. TestAmerica Sacramento works with clients to ensure that the canisters meet their data quality objectives, by providing canisters evaluated to the reporting limit or method detection limit as required by their program.”

19.4.4. Inserted Section 17.11 to read, “Method TO-15 recommends maintaining control charts of the %D values for CCV standards. Due to limitations of the LIMS control chart module, these control charts are maintained using the % recovery values for the CCVs. This modification still permits monitoring for adverse trends.”

19.4.5. Section 17.1.2, inserted the sentence, “These compounds are included in the initial calibration at a single concentration for each calibration point.”

19.5. WS-MSA-0015, Revision 1.3, Effective 08/15/2014

19.5.1. Section 8, revised second row of table to reflect the more recent "Advisory, Active Soil Gas Investigations" (from 2012 rather than 2003). Reference in 16.5 also changed.

19.5.2. Inserted Section 5.1.2, safety requirements when transferring sample from air bags into syringes or canisters.

19.5.3. Section 8 – in accordance with the most recent DTSC advisory, changed the holding time to 30 days for canisters under DTCS requirements as well.

19.5.4. Changed Section 7.2.2 from 'concentration of 250 ppbv…' to 'concentration of 300 ppbv…'.

19.5.5. Changed Section 7.3.1.1 from 125 µL to 50 µL Distilled or Nanopure water.

19.5.6. Inserted Section 9.7.1, referring to DoD requirements.

19.5.7. Added Section 10.2.5.1, "The coefficient of determination for a line fit must be greater than or equal to 0.990

19.5.8. Added Section 10.2.5.2, The absolute value of the intercept (printed on the calibration curve plot in Chrom) should be less than ½ the reporting limit (-RL ≤ intercept ≤ +RL). If the intercept is outside the limits, any values below the reporting limit must be evaluated to ensure that false positives or false negatives are not being reported.

19.5.9. Changed Section 10.2.7 to – "The nominal concentrations of the ICAL standards are typically 0.30, 0.40, 0.80, 2.0, 4.0, 8.0, 20, 40 and 60 ppbv, but these may vary depending on the certified mix used to prepare the standards or the volume trapped. The low standard must be at or below the RL. The standards are analyzed by preparing stock standards at the required concentration or by varying the trapped volume of the working standards from the default volume of 250 mL. For example, the 0.30, 0.40, and 0.80 ppbv standards are analyzed by trapping 30, 40, and 80 mL, respectively, of a 2.5 ppbv working standard."

19.5.10. Removed Section 11.2.4, 11.2.4.1, and 11.2.4.2, which discussed the laboratory default to analyze air sample bags at a 20x dilution.

19.5.11. Removed the subheadings from Section 11.4 (Screening).

19.5.12. Section 11.7.2, appended the following, "The sequence is verified by another analyst. This analyst verifies the autosampler sequence, port position, chem.

station sequence, and Chrom worklist. The analyst annotates in the instrument maintenance log if the sequence has been verified."

19.5.13. Changed Section 11.7.4 from – 'If the default volume is 250 mL then 410 mL should be trapped' to 'If the default volume is 250 mL then 510 mL should be trapped.'

19.5.14. Combined GC operating conditions and BFB operating conditions (Attachment 2 and Attachment 3) as they are the same. Renumbered the attachments.

19.5.15. Updated Attachments 7, 8, and 10 to current versions.

19.5.16. Editorial comments.

19.5.17. Inserted Attachment 11 – GRO Analysis using Method TO-15

19.5.18. Editorial changes.

Attachment 1: Standard Mix Analytes and Characteristic Ions

Analytes	CAS #	Quant	Confirmation	RL (ppb v/v)
1,1,1,2-Tetrafluoroethane	811-97-2	86	69, 51	1.0
1,1,1-Trichloroethane	71-55-6	97	99, 61	0.30
1,1,2,2-Tetrachloroethane	79-34-5	83	85, 131	0.40
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	101	151, 103	0.40
1,1,2-Trichloroethane	79-00-5	97	83, 85	0.40
1,1-Dichloro-1-fluuoroethane	1717-00-6	81	61, 45	0.40
1,1-Dichloroethane	75-34-3	63	65, 83	0.30
1,1-Dichloroethene	75-35-4	61	96, 98	0.80
1,1-Dichloropropene	563-58-6	75	110, 39	0.40
1,1-Difluoroethane	75-37-6	51	65	0.40
1,2,3-Trichlorobenzene	87-61-6	180	182, 145	2.0
1,2,3-Trichloropropane	96-18-4	110	97, 75	0.40
1,2,4-Trichlorobenzene	120-82-1	180	182, 145	2.0
1,2,4-Trimethylbenzene	95-63-6	120	105, 77	0.80
1,2-Dibromo-3-chloropropane	90-12-8	157	155, 75	2.0
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	135	85, 87	0.40
1,2-Dichlorobenzene	95-50-1	146	148, 111	0.40
1,2-Dichloroethane	107-06-2	62	49, 64	0.80
1,2-Dichloropropane	78-87-5	76	63, 62	0.40
1,3,5-Trimethylbenzene	108-67-8	120	105, 77	0.40
1,3-Dichlorobenzene	541-73-1	146	148, 111	0.80
1,3-Dichloropropane	142-28-9	76	41,78	0.80
1,4-Dichlorobenzene	106-46-7	146	148, 111	0.40
1,4-Difluorobenzene	540-36-3	114	88, 63	
1,4-Dioxane	123-91-1	88	58	0.80
1.1.1.2-Tetrachloroehtane	630-20-6	131	133, 95	0.40
2,2-Dichloropropane	78-87-5	77	97, 41	0.80
2-Butanone (MEK)	78-93-3	72	43, 57	0.80
2-Chlorotoluene	95-49-8	126	91, 89	0.40
2-Hexanone	591-78-6	58	43, 85100	0.40
2-Methyl-2-propanol	75-65-0	59	57, 41	2.0
3-Chloro-1-propene (Allyl Chloride)	107-05-1	41	76, 78	0.80
4-Ethyltoluene	622-96-8	120	105, 77	0.40
4-Isopropyltoluene	99-87-6	119	134, 91	0.80
4-Methyl-2-pentanone (MIBK)	108-10-1	43	58, 100	0.40
Acetone	67-64-1	43	58	5.0
Acrolein	107-02-8	56	55, 53	2.0
Alpha Methyl Styrene	98-83-9	118	103, 117	0.40
Benzene	71-43-2	78	77, 52	0.40

Analytes	CAS #	Quant	Confirmation	RL (ppb v/v)
Benzyl chloride	100-44-7	91	126, 63	0.80
Bromobenzene	108-86-1	156	77, 158	0.80
Bromoform	75-25-2	173	175, 171	0.40
Bromomethane	74-83-9	94	96, 79	0.80
Butadiene (1,3-Butadiene)	106-99-0	39	54, 53	0.80
Butane	106-97-8	43	41, 58	0.40
Carbon disulfide	75-15-0	76	78, 44	0.80
Carbon tetrachloride	56-23-5	117	119, 121	0.80
Chlorobenzene	108-90-7	112	114, 77	0.30
Chlorodibromomethane	124-48-1	129	127, 131	0.40
Chlorodifluoromethane	75-45-6	51	67, 50	0.80
Chloroethane	75-00-3	64	49, 66	0.80
Chloroform	67-66-3	83	85, 47	0.30
Chloromethane	74-87-3	50	52	0.80
cis-1,2-Dichloroethene	156-59-2	96	61, 98	0.40
cis-1,3-Dichloropropene	10061-01-5	75	77, 39	0.40
Cyclohexane	110-82-7	84	56, 69	0.40
Cyclohexanone	108-94-1	55	42, 98	0.80
Dibromomethane	74-95-3	174	93, 95	0.40
Dichlorobromomethane	75-27-4	85	83, 129	0.30
Dichlorodifluoromethane	75-71-8	85	87, 50	0.40
Dichlorofluoromethane	75-43-4	67	69	0.40
Ethanol	64-17-5	46	45	1.0
Ethyl acetate	141-78-6	43	61, 70	0.30
Ethylbenzene	100-41-4	91	106, 65	0.40
Ethylene Dibromide (EDB)	106-93-4	107	109, 81	0.80
Hexachlorobutadiene	87-68-3	225	223, 227	2.0
Hexane	110-54-3	43	57, 86	0.80
Iodomethane	74-88-4	142	127	0.40
Isooctane (2,2,4-Trimethylpentane)	540-84-1	57	41, 56	0.40
Isopropyl alcohol	67-63-0	45	4359	0.80
Isopropyl ether	108-20-3	45	87, 59	0.80
Isopropylbenzene	98-82-8	120	105, 79	0.80
Methyl methacrylate	80-62-6	69	41, 100	0.80
Methyl tert-butyl ether	1634-04-4	73	57, 41	0.80
Methylene Chloride	75-09-2	49	84, 86	0.40
m-Xylene & p-Xylene	179601-23-1	91	106, 77	0.80
Naphthalene	91-20-3	128	102, 129	0.80
n-Butanol	71-36-3	56	41, 43	2.0
n-Butylbenzene	104-51-8	92	91, 134	0.40
n-Heptane	142-82-5	43	41, 100	0.80

Analytes	CAS #	Quant	Confirmation	RL (ppb v/v)
n-Nonane	111-84-2	43	57, 85	0.80
n-Octane	111-65-9	43	41, 85	0.40
N-Propylbenzene	103-65-1	91	120, 65	0.40
o-Xylene	95-47-6	91	106, 105, 78	0.40
Pentane	109-66-0	43	57, 72	0.80
Propane	74-98-6	43	42, 39	0.40
Propane, 2-methyl	75-28-5	43	41	0.40
Propene	115-07-1	41	39, 42	0.40
sec-Butylbenzene	135-98-8	105	134, 91	0.40
Styrene	100-42-5	104	78, 103	0.40
Tert-amyl methyl ether (TAME)	994-05-8	73	55, 87	0.80
Tert-butyl ethyl ether	637-92-3	59	87, 57	0.80
tert-Butylbenzene	98-06-6	91	119, 134	0.80
Tetrachloroethene	127-18-4	166	164, 131	0.40
Tetrahydrofuran	109-99-9	42	71, 72	0.80
Toluene	108-88-3	91	92, 65	0.40
trans-1,2-Dichloroethene	156-60-5	61	96, 98	0.40
trans-1,3-Dichloropropene	10061-02-6	75	77, 39	0.40
Trichloroethene	79-01-6	130	95, 132	0.40
Trichlorofluoromethane	75-69-4	101	103, 66	0.40
Vinyl acetate	108-05-4	43	86, 42	0.80
Vinyl bromide	593-60-2	106	108, 81	0.80
Vinyl chloride	75-01-4	62	64, 61	0.40
Xylenes, Total	1330-20-7	NA	NA	1.20
Internal Standards				
Chlorobromoethane	107-04-0	130	49.128	
1,4-Difluoroethane	540-36-3	114	88, 63	
Chlorobenzene-d5	3114-55-4	117	82. 54	
Surrogates				
1,2-Dichloroethane-d4	3855-82-4	85	87, 102	
Toluene-d8	2037-26-5	100	98	
4-Bromofluorobenzene	460-00-4	95	174, 176	

Attachment 2: GC Operating Conditions, BFB and EPA TO-15

Method file: TO15				
Method File List				
GC Type: 6890				
Run type: Scan, GC, E1				
Column: Cap				
Split Ratio: 40.5:1				
	Inj.P	**Intfc**	**Source**	
Temp, °C	**150°C**	**220°C**	**NA**	
GC/DIP				
Initial Column Temperature / Hold time	**35°C for 5 minutes**			
Temperature Profile	**35°C - 110°C at 6.0°C /minute, hold for 0.10 minute, 110°C - 220°C at 8.0°C, hold for 1 minute**			
Post Time	**5.0 minutes**			
Oven equilibration Time: 0 min				
Run time: 37.35 min				
Scan Start time: 3.95 min				
Scan Parameters:				
Mass Range: 35 to 300				
Multiplier voltage: varies				
Number of samples: 2				
Threshold: 200 counts				

Attachment 3: BFB Acceptance Criteria, EPA TO-14A

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5.0 to 9.0% of mass 95
173	<2.0% of mass 174
174	>50% of mass 95
175	5.0 to 9.0% of mass 174
176	>95% but <101% of mass 174
177	5.0 to 9.0% of mass 176

Attachment 4: BFB Acceptance Criteria, EPA TO-15

Mass	Ion Abundance Criteria
50	8.0 to 40% of mass 95
75	30 to 66% of mass 95
95	Base Peak, 100% Relative Abundance
96	5.0 to 9.0% of mass 95
173	<2% of mass 174
174	50 to 120% of mass 95
175	4.0 to 9.0% of mass 174
176	93% to 101% of mass 174
177	5.0 to 9.0% of mass 176

Attachment 5: Internal Standards

Bromochloromethane
1,4-Difluorobenzene
Chlorobenzene-d5

Attachment 6: Surrogate Standards

1,2-Dichloroethane-d4
Toluene-d8
4-Bromofluorobenzene

Attachment 7: Example GC/MS Initial Calibration Curve Review Checklist

TestAmerica
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Sacramento

ICAL Review Checklist
Volatile Air GCMS

Method & Instrument ID: _____ **ICAL Date:** _____
Chrom Worklist #: _____ **Calibration ID:** _____ **TALS Analysis Batch:** _____
Method (Check the applicable box)
☐ TO-14A / TO-15 Modified SCAN ☐ TO-15 Scan ☐ TO-15 SIM ☐ TO-15 SIM (Special Project)

Acceptance criteria are found in the applicable laboratory SOP or in TALS. If item is No, create an NCM.

Review Items	Level 1		NA	Level 2
General Criteria	Yes	No		
Standards analyzed within 24 hour tune time.				
Chrom Peak Review calibration reports (F6) reviewed for error flags				
Retention time correct for isomers/coeluters and all other analytes • Dichlorodifluoromethane / 1,2-Ddichlorofluoroethane • Trichlorofluoromethane / 1,1,2-Trichlorofluoroethane • Hexane / Vinyl acetate • 2-Methyl butane / Acrolein • 1,1-Dichloroethene / cis-1,2-Dichloroethene / trans-1,2-Dichloroethene • 1,2-Dichloroethane / Benzene • cis-1,3-Dichloropropane / trans-1,3-Dichloroproapne • Ethylbenzene / m/p-Xylene / o-Xylene • 4-Ethyl toluene / 1,3,5-Trimethylbenzene / 1,2,4-Trimethylbenzene • tert-Butylbenzene / 4-Isopropyltoluene • 1,3-Dichlorobenzene / 1,4-Dichlrobenzene / 1,2-Dichlorobenzene • 1,2,4,5-tetramethylbenzne / 1,2,3,4-tetramethylbenzene • 1,2,4-Trichlorobenzene / 1,2,3-Trichlorobenzene				
Curve reviewed in Chrom for all analytes and all appropriate leves are included/excluded				
Uploaded all calibration levels to TALS after any changes were made in Peak Review				
Method for this worklist set as Most Recent Method				
ICAL locked in Chrom and in TALS				
ICV passes -See criteria below				
Manual Integrations clearly identified, initialed, dated and reason given.				
SIM Criteria				
PFTBA tune documentation present in Chrom & TALS and meets criteria				
RSD < 30% (≤ 40% for up to 2 analytes.				
Linear regressions >0.995 and intercept <+/- ½ RL/IS amount, (minimum of 5 points curve).				
All internal standards are within 60-140% of ICAL midpoint.				
ICV (Second Source) meets 70-130% criteria (60-140%) for up to 2 analytes,				
Scan Criteria				
BFB Tune documentation present in Chrom & TALS and meets criteria				
For GRO: WS-GRO report (F8) reviewed to ensure IS/Surrogate subtraction from area sum.				
RSD < 30% (≤ 40% for up to 2 analytes, and ≤ 55% for up to 4 poor performers defined in SOP)				
Linear regressions >0.995 and intercept <+/- ½ RL/IS amount, (minimum of 6 points curve).				
All internal standards are within 60-140% of ICAL midpoint (for TO-15 / TO-15 Modified) or within 50-200% of ICAL midpoint (for TO-14A)				
ICV (Second Source) meets 70-130% criteria (60-140% for up to 2 analytes, and 45-155% for up to 4 poor performers defined in SOP)				

	Repeat Failure from Prev ICAL	
ICAL compounds outside RSD criteria (write compound and %RSD	Yes	No
_____		

ICV (second source) compounds outside RSD criteria (write compound and %D.	Yes	No
_____		

1st Level Reviewer: _____ Date: _____
2nd Level Reviewer: _____ Date: _____
Comments: _____

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Attachment 8: Example GC/MS Technical Data Review Checklist

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sacramento

MS VOA AIR Data Review Checklist

Job(s):_____ Instrument ID: _____
☐TO-14A ☐TO-14A MOD ☐TO-15 ☐TO-15 MOD ☐TO-15 SIM
ICAL Batch: _____ TALS Batch:_____

Review Items	Level 1 Yes	Level 1 No	Level 2	NA
Initial Calibration				
1. Is ICAL locked in Chrom & TALS?				
2. Is ICV properly linked in TALS for L3/L4 jobs?				
Continuing Calibration				
1. BFB tune documentation meets criteria? The PFTBA Tune Documentation is attached in TALS (SIM methods only)?				
2. All Internal Standards within 50-200% of ICAL mid-point (TO-14A/TO-14A MOD) or 60-140% (TO-15/ TO-15 MOD?				
3. Does the %D meet:30%D for standard program, and 20%D for DoD?				
4. Isomeric pairs checked for correct peak assignment? • Dichlorodifluoromethane / 1,2-Ddichlorofluoroethane • Trichlorofluoromethane / 1,1,2-Trichlorofluoroethane • 2-Methyl butane / Acrolein • 1,1-Dichloroethene / cis-1,2-Dichloroethene / trans-1,2-Dichloroethene • Hexane / Vinyl acetate • 1,2-Dichloroethane / Benzene • cis-1,3-Dichloropropane / trans-1,3-Dichloroproapne • Ethylbenzene / m/p-Xylene / o-Xylene • 4-Ethyl toluene / 1,3,5-Trimethylbenzene / 1,2,4-Trimethylbenzene • tert-Butylbenzene / 4-Isopropyltoluene • 1,3-Dichlorobenzene / 1,4-Dichlorobenzene / 1,2-Dichlorobenzene • 1,2,4,5-tetramethylbenzne / 1,2,3,4-tetramethylbenzene • 1,2,4-Trichlorobenzene / 1,2,3-Trichlorobenzene				
Client Samples & QC Sample Results				
1. Was analysis done within holding times?				
2. Are Chromatograms reviewed and spectra verified?				
3. Are positive results within calibration range?				
4. Are all positive results within RT windows?				
5. All target cpds in MB < RL (< ½ RL for DoD)? Requires NCM if "no."				
6. Are surrogate recoveries for MB and LCS/LCSD within control limits?				
7. Are target constituents in LCS/LCSD within control limits?				
8. Are all Chrom graphics uploaded?				
9. Are all QC samples properly linked in TALS?				
10. Do the Internal Standards meet criteria +/-50% to +/-200% (TO-14A / TO-14A MOD), +/-60% to +/- 140% (TO-15/TO-15 MOD)?				
11. Do results (e.g., dilutions) make sense?				
12. Are MS/MSD recoveries and RPDs within control limits?				
13. Have all flags been reviewed for appropriateness?				
14. All manual integrations appropriate and documented?				
15. Are non-conformances documented as NCMs?				
16. Are client sample surrogate failures flagged and NCM written?				
17. Dilutions due to target cpds? ____ Dilutions due to non-targets? ____				
18. Has QC checker been run?				

1st Level Reviewer / Date:_____ 2nd Level Reviewer / Date: _____

Comments: _____

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Attachment 9: Schedule for Routine Maintenance of Analytical Instrument

Frequency	Maintenance Item
Daily	Check baseline level with analysis of blanks. Inspect chromatogram to verify symmetrical peak shape and adequate resolution between closely eluting peaks. Autosampler: Check for proper operation. Leak check system.
As needed	Replace septum. Clean injector port. Break off front portion of capillary columns. Replace column if this fails to restore column performance or when column performance (e.g. peak tailing, poor resolution, high backgrounds, etc.) indicates it is required. Check level of oil in mechanical pumps and diffusion pump if vacuum is insufficient. Add or change oil, if needed. Replace the exhaust filters on the mechanical rough pump every 1-3 years, or as needed. Replace electron multiplier when the tuning voltage approaches the maximum and/or when sensitivity falls below required levels. Check ion source and analyzer (clean, replace parts as needed). Clean source, including all ceramics and lenses - as is indicated by a variety of symptoms including inability to properly tune, poor response, and high background contamination. Repair/replace jet separator. Replace filaments when burnt out or performance indicates need for replacement.

Attachment 10: Canister Pressurization Logbook (Example Page)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sacramento

Canister Pressurization Log

Date	Sample ID	Can #	Initial Press. (psig)	Initial Press. (psia)	Final Press. (psig)	Final Press. (psia)	Gauge ID	Initial	Comments
							A		
							B		
							A		
							B		
							A		
							B		
							A		
							B		
							A		
							B		
							A		
							B		
							A		
							B		
							A		
							B		
							A		
							B		
							A		
							B		

A = Gauge CD5437; B = Gauge _____ [Calculation: psig + 14.7 = psia]

PAGE 1

Reviewed by /Date: _____

QA-813 r1 GEC 7/21/2014

1. SCOPE AND APPLICATTION

1.1. This method describes the analysis of volatile petroleum hydrocarbons. The procedure used for the petroleum hydrocarbons is based on SW-846. Refer to Table A1 for the individual analytes normally determined by these procedures.

1.2. Compounds within the scope of this method have boiling points below 218°C. Classes of compounds best suited for evaluation by this analysis include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

2. SUMMARY OF METHOD

Refer to Section 2 of the main body of this SOP for a summary of the method.

3. DEFINITIONS

Refer to Section 3 of the main body of this SOP for a summary of the method.

4. INTERFERENCES

Refer to Section 4 of the main body of this SOP for interferences.

5. SAFETY

Refer to Section 5 of the main body of this SOP for Safety Information.

6. EQUIPMENT AND SUPPLIES

Refer to Section 6 of the main body of this SOP for equipment and supplies.

7. REAGENTS AND STANDARDS

All reagents must be ACS reagent grade or better unless otherwise specified.

7.1. Reagents

7.1.1. UHP Helium for carrier gas

7.1.2. UHP H_2 for detector combustion

7.1.3. Zero-grade air for detector combustion

7.1.4. UHP N_2 for sample preparation, standard preparation, and method blanks

7.1.5. Liquid N_2

7.2. Standards – Neat standards are good for 1 year from date purchased or if a vendor supplied standard has an earlier expiration date then that date is used.

7.2.1. Certified BTEX, MTBE, and alkane standards in pressurized gas cylinders and neat liquids, obtained from select NIST-approved vendors.

7.2.2. Certified Hexane standards in pressurized gas cylinder and neat liquid, obtained from select NIST-approved vendors.

7.2.3. Certified neat unleaded gasoline standards, obtained from select NIST-approved vendors.

7.3. Standard Preparation

Standard preparation activities are performed accordance with TestAmerica SOP WS-QA-0017.

7.3.1. Dilutions of standards are made on a volume/volume basis using serial dilution methodologies. UHP N_2 is used as the diluent gas.

7.3.2. Primary gas standards are either purchased from manufacturers in pressurized, pre-mixed gas cylinders, or prepared in passivated canisters or air sample bags from neat liquid standards.

7.3.2.1. Primary Gas Standard Prepared in Canisters - To prepare a primary gas standard from neat liquids, an aliquot of the compound is injected into a clean and evacuated (-30 inches of mercury) passivated canister. The density of the compound is used to determine the mass injected. The canister is pressurized using UHP N_2 and is then allowed to equilibrate.

7.3.2.2. Primary Gas Standard Prepared in Air Sample Bags - To prepare a primary gas standard from neat liquids, an aliquot of the compound is injected with a volumetric gas-tight syringe into a new and clean air sample bag. The air sample bag is filled with UHP N_2 to the appropriate volume using a volumetric gas-tight syringe. The air sample bag standard is then allowed to equilibrate.

To calculate the concentration of the standard prepared:

$$ppmv = \frac{\left(D \times V_1 \times 24.45 \times 10^6\right)}{\left(MW \times V_2\right)}$$

Where:

V_1 = aliquot of neat liquid (mL)

D = density of neat liquid (g/mL)

V_2 = final volume in passivated canister or air sample bag (L)

24.45 = molar volume (L/mole) at STP

10^6 = conversion factor

MW = molecular weight (g/mole)

7.3.3. Working gas standards are good for 6 months from date of preparation. They are prepared in passivated canisters or air sample bags by making dilutions of the primary pre-mixed gas cylinders (from vendors) or by making dilutions of the prepared primary gas standard prepared from the neat liquid standards (see Section 7.3.2).

7.3.3.1. Working Gas Standard Prepared in Canisters - To prepare a working gas standard, an aliquot of the prepared primary gas standard or of the pre-mixed primary gas standard is transferred to a clean and evacuated passivated canister. The aliquot is metered in by measuring the vacuum of the canister as the aliquot is being transferred. The ratio of the final canister pressure and the pressure transferred is the dilution factor. The canister is pressurized with UHP N_2 and is then allowed to equilibrate.

7.3.3.2. Working Gas Standard Prepared in Air Sample Bags - To prepare a working gas standard, an aliquot of the prepared primary gas standard or of the pre-mixed primary gas standard is transferred to a new and clean air sample bag. The aliquot is transferred by direct injection with a volumetric gas-tight syringe. The air sample bag is filled with UHP N_2 to the appropriate volume using a volumetric gas-tight syringe. The air sample bag standard is then allowed to equilibrate.

7.3.3.3. To calculate the concentration of the standard prepared:

$$ppmv = C_{ps} \times P_i / P_f$$

Where:

C_{ps} = concentration of compound in primary gas standard, ppmv

P_i = aliquot of primary gas standard used in psia or in mL if using air sample bag

P_f = final pressure of canister in psia or final volume in mL if using air sample bag

7.3.4. Gasoline Calibration Standards

7.3.4.1. The primary standards are prepared in passivated canisters from neat unleaded gasoline. Gasoline from one vendor will be used to prepare two or more gasoline calibration standards. The second

source LCS is prepared from unleaded gasoline obtained from a different lot number.

7.3.4.2. A 10-, 25-, 50-, or 100-µL gas-tight syringe is used to transfer the neat gasoline into the septum-capped evacuated canister. The total (barrel + needle) syringe volume is accounted for.

8. SAMPLE PRESERVATION AND STORAGE

Refer to Section 8 of the main body of this SOP for information regarding sample preservation and storage.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the main body of this SOP for general quality control requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the % RSD of the response factor or calibration factor of each analyte is ≤ 30%. If an analyte exceeds the criteria, then a regression line (linear or curved) may be attempted.

10.1.1. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits should only be used if the analyst has reason to believe that the average RF model does not fit the **normal** concentration/response behavior of the detector.

10.1.2. Average response factor

The average response factor may be used if the average percent relative standard deviation (%RSD) of all the response factors taken together is ≤ 30%. The equation for average response factor is:

Equation A1

$$\text{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.1.3. Linear regression

The linear fit uses the following function:

Equation A2

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response

x = Concentration

a = Slope

b = Intercept

10.1.4. Quadratic curve

The quadratic curve uses the following function:

Equation A3

$$x = \frac{-b + \sqrt{b^2 - 4a(c - y)}}{2a}$$

Where: x = concentration

y = instrument response

a = 2nd order coefficient (curvature)

b = 1st order coefficient (slope)

c = constant (intercept)

10.2. Evaluation of calibration curves

The %RSD from the calibration curve is used to evaluate the initial calibration. If a regression line is used, the coefficient of determination (r2) shall be greater than or equal to 0.990, or the correlation coefficient (r) shall be greater than or equal to 0.995, whichever is appropriate to the regression fit used.

10.3. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response should be less than ± ½ the reporting limit for the analyte.
- The RSD for average response factors for each component must be ≤ 20%.
- When RSD is inappropriate, either the correlation coefficient (r) must be ≥ 0.995, or the coefficient of determination (r^2) must be ≥ 0.990.

10.4. Initial Calibration (ICAL)

10.4.1. At the beginning of each initial calibration curve for gasoline or other hydrocarbon fuel mixtures, the carbon range is established from the n-alkanes in the calibration standard. The start and end points for the peak summing range is the retention time at the apex of the beginning and ending carbon

range of the fuel mixture (e.g RT of C6 to RT of C12 measured at the beginning of the start peak and the end of the end peak.

10.4.2. The initial calibration for the GRO curve consists of 6 calibration standards (concentrations listed in Table A3)

10.5. Quantitating hydrocarbon mixtures:

Starting and ending retention times for quantitation are determined for each fuel as per 10.4.1. The peak areas between the starting and ending times are summed and 1,4-Difluorobenzene is used to generate a response factor. This factor is used to quantitate sample results, and depending on the client requirements, this factor may be applied to the same retention range as the standard, or to a different range.

10.6. Integration

10.6.1. When evaluating the initial calibration, also evaluate hydrocarbon pattern integration.

10.6.1.1. The integrated peaks should run from the point in the chromatogram prior to peaks to a region following the mixture's peaks in a fairly straight line.

10.6.2. The default integration parameters generated as a result of evaluating the initial calibration should remain in effect until the initial calibration is reanalyzed.

10.7. Evaluate the initial calibration as per 10.1 and 10.3.

10.8. A second source standard is analyzed immediately following the initial calibration. The acceptance criteria for the second source standard is ± 30% from the expected value.

10.9. Continuing Calibration Verification (CCV)

10.9.1. A CCV (5000ppbv or another mid-level standard) is analyzed at the beginning of each 24 hour analytical sequence. The integration for the GRO CCV follows the same technique as stated in 10.6.

10.9.1.1. CCVs associated with DoD/DOE QSM samples are analyzed daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.

10.9.2. The acceptance criteria for the CCV is ± 30% D.

11. PROCEDURE

11.1. Refer to Section 11 of the main body of this SOP for information regarding sample preparation and other procedures.

12. CALCULATIONS/DATA REDUCTION

12.1. Refer to Section 12 of the main body of this SOP for general information regarding data analysis and calculations.

12.2. Gasoline is quantitated using the area between two marker peaks as specified in Table A2.

12.3. Calculate results in samples as in Section 12 of the main portion of this SOP.

13. METHOD PERFORMANCE

Refer to Section 13 of the main body of this SOP for method performance criteria.

14. POLLUTION CONTROL

Refer to Section 14 of the main body of this SOP for information relating to pollution control.

15. WASTE MANAGEMENT

Refer to Section 15 of the main body of this SOP for information relating to waste management.

16. REFERENCES/CROSS REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Sections 5000, 5030B, 5035, 8000B, and 8015B.

16.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, March 2003, Section 8000C.

16.3. Leaking Underground Fuel Tank Field Manual, State of California, October, 1989

17. METHOD MODIFICATIONS

17.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.2. This method is performed on a GC/MS, with surrogate values calculated using Method TO-14A/TO-15, and the TPH values calculated using the total area chromatogram. All

of the reference methods are based on GC-FID as the detector and the limitations thereof.

18. ATTACHMENTS

18.1. Table A1 – Standard Analyte List

18.2. Table A2 – Volatile Petroleum Hydrocarbon Quantitation Ranges.

18.3. Table A3 - Calibration Standard Concentrations

18.4. Table A4 - LCS Spiking

.

Table A1		
Standard Analyte List		
Compound	CAS Number	Reporting Limit (ppbv/v)
Gasoline Range Organics (GRO)	NA	100

Table A2		
Volatile Petroleum Hydrocarbon Quantitation Ranges.		
Regulatory Method GRO	Quantitation Range	
	Start	End
GRO	n-C3	n-C12
nC4-nC12	nC4	nC12
C4-C12	n-C4	n-C12

[1] *The method specifies that the peak summing window must start at the start of the n-C6 peak and finish at the start of the n-C10 peak.*

Table A3						
Calibration Standard Concentrations (ppbv/v)						
Component	1	2	3	4	5	6
Gasoline	100	500	1000[1]	5,000	10,000	20,000

[1]*Designates the mid-level standard concentration used for the ICV and CCVs following the initial CCV of a sequence.*

Refer to the main body of this SOP for surrogate details.

Table A4	
LCS Spiking	
Component	Concentration (ppbv)
GRO	5000

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Chlorinated Pesticides [Methods 8081A, 8081B]

Approvals

Signatures on File

Joan Protasio Date
Semivolatile Organic Department Manager

Manjit Nijjar Date
Health & Safety Manager / Coordinator

Terri Torres Date
Quality Assurance Manager

Dennis Bean Date
Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1. This standard operating procedure (SOP) describes the determination of chlorinated pesticides using the methodology described in EPA SW-846 Method 8081A and 8081B.

1.2. This SOP is applicable to the gas chromatographic (GC) analysis of extracts of soil and water samples. Table 1 lists the compounds that can be determined by this method and their associated routine reporting limits (RLs).

1.3. This SOP does not include the procedures for extracting soil and water samples. Refer to the following SOPs for sample extraction procedures:

TA-OP-0301	Liquid-Liquid Extraction by Separatory Funnel, SW846 3510C and EPA 600 Series
TA-OP-0302	Sonication Extraction Procedure, SW846 3550B
TA-OP-0367	Microwave Extraction Procedure, SW846 3546

1.4 Analytes, Matrix(s), and Reporting Limits

See Table 1 for analytes and *TALS for the current* reporting limits by matrix.

2.0 Summary of Method

2.1 Sample Preparation

2.1.1 Chlorinated pesticides are extracted from a one-liter, or 250 mL (for LVI) water sample with methylene chloride using a separatory funnel (Method 3510C). Detailed instructions are given in SOP~~s~~ TA-OP-0301. The methylene chloride extract is exchanged to hexane as described in the appropriate extraction SOP.

2.1.2 Chlorinated pesticides are extracted from a 10-gram soil subsample into hexane by sonication (Method 3550B) or by microwave extraction (Method 3546). Detailed instructions are given in SOP TA-OP-0302.

2.1.3 SOPs TA-OP-0353 and TA-OP-0366 provide instructions for the cleanup of sample extracts. Clean-up is performed if necessary. All extracts are in hexane and the final extract volume is 10-mL for *soils and* one-liter samples, or 2.5 mL for LVI samples.

2.2 Analysis

2.2.1 Samples are analyzed using a gas chromatograph equipped with dual columns and dual microelectron capture detectors (µECDs).

2.2.2 The instrument is calibrated using *internal standards (1-Bromo-2-nitrobenzene)*. Compounds are identified by their retention time on the columns.

2.2.3 Positive results from the primary column are confirmed with a second, dissimilar column.

3.0 Definitions

3.1 Single-Component Pesticides: A pesticide formulation that consists of a single chemical compound. Most of the analytes determined by this procedure are single-compound pesticides.

3.2 Multi-Component Pesticides: A pesticide formulation that consists of more than one chemical compound. Toxaphene and Technical Chlordane are production mixtures of

multiple compounds. Toxaphene is manufactured by the chlorination of camphenes, which produces a variety of compounds, not all of which are chromatographically resolved. Technical Chlordane is produced by the chlorination of a mixture of camphenes and pinenes.

3.3 Chlordane: As just described, Technical Chlordane is a mixture of compounds. Method 8081A, Section 7.6.2 notes that it includes at least 11 major components and 30 minor components, and adds "the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch." The laboratory has found that manufacturing lots of Technical Chlordane produced at different times or at different production facilities have different ratios of the key components. For this reason, it is more common to analyze for the major components of technical Chlordane (α-Chlordane, γ-Chlordane, and heptachlor) instead of analyzing for the total mixture.

3.4 The quality control terms used in this procedure are consistent with SW-846 terminology. Definitions are provided in the glossary of the TestAmerica Seattle Laboratory Quality Manual (LQM).

4.0 Interferences

4.1 Contamination by carryover can occur when a low concentration sample is analyzed immediately following a high concentration sample. It is the laboratory's policy to reanalyze any samples that follow an unusually concentrated sample and that show detectable levels of the same compounds that appeared in the preceding concentrated sample.

4.2 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3 Sulfur will interfere chromatographically, and when observed, is removed. See SOP TA-OP-0353 for the sulfur cleanup procedure. The Lot# of the reagent used to perform the cleanup will be documented in an NCM.

4.4 Soil and water sample extracts can be subject to Florisil cleanup *which* can also be used to remove similar interferences. See SOP TA-OP-0366 for the Florisil Cleanup procedure. The Lot# of the cartridge used to perform the cleanup will be in an NCM or the batch worksheets.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.2 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.3 The ECD contains a ^{63}Ni radioactive source. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the facility's radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the EH&S Coordinator shall be immediately notified.

5.1.4 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. As a safety precaution, all standards, samples, and extracts are handled in an approved fume hood.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects are exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness, and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
(1) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 An analytical system complete with a gas chromatograph and dual ECD (Ni-63) detectors is required. A data system capable of measuring peak area and/or height is required.

6.1.1 Data acquisition system: Agilent's ChemStation, is used for data acquisition and storage on machine-readable media. Since no processing is done by

ChemStation and since there are no audit trail functions associated with data acquisition, the audit trail feature for ChemStation may be either enabled or disabled. The other component, Chrom, is used for data processing such as the measurement of peak area or peak height. By design, the audit trail feature for Chrom is always enabled.

6.1.2 Data processing: Chrom version 1.2 or higher

6.1.3 TestAmerica LIMS (TALS), current version

6.2 Columns

6.2.1 Guard Column: Agilent FS deactivated guard column, 5 meters long. Catalog number 160-2255-5.

6.2.2 Primary Column: ZB-CLPesticides-1, 30 m X 0.25 mm ID X 0.25 um Phenomenex or equivalent

6.2.3 Secondary Column: ZB-CLPesticides-2, 30 m X 0.25 mm ID X 0.20 um Phenomenex or equivalent

6.2.4 Additional columns that can be used for confirmation include: DB 35MS and DB XLB, Restek, or equivalent.

NOTE: Other columns may be used. These were the columns in place at the time the SOP was prepared.

6.3 Autosampler vials, crimp-top or screw top cap with PTFE-faced septa

6.4 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

6.5 Software

6.5.1 Data acquisition system: Agilent's ChemStation, is used for data acquisition and storage on machine-readable media. Since no processing is done by ChemStation and since there are no audit trail functions associated with data acquisition, the audit trail feature for ChemStation may be either enabled or disabled. The other component, Chrom, is used for data processing such as the measurement of peak area or peak height. By design, the audit trail feature for Chrom is always enabled.

6.5.2 Data processing: Chrom version 1.2 or higher

6.5.3 TestAmerica LIMS (TALS), current version

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

Reagents

7.2 Hexane, pesticide grade; each lot tested for purity prior to use per SOP S-T-001.

7.3 Carrier gas, ≥ 99.99999% pure hydrogen

7.4 Make-up gas, ≥ 99.99980% pure nitrogen

Standards

7.5 Standards Verification

All standards are subject to verification using a second-source standard before they are used for sample analysis. This process is also described in SOP TA-QA-0619.

7.6 Storage of Stock Standards

7.6.1 Commercial standards are received in flame-sealed ampoules or neat, 100% concentration, solutions. Stock standards are stored as directed by manufacturer. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.6.2 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced at least every one year or sooner if comparison with check standards indicates a problem. Endosulfan I and II appear to degrade in the presence of methanol. Delta-BHC appears to degrade in the presence of acetone.

7.7 Calibration Stock Standards

All calibration stock standards are obtained from commercial sources.

NOTE: The availability of the specific commercial standard solutions upon which the following sections are based may change at any time. As a result, it may be necessary to alter the dilution scheme presented herein to accommodate changes in stock standard concentrations. It may be also necessary to switch which source is the primary and secondary stock. All such changes are documented in the standards preparation records in the TALS Reagent module.

7.7.1 Internal Standard, Stock standard, 1000 ug/mL

The stock 1-Bromo-2-nitrobenzene internal standard is purchased from Restek, Catalog number 32279. An alternative Ultra Scientific product is available, Catalog number PPS-350.

7.7.2 CLP Organochlorine Pesticide Mix Stock Standard, 2,000 µg/mL

The routine pesticide mix stock standard contains all of the “routine” single-component pesticides (Restek Cat# 32415 or equivalent), as identified in Table 1 with the addition of Hexachlorobutadiene (Restek Cat# 31435 or equivalent) and Hexachlorobenzene (Restek Cat# 32231 or equivalent) at 1000 µg/mL Pesticide Surrogate Spike Mix Stock Standard, 200 µg/mL

The surrogate mix stock standard contains decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX) (Restek Cat# 32000 or equivalent).

7.7.3 Toxaphene Stock, 2000 µg/mL

The Toxaphene stock standard contains a specific production mixture of Toxaphene. (Restek Cat# 32071 or equivalent) This mixture does not necessarily match all possible production mixtures that could be found in the environment. This can present problems for Toxaphene quantitation (see Section 12).

7.7.4 Chlordane Stock, 1000 µg/mL

The Chlordane stock contains Technical Chlordane. (Restek Cat# 32021 or equivalent)

7.7.5 Non-Routine Compounds

Other, non-routine compounds not listed in this section may be requested by a client and may be added to this procedure.

7.7.5.1 In these cases, all stock solutions will be obtained from commercial sources and will be verified with a second-source standard as described in Section 7.5 above.

7.7.5.2 Non-routine standards will be stored and treated as described in Section 7.6 above.

7.7.5.3 Subsequent dilutions of specially requested compounds will be determined in a manner consistent with the client's recommendations for number of calibration points, inclusion of reporting limit, and concentration range adequate to represent the linearity of the instrument.

7.7.5.4 These specially requested non-routine compounds either may be added to the dilution scheme used for routine compounds or may be prepared as a separate calibration.

7.7.5.5 All standards preparation for non-routine compounds shall be documented using the same method that is used for routine compounds.

7.8 Intermediate Level Calibration Standards

7.8.1 Pesticide ICAL Stock Standard, 20,000 µg/L. The intermediate level calibration standard for routine pesticide compounds including Hexachlorobenzene and Hexachlorobutadiene is prepared by diluting the CLP Organochlorine Pesticide Mix (Section 7.7.1) and the Pesticide Surrogate Spike Mix (Section 0) stock standards in hexane as follows (all compounds are the same final concentration):

Pesticide ICAL Stock Standard

Pesticide Mix (mL)	Hexachloro butadiene (mL)	Hexachloro benzene (mL)	**Surrogate Mix (mL)**	**Final Volume (mL)**	**Final Conc of Each Pesticide (µg/L)**
0.100	0.200	0.200	1.0	10	20,000

7.9 Working Level Internal Standard

7.9.1 A 10,000 ug/L working internal standard is prepared by diluting 1 mL of the stock standard into a 100.00 mL volumetric flask. The working standard is then transferred to amber-colored vials or store with minimal light exposure, because the 1-Bromo-2-nitrobenzene is photosensitive.

7.9.2 For all initial calibration and verification standards, 1 mL of the working internal standard solution is added to each calibration standard level when preparing 100 mL of each standard.

7.10 Working Level Calibration Standards

7.10.1 Pesticide Calibration Standards

The following volumes of the 20,000 µg/L Pesticide ICAL Stock standard (Section 7.8.1) are diluted to 10 mL with hexane to produce calibration standards at 7 concentration levels, as summarized in the following table:

Pesticide Working Level Calibration Standards

Level	Volume of Mix C Intermediate Std (mL)	Volume of Working IS Std (uL)	Final Concentration (Analyte/IS) (µg/L)
7	0.200	100	400/100
6	0.100	100	200/100
5	0.050	100	100/100
4*	0.025	100	50/100
3	0.0025	100	5/100
2	0.0010	100	2/100
1	0.0005	100	1/100
* This level is used as the Continuing Calibration Verification (CCV) standard. It is recommended to create a working level of this standard with no IS added, in order to prepare the lower concentration standard levels.			

7.10.2 Toxaphene Working Level Calibration Standards

The 1,000 µg/mL purchased Toxaphene stock standard (Section 7.7.3) is diluted 1:100 in hexane yielding a 10 ug/mL Toxaphene ICAL stock that is then diluted with hexane to the final volumes indicated in the following table:

Toxaphene Working Level Calibration Standards

Level	Volume of Stock Std (mL)	Volume of Working IS Std (uL)	Final Volume (mL)	Final Concentration (TOX/IS) (µg/L)
1	0.01	100	10	10/100
2	0.1	100	10	100/100
3	0.2	100	10	200/100
4*	0.5	100	10	500/100
5	1.0	100	10	1000/100
6	2.0	100	10	2000/100
* This level is used as the CCV standard. To make additional volume of this standard, dilute 1.0 mL of the ICAL stock with hexane to a final volume of 200 mL.				

7.10.3 Technical Chlordane Working Level Calibration Standards

The 1,000 µg/mL purchased Technical Chlordane stock standard (Section 7.7.4) is diluted 1:100 in hexane yielding a 10 ug/mL Technical Chlordane ICAL stock that is then diluted with hexane to the final volumes indicated in the following table:

Chlordane Working Level Calibration Standards

Level	Volume of Stock Std (mL)	Volume of Working IS Std (uL)	Final Volume (mL)	Final Concentration (TCHL/IS) (µg/L)
1	0.010	100	10	10/100
2	0.020	100	10	20/100

Level	Volume of Stock Std (mL)	Volume of Working IS Std (uL)	Final Volume (mL)	Final Concentration (TCHL/IS) (µg/L)
3	0.050	100	10	50/100
4*	0.100	100	10	100/100
5	0.200	100	10	200/100
6	0.400	100	10	400/100
* This level is used as the CCV standard. To make additional volume of this level, dilute 2 mL of the stock standard with hexane to a final volume of 200 mL.				

7.10.4 Extended List Pesticides Calibration Standards

The extended list of pesticides analytes consists of 2,4-DDx compounds, oxy-Chlordane, cis- and trans-Nonachlor and Mirex. The primary source stock standards are obtained from various vendors, as indicated in the following table:

Extended List Pesticides Stock Source Information

Analyte Name	Vendor	Catalog Number	Analyte Concentration (mg/L)
2,4-DDx, combined	O2Si	131220-01	1000
oxy-Chlordane	O2Si	030353-03	1000
cis-Nonachlor	SPEX	S-2765	1000
trans-Nonachlor	SPEX	S-2770	1000
Mirex	Ultra Sci.	PST-720M100A01	100

7.10.5 Stock Level Extended List Pesticide Calibration Standard, 2000 ug/L

Prepare the 2000 ug/L stock calibration standard by diluting the standards listed in the table above in a 100 mL volumetric flask per the following table:

Analyte Standard	Volume Added (mL)	Final Concentration (ug/L)
2,4-DDx combo	0.200	2000
oxy-Chlordane	0.200	2000
cis-Nonachlor	0.200	2000
trans-Nonachlor	0.200	2000
Mirex	2.000	2000

7.10.6 Working Level Extended List Pesticide Calibration standards

Prepare the six calibration standard levels as outlined in the following table:

Extended List Pesticides Working Level Calibration Standards

Level	Volume of Stock Std (mL)	Volume of Working IS Std (uL)	Final Volume (mL)	Final Concentration (XOCP/IS) (µg/L)

Level	Volume of Stock Std (mL)	Volume of Working IS Std (uL)	Final Volume (mL)	Final Concentration (XOCP/IS) (µg/L)
1	0.010	100	10	2/100
2	0.020	100	10	5/100
3	0.050	100	10	10/100
4*	0.100	100	10	20/100
5	0.500	100	10	100/100
6	1.00	100	10	200/100
* This level is used as the CCV standard. To make additional volume of this level, dilute 2 mL of the stock standard with hexane to a final volume of 200 mL.				

7.11 Second-Source Standards for Initial Calibration Verification (ICV)

The second-source stock standards are purchased from a vendor different from the one that supplied the stock calibration standards.

7.11.1 Pesticide ICV Stock Standard, 1,000 µg/mL

Commercial standards containing all single-component pesticide compounds are obtained from a vendor different from the one that supplied the calibration stock standard. Typically, the standards are obtained from Ultra Scientific (CC-2563) for the pesticide mix and Spex or O2SI for Hexachlorobutadiene and Hexachlorobenzene.

7.11.2 Surrogate ICV Stock Standards, 200 µg/mL

Commercial standards are obtained containing decachlorobiphenyl (DCBP) and tetrachloro-m-xylene (TCMX).

7.11.2.1 Instrument blank standard: CCB and/or ICB, 20 ug/L DCB and TCMX

The CCB/ICB standard is prepared by diluting 10uL of the stock surrogate standard and 1mL of the working internal standard solution into a 100mL volumetric flask.

7.11.3 ICV Intermediate Level Standards, 20,000 µg/L

The intermediate level calibration standard for routine pesticide compounds is prepared by diluting the pesticide mix, Hexachlorobenzene, and Hexachlorobutadiene, and surrogate stock standards (Sections 7.11.1 and 7.11.2) with hexane to a final volume of 100 mL as summarized in the table below. All compounds in the intermediate standard are at the same final concentration, i.e. 20.0 µg/mL.

Second-Source ICV Intermediate Standard

Vol of Pesticide Stock (mL)	Vol of HCB/HCBD Stock (mL)	Vol of Surrogate Stock (mL)	Final Volume (mL)	Final Conc (µg/L)
0.100	0.200	1.00	10	20,000

7.11.4 Routine Pesticide ICV Working Level Standard, 50 µg/L

The working level ICV standard for the routine pesticide compounds is prepared by diluting the ICV intermediate standard (Section 7.11.2.1) in hexane follows:

250uL of the ICV Intermediate Standard and 100uL of the working internal standard solution are brought to a final volume of 10mL in Hexane.

7.11.5 Toxaphene ICV Stock Standard, 2,000ug/mL

Typically this standard is purchased from Restek (cat#32015).

7.11.6 Toxaphene ICV Intermediate Standard, 100ug/mL

500uL of Toxaphene ICV Stock Standard is brought to a final volume of 10mL in Hexane.

7.11.7 Toxaphene ICV Working Standard, 500 ug/L

50uL of Toxaphene ICV Intermediate Standard and 100uL of the working internal standard solution are brought to a final volume of 10mL in Hexane.

7.11.8 Technical Chlordane ICV Stock Standard, 1000ug/mL

Typically this standard is purchased from Restek (cat#32021)

7.11.9 Technical Chlordane ICV Intermediate Standard, 10ug/mL

100uL of Technical Chlordane ICV Stock is brought to a final volume of 10mL in Hexane.

7.11.10 Technical Chlordane Working Standard, 100 ug/L

100uL of Technical Chlordane ICV Intermediate standard and 100uL of the working internal standard solution are brought to a final volume of 10mL in Hexane.

7.12 Continuing Calibration Verification (CCV) Standards

The level 4 Pesticide working calibration standard (Section 7.10.1), the level 4 Toxaphene working calibration standard (Section 7.10.2), and the level 4 Chlordane working calibration standard (Section 7.10.3) are used as the CCV standards.

7.13 RL Standard

The lowest concentration calibration standard (i.e., Level 1) is used as the RL standard.

7.14 Working Spike Solution, 2,000 µg/L

A second source stock standard is purchased at 1,000 ug/mL in hexane (to avoid degradation of d-BHC). An intermediate stock is prepared by diluting 200 µL of the stock with hexane to a final volume of 10 mL resulting in a final concentration of 20,000 µg/L.

The working spike solution is prepared by diluting 1.0 mL of the intermediate stock standard with acetone to a final volume of 10 mL in a volumetric flask to yield a concentration of 2,000 ug/L, as summarized in the following table:

Working Spiking Solution

Volume of Pesticide Mix Stock (mL)	Conc of Intermediate Pesticide Stock (µg/L)	Final Volume (mL)	Final Working Concentration (µg/L)
1.0	20,000	10.0	2,000

7.14.1 LVI Working Spike Solution, 250 ug/L

The LVI working spike solution is prepared by diluting 1.25 mL of the aforementioned working spike solution prepared at 2,000 ug/L in acetone. This standard level may also be used for MDL, MDLV and LOQV study samples.

7.14.2 LCS Spike Solution

The LCS and LCSDs for batches of aqueous samples is prepared by adding 0.1 mL of the working spike solution to one liter of reagent water for extracts with a 10 mL final volume (or 10 µL for samples with a 1 mL final volume). The LCS for batches of soil samples is prepared by adding 0.1 mL of the working spiking solution to 10 g of Ottawa sand. The LCS for batches of LVI waters is prepared by added 0.1 mL or 0.2 mL of the working LVI spiking solution to 125 mL or 250 mL of reagent water, respectively.

7.14.3 Matrix Spike (MS) Spike Solution

Matrix spikes (MS and MSD) are prepared by adding 0.1 mL of the working spike solution to one liter of an aqueous sample or to a 10-gram soil subsample. For LVI water samples, 0.1 mL or 0.2 mL of the working LVI spiking solution is added to 125 mL or 250 mL of water sample, respectively.

7.15 Toxaphene and Technical Chlordane Spike Solutions

7.15.1 A Toxaphene stock standard solution at a concentration of 2,000 µg/mL is purchased from commercial sources.

7.15.1.1 The working Toxaphene spike solution is prepared in a 10 mL volumetric flask by adding 0.250 mL of the stock solution and diluting to volume with acetone.

7.15.1.1.1. The working Toxaphene LVI spike solution is prepared in a 10 mL volumetric flask by adding 1.25 mL of the working Toxaphene spike solution, as prepared in section 7.15.1.1 above, and diluting to volume with acetone.

7.15.1.2 Aqueous LCSs are prepared by adding 0.1 mL of the Toxaphene spike solution to 1.0 liter of reagent water. Aqueous LVI sample LCSs are prepared by adding 0.1 mL of the working Toxaphene LVI spike solution to 125 mL of reagent water, or 0.2 mL of the working Toxaphene LVI spike solution to 250 mL of reagent water. Soil LCSs are prepared by adding 0.1 mL of the Toxaphene spike solution to 10 grams of Ottawa sand.

7.15.1.3 Aqueous MS/MSDs are prepared by adding 0.1 mL of the Toxaphene spike solution to 1.0 liter of the selected aqueous sample. Aqueous MS/MSDs for LVI samples are prepared by adding 0.1 mL of the working Toxaphene LVI spike solution to 125 mL of the selected sample, or 0.2 mL of the working Toxaphene LVI spike solution to 250 mL of the selected sample.

Soil sample MS/MSDs are prepared by adding 0.5 mL of the Toxaphene spike solution to 10 grams of the selected soil subsample.

7.15.2 A Technical Chlordane stock standard solution at a concentration of 1,000ug/mL is purchased from commercial sources.

7.15.2.1 The working Technical Chlordane spike solution is prepared in a 10mL volumetric flask by adding 100uL of the stock solution and diluting to volume with acetone.

7.15.2.1.1. The working Technical Chlordane LVI spike solution is prepared in a 10 mL volumetric flask by adding 1.25 mL of the working Technical Chlordane spike solution, prepared in section 7.15.2.1 above, and dilution to volume with acetone.

7.15.2.2 Aqueous LCSs are prepared by adding 0.1 mL of the Technical Chlordane spike solution to 1.0 liter of reagent water. Aqueous LVI sample LCSs are prepared by adding 0.1 mL of the working Technical Chlordane LVI spike solution to 125 mL of reagent water, or 0.2 mL of the working Technical Chlordane LVI spike solution to 250 mL of reagent water. Soil LCSs are prepared by adding 0.1 mL of the Technical Chlordane spike solution to 10 grams of Ottawa sand.

7.15.2.3 Aqueous MS/MSDs are prepared by adding 0.1 mL of the Technical Chlordane spike solution to 1.0 liter of the selected aqueous sample. Aqueous LVI sample MS/MSDs are prepared by adding 0.1 mL of the working Technical Chlordane LVI spike solution to 125 mL of the selected sample, or 0.2 mL of the working Technical Chlordane LVI spike solution to 250 mL of the selected sample. Soil sample MS/MSDs are prepared by adding 0.5 mL of the Technical Chlordane spike solution to 10 grams of the selected soil subsample.

7.16 Surrogate Spike Solution, 2,000 µg/L

7.16.1 The surrogate stock solution, containing 200 µg/mL each of decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX), is purchased from commercial sources.

7.16.2 The working surrogate spike solution is prepared in a 100 mL volumetric flask by adding 1.0 mL of the stock solution and diluting to volume with acetone. This produces a 10,000 µg/L solution.

7.16.2.1 The working LVI surrogate spike solution is prepared in a 10 mL volumetric flask by adding 1.25 mL of the working surrogate spike solution, prepared in section 7.16.2 above, and diluting to volume with acetone. This produces a 1,250 ug/L solution.

7.16.3 For aqueous sample batches, 0.1 mL of the surrogate spike solution is added to each one-liter sample and QC sample. For aqueous LVI sample batches, 0.1 mL or 0.2 mL of the working LVI surrogate spike solution is added to each 125 mL or 250 mL sample, respectively. For soil sample batches, 0.1 mL of the surrogate spike solution is added to each 10-gram soil subsample and QC sample.

7.17 Column Degradation Mix (Performance Evaluation Mixture, PEM)

7.17.1 The DDT/Endrin breakdown stock standard solution is obtained from commercial sources, with 4,4'-DDT at 200 µg/mL and Endrin at a concentration of 100 µg/mL in MTBE.

7.17.2 The working PEM solution is prepared in a 100 mL volumetric flask by diluting 0.100 mL of the stock solution in hexane, as summarized in the following table:

Column Degradation Mix (PEM) Spike Solution

Compound	Volume of Stock (mL)	Final Volume (mL)	Final Concentration (µg/L)
Endrin	0.100	100	50
4,4'-DDT			100

7.18 Primer Mix

The concentration of the column primer mix is not critical. It generally consists of a mixture of CCV, old ICAL standards, and /or old soil LCS extracts. The primer mix is used to initialize the column and does not affect calibration or quantitation.

7.19 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned, amber glass bottles fitted with a Teflon-lined cap. To achieve routine reporting limits, a full one liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Soil samples are collected in 8-ounce, pre-cleaned, wide-mouth jars with a Teflon-lined lid.

8.3 Samples are stored at 0-6°C.

8.4 Extracts are refrigerated at 0-6°C.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	1 Liter 125 mL or 250 mL	Cool 0-6°C	7 Days	40 Days from extraction	40 CFR Part 136.3
Soils	Glass	30 grams	Cool 0-6°C	14 Days	40 Days from extraction	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Seattle SOP TA-QA-0620, Quality Control Program.

9.1.2 Project-specific requirements can override the requirements presented in this

section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See QC SOP TA-QA-0620 for further details.

CCB Instrument blank with surrogate added. Needs to be run after a CCV unless a MB is run first. If the CCB is run it needs to be evaluated with results less than the RL for the target list and passing surrogate criteria and uploaded to TALS.

9.3 Internal Standard (IS)

The 1-Bromo-2-nitrobenzene is added to all samples at an on-column concentration of 100 ug/L. Typically, 10 uL of the standard is added to a 1 mL sample extract aliquot.

Acceptance Criteria: The IS must recover within 50-200% of its true value. In addition, the retention time of the IS in each sample fall within +/- 0.50 minutes when compared to the IS in the CCVIS standard.

Corrective Action: If the recovery of the IS falls outside of the recovery limits, the sample chromatograms should be evaluated for sample matrix interference. If the recovery fails high, then the affected samples need to be re-analyzed at a dilution until the IS recovery falls within acceptance limits. If the recovery fails low and the sample is non-detect for all target analytes, then the analyst may narrate the deficiency in an NCM and report the data. If the retention time shifts outside of the acceptance limit, then re-analyze the extract for confirmation of the shift. Evaluate the sample chromatogram and determine if the sample should be re-analyzed at a dilution. If re-analysis confirms the retention time shift, narrate the deficiency in an NCM and report the data.

9.4 Method Blank (MB)

At least one method blank must be processed with each preparation batch. The method blank for batches of aqueous samples consists of 1.0 liter of reagent water, and for batches of soil samples, consists of 10 grams of Ottawa sand, both of which are free of any of the analyte(s) of interest. The method blank is processed and analyzed just as if it

were a field sample.

Acceptance Criteria: The result for the method blank must be less than the reporting limit for the analyte(s) of interest or less than 10% of the analyte concentration found in the associated samples, whichever is higher. Note that some programs (e.g., *DOD,* BP LaMP, Navy and USACE) require that the maximum blank concentration must be less than one-half of the reporting limit or less than 10% of the sample concentration.

Corrective Action: If target analytes in the blank exceed the acceptance limits, the source of the contamination must be investigated. All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If the analyte was not detected in the samples, then the data may be reported with qualifiers (check project requirements to be sure this is allowed**)** and it must be addressed in the project narrative.

9.5 Laboratory Control Sample (LCS)

At least one LCS must be processed with each preparation batch. For aqueous sample batches, the LCS consists of reagent water to which the analyte(s) of interest are added at a known concentration. For soil sample batches, the LCS consists of reagent sand to which the analyte(s) of interest are added at a known concentration. See Section 7.14 for the preparation of LCSs. The LCS is carried through the entire analytical procedure just as if it were a sample. In the case where insufficient volume is provided for the extraction of an MS/MSD, an LCSD will also be prepared.

Acceptance Criteria: The recovery results for the LCS must fall within the established control limits. Control limits are set at ± 3 standard deviations around the historical mean. Where required, project-specific limits may be used in place of historical limits. Current control limits are maintained in the LIMS.

When there are more than 11 analytes in the LCS, then NELAC allows a specified number of results to fall beyond the LCS control limit (3 standard deviations), but within the marginal exceedance (ME) limits, which are set at ± 4 standard deviations around the mean of historical data. The number of marginal exceedances is based on the number of analytes in the LCS, as shown in the following table:

# of Analytes in LCS	# of Allowed MEs
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

If more analytes exceed the LCS control limits than is allowed, or

if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be random. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem. The source of the error must be identified and corrective action taken. See SOP QA-0600 for additional information on control charting marginal exceedances.

Corrective Action: If LCS recoveries are outside of the established control limits, the system is out of control and corrective action must occur. If recoveries are above the upper control limit and the analyte(s) of interest is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Refer to Section 7.12.2 for preparation of matrix spikes. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

Acceptance Criteria: The recovery results for the MS and MSD must fall within the established control limits, which are set at ± 3 standard deviations around the historical mean. The relative percent difference (RPD) between the MS and MSD must be less than the established RPD limit, which is set at 3 standard deviations above the historical mean. Current control limits are maintained in the LIMS.

Corrective Action: If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of analytical problems, and qualified results may be reported. The situation must be described in an NCM and in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

9.7 Surrogate Spikes

Every field sample, QC sample (i.e., method blank, LCS, LCSD, MS, and MSD), and instrument blanks is spiked with DCB and TCMX surrogate compounds. Refer to Section 7.16 for preparation of the surrogate spike solution.

Acceptance Criteria: The recovery of each surrogate must fall within established statistical limits, which are set at ± 3 standard deviations around the historical mean.

Corrective Action: If surrogate recoveries in the method blank are outside the established limits, verify calculations, standard solutions, and acceptable instrument performance. High surrogate recoveries in the blank might be acceptable if the surrogate recoveries for the field samples and other QC samples in the batch are acceptable. Low surrogate recoveries in the blank require re-preparation and reanalysis of the associated samples, unless sample surrogate recoveries are acceptable and targeted compounds are not detected.

If surrogate recoveries fail, verify calculations, standard solutions, and acceptable instrument performance. High recoveries may be due to a co-eluting matrix interference, which can be confirmed by examining the sample chromatogram. Low recoveries may be due to adsorption by the sample matrix (i.e., clay particles, peat/ organic material in the sample or wet samples). Recalculate the data and/or reanalyze the extract if the checks reveal a problem.

If matrix interference is not obvious from the initial analysis, it is necessary to re-prepare / reanalyze a sample only once to demonstrate that poor surrogate recovery is due to a matrix effect, as long as it can be shown that the analytical system was in control.

NOTE: For LAMP samples, if the surrogate percent recovery fails, the recovery must be confirmed by re-extraction and reanalysis with the following exceptions:

- The lab has unequivocally demonstrated a sample matrix effect and informed the LAMP representative.
- The recovery exceeds the upper control limits and all target analytes in the sample are non-detect.

9.8 Instrument QC is evaluated in section 10 of this SOP.

9.9 Any extra QA that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Calibration and Standardization

10.1 TestAmerica Seattle gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

10.1.1 Use the ChemStation chromatography data system to set up GC conditions for calibration. See Table 2 for typical operating conditions. Actual instrument operating conditions are posted in each maintenance logbook.

10.1.2 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.1.3 After processing the calibration data, link the associated initial calibration verification to the first set of samples run after the calibration, and submit the calibration report to a qualified peer or the group leader for final review.

10.2 Column Degradation Evaluation (Performance Evaluation Mixture, PEM)

10.2.1 Each day of operation, before any calibration or calibration verification standards are analyzed, the column degradation evaluation mix (PEM) must be analyzed. In addition, some programs require injection of the degradation evaluation mix more frequently. The degradation check must be performed whether or not DDT, Endrin, or degradation compounds are designated as target analytes. The purpose of the evaluation is to determine whether instrument/column maintenance is needed. The preparation of this standard is described in Section 7.17.

10.2.2 The results of the analysis of the PEM standard solution are used to calculate column degradation in terms of DDT percent breakdown (%B) and Endrin %B as follows:

$$\text{DDT } \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100\% \qquad \text{Equation 1}$$

Where A_{DDD}, A_{DDE}, and A_{DDT} are the peak responses for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT, respectively, in the EVAL B chromatogram.

$$\text{Endrin } \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100\% \qquad \text{Equation 2}$$

Where A_{EK}, A_{EA}, and A_{E} are the peak responses for endrin ketone, endrin aldehyde, and endrin, respectively, in the PEM chromatogram.

10.2.3 Acceptance Criteria

The %Breakdown for each of these two compounds, DDT and endrin, must be less than 15%.

10.2.4 Corrective Action

If the breakdown of DDT and/or endrin exceeds the 15% limit, corrective action must be taken. This action may include any or all of the following:

- Replacing the injection port liner
- Replacing the septa.
- Cutting off a portion of the injection end of the column or guard column.
- Replacing the GC column or guard column
- Replacing the y-splitter
- Replace inlet seal

After taking the appropriate corrective action, the degradation evaluation standard must be reanalyzed and must pass acceptance criteria before conducting any calibration events.

10.3 The laboratory uses seven calibration levels (as shown in Table 3) for the single-component pesticides. The lowest point on the calibration curve is at or below the reporting limit (RL). The highest standard defines the highest sample extract concentration that may be reported without dilution. The preparation of the calibration standards is described in Section 7.910.

10.4 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours and within 12 hours of the PEM breakdown check standard.

10.5 Calibration for the multi-peak component analytes, Toxaphene and Technical Chlordane, begins with a single-point calibration. If any multi-peak components are found to be present in the samples, a calibration for the multi-component analyte(s) is conducted with a minimum of five calibration levels. The samples are then reanalyzed using the full calibration curve that brackets the quantitation range.

NOTE: Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems found must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious mis-injection explained in the run log), then one point might be rejected, but only if all of the following conditions are met:

- The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and
- The lowest remaining calibration point is still at or below the project reporting limit; and
- The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and
- The calibration must still have the minimum number of calibration levels required by the method, i.e., five levels for calibrations modeled with average calibration factors or linear regressions, or six levels for second-order curve fits.

10.6 External Standard Calibration

External standard calibration involves the comparison of instrument responses (e.g., peak area or peak height) from the target compounds in the sample to the responses of the target compounds in the calibration standards. The ratio of the detector response to the amount or concentration of target analyte in the calibration standard is defined as the calibration factor (CF), as follows:

$$CF = \frac{A_S}{C_S} \qquad \text{Equation 3}$$

Where:

A_s = Peak area (or height) of the analyte or surrogate in the calibration standard.

C_s = Concentration of the analyte or surrogate, in ng/mL, in the injected calibration standard.

10.7 Internal Standard Calibration

Internal standard calibration involves the inversely related comparison of the IS response to the associated target analytes. The IS analyte is added to all calibration level standards at a final, on-column concentration of 100 ug/L.

10.8 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors or as calibration curves, using a systematic approach to selecting the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until the calibration acceptance criteria are met.

10.8.1 Linear Calibration Using Average Calibration Factor (CF)

Tabulate the peak area response for each target analyte in each calibration level against the concentration injected. For each analyte in each calibration standard, calculate the calibration factor (CF) as shown in Equation 3 above. The calibration factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

For each target analyte, calculate the average calibration factor as follows:

$$AverageCalibrationFactor = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n} \qquad \text{Equation 4}$$

Where:

CF_i = Calibration factor for the i^{th} calibration level.

n = The number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{CF}} \times 100\% \qquad \text{Equation 5}$$

Where SD is the standard deviation of the average CF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)^2}{n-1}} \qquad \text{Equation 6}$$

10.8.2 Evaluation of the Average Calibration Factor

The calibration relationship can be graphically represented as a line through the origin with a slope equal to the average calibration factor. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered. SW-846 Method 8000B allows evaluation of the grand average RSD across all compounds, but some programs (e.g., AFCEE) require evaluation of each compound individually.

Acceptance Criteria: The RSD must be ≤ 20%.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

10.8.3 Linear Calibration Using Least-Squares Regression

Calibration using least-squares linear regression produces a straight line that does not necessarily pass through the origin. The calibration relationship is constructed by performing a linear regression of the instrument response (peak area or peak height) versus the concentration of the standards. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). A weighted least squares regression may be used if at least three multi-point calibrations have been performed. The weighting used is the reciprocal of the square of the standard deviation. The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = ax + b \qquad \text{Equation 7}$$

Where:

y = Instrument response (peak area or height).

x = Concentration of the target analyte in the calibration standard.

a = Slope of the line.

b = The y-intercept of the line.

For an external standard calibration, the above equation takes the following form:

$$A_s = aC_s + b \qquad \text{Equation 8}$$

To calculate the concentration in an unknown sample extract, the regression equation (Equation 6) is solved for concentration, resulting in the following equation, where C_s is now C_e, the concentration of the target analyte in the unknown sample extract.

$$C_e = \frac{A_e - b}{a} \qquad \text{Equation 9}$$

Where:

A_s = Area of the chromatographic peak for the target analyte in the calibration standard.

A_e = Area of the chromatographic peak for the target analyte in the sample extract.

a = Slope of the line as determined by the least-squares regression.

C_s = Concentration of the target analyte in the calibration standard.

C_e = Concentration of the target analyte in the sample extract.

b = Intercept of the line as determined by the least-squares regression.

10.8.4 Linear Regression Evaluation

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum "Clarification Regarding Use of SW-846 Methods", Attachment 2, Page 9, includes the statement "The Agency further recommends the use of a weighted regression over the use of an unweighted regression."

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than the reporting limit, and preferably less than the MDL.

Also examine the residuals, paying particular attention to the residuals at the low end of the curve. If the intercept or the residuals are large, a second-order regression should be considered.

The linear regression must have a correlation coefficient (r) ≥ 0.990. Some programs (e.g., DoD) require a correlation coefficient ≥ 0.995.

Corrective Action: If the correlation coefficient falls below the acceptance limit, linear regression cannot be used and a second-order regression should be attempted.

10.8.5 Non-Linear Calibration

When the instrument response does not follow a linear model over a sufficiently wide working range, or when the previously described calibration approaches fail acceptance criteria, a non-linear, second-order calibration model may be employed. The second-order calibration uses the following equation:

$$y = ax^2 + bx + c \qquad \text{Equation 10}$$

Where a, b, and c are coefficients determined using a statistical regression technique; y is the instrument response; and x is the concentration of the target analyte in the calibration standard.

Note: It is not acceptable to utilize a quadratic calibration fit for ECD methods. If the instrument does not support a linear calibration, instrument maintenance is required.

See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

10.9 Initial Calibration Verification (ICV), 50 µg/L for most compounds

A mid-level standard that is obtained from a source different from that of the calibration standards (second-source standard) is used to verify the initial calibration (see Section 7.10.4). The ICV standard is analyzed immediately following the initial calibration (ICAL).

Acceptance Criteria: The result for the target analyte(s) in the ICV standard must be within ± 20% of the expected value(s). (ICV 15% LaMP)

Corrective Action: If this is not achieved, the ICV standard, calibration standards, and instrument operating conditions should be checked. Correct any problems and rerun the ICV standard. If the ICV still fails to meet acceptance criteria, then repeat the ICAL.

10.10 Calibration Verification

10.10.1 Continuing Calibration Verification (CCV), 50 µg/L for most compounds

The mid-level calibration standard is analyzed as the continuing calibration verification (CCV) standard (see Section 01). At a minimum, this is analyzed *at the beginning of an analytical sequence* every 12 hours (or 20 sample injections, whichever is more frequent). *If there are more than 20 samples in an analytical sequence, CCVs must be run before the next bracket. Closing CCVs are not required since internal standard is used.*

NOTE: For samples analyzed under the DoD QSM and LaMP, CCVs are analyzed prior to sample analysis, after every ten samples , and at the end of the sequence.

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

NOTE: Samples are defined as field samples and batch QC (MB, LCS, MS) and do not include CCVs, PEMs, CCBs, instrument blanks, etc.

10.10.2 RL Standard

It may also be appropriate to analyze a standard prepared at or below the reporting limit (RL) for the method at the end of the analytical sequence, as a minimum). This standard can be used to rule out false negatives in non-DOD client samples in cases where the %D for one or more of the analytes in a bracketing CCV falls below the lower acceptance limit. The results for the RL standard are not evaluated unless the previous CCV fails acceptance criteria.

10.10.3 Acceptance Criteria for Continuing Calibration Verification (CCV)

10.10.3.1 Detected Analytes (≥ RL)

For any analyte detected at or above the reporting limit (RL) in client samples, the percent difference (%D) for that analyte in the preceding - CCVs, on the column used for quantitation, must be within ± 20%. *Closing CCVs are not required since internal standard is used.*

NOTE: *DoD and LaMP samples require closing CCVs.*

If a failing CCV is followed by a second verifying CCV and the subsequent calibration verification injection also fails, a new initial calibration curve must be processed. (i.e., no more than two consecutive injections of the calibration verification may be processed.

Refer to Section 12 for which result to report.

The %D is calculated as follows:

$$\%D = \frac{\text{Measured Conc} - \text{Theoretical Conc}}{\text{Theoretical Conc}} \times 100$$ Equation 11

10.10.3.2 Analytes Not Detected (< RL)

For any analyte not detected in client samples, the %D for that analyte in the bracketing CCVs should also be within ± 20%.

However, if the CCV %D exceeds 20% and the sample results are ND, it still may be possible to report sample results for non-DOD projects. In this case, the client should be consulted and an NCM written.

For DOD samples, a high biased CCV with non-detects in the samples is only acceptable to report if approval is granted by the client. Otherwise, samples associated with a high failing CCV need to be re-analyzed.

If the CCV %D falls below 20% and sample results are ND, but the target analytes are detected in the RL Standard, it may still be possible to report sample results for non-DOD projects, since the detection of the analyte(s) in the RL Standard indicate that there was sufficient sensitivity to detect the analyte(s) in the samples. In this case, the client should be consulted and an NCM written.

NOTE: If samples are DOD they must be diluted and re-analyzed until capping CCV %D falls within 20%. Only when a sample cannot be re-analyzed is it acceptable to flag/qualify data and request a variance.

10.11 Retention Time Windows

10.11.1 Initial determination of Retention time windows.

10.11.1.1 The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV in the daily analytical sequence, whichever is more recent.

10.11.1.2 Evaluate the deviation from expected retention time for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours.

10.11.1.2.1. If three days of analytical data are not available, use a default RT window of 0.01 minutes. At the end of the batch evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.

10.11.1.3 Calculate the mean and standard deviation of the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RT_i - \overline{RT}\right)^2}{n-1}}$$

Where:

RT_i = Retention time for the i^{th} injection.
n = Number of injections (typically 3).
SD = Standard deviation.

Note: This can be done automatically utilizing the Control Chart feature in TALS.

10.11.1.4 Multiply the maximum deviation by 1.5. This is the retention time window, unless the result is less than 0.01 min, in which case the window is set at 0.01 min . For example, if the maximum RT deviation for a specific analyte is 0.008 min, then the RT window is set at +/- 0.012 min.

10.11.1.4.1. NOTE: For the multi-component analytes, for example Toxaphene and Technical Chlordane,, the maximum deviation must be evaluated for each of the 3 to 5 major peaks used for sample calculations.

10.11.2 Ongoing evaluation of retention time windows

10.11.2.1 Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV of the day. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the retention time window (except as discussed below).

10.11.2.1.1. 10.11.1.1 Matrix spike analytes may fall outside the retention time window if there is a large non-target peak coeluting with the analyte in the matrix spike

10.11.2.2 If any analytes fall outside the retention time window in CCVs, LCS or matrix spikes (except as discussed above for matrix spikes) then the RT windows for those analytes shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

10.11.2.3 Retention time windows should be reliably narrower than +/- 0.03 minutes. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained.

10.11.3 Sample Retention Time Criteria

10.11.3.1 The surrogate should fall within the established RT window. Target analyte peaks should be within the established RT window to be reported as such. If the surrogate RT indicates an RT shift, it may be necessary to evaluate the affected sample with a wider window relative to the surrogate RT shift and report with a NCM about the retention time shift. It may be necessary to run the sample at a dilution to lower any matrix effects causing the RT shift.

11.0 Procedure

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

11.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.3 Sample Preparation

11.3.1 Sample preparation for aqueous samples is described in SOP~~s~~ TA-OP-0301.

11.3.2 Sample preparation for solid samples is described in SOP TA-OP-0302 and TA-OP-0367.

11.3.3 Sample preparation for waste samples is described in SOP TA-OP-0314.

11.3.4 Cleanup of sample extracts are described in SOPs *TA-OP-0353 (Sulfur Cleanup),* TA-OP-0364 (Silica Gel cleanup) and TA-OP-0366 (Florisil cleanup). Lot# of reagent(s) used for cleanup must be noted were applicable in the TALS batch or NCM.

11.3.5 The final extract volume in hexane is 10 mL *or 2.5 mL for LVI waters*.

11.3.6 Use hexane to dilute sample extracts, if necessary.

11.4 Gas Chromatography

Typical chromatographic conditions for this method are presented in Table 2; actual conditions can be found in the instruments maintenance logbook. Use the ChemStation interface to establish instrument operating conditions for the GC. Raw data are processed using the Chrom software. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the software.

11.5 Sample Introduction

All extracts and standards are allowed to warm to room temperature before injection. An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract. Samples, standards, and QC samples must be introduced using the same procedure. Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

11.6 Analytical Sequence

An analytical sequence starts with a PEM standard, followed by a minimum five-level initial calibration (ICAL) or a daily calibration verification. Refer to Table 3 for the calibration levels used.

11.6.1 Prior to analyzing any calibration or calibration verification standards, the column degradation evaluation (PEM) standard is injected and the results are evaluated as described in Section 10.2. The PEM standard must be injected and evaluated every 12 hours in an analytical sequence.

11.6.2 The daily calibration verification includes analysis of the 12-hour calibration sequence and updating the retention time windows (see Section 10.11).

11.6.3 The following is a typical analytical sequence:

- Primer
- Hexane blank
- PEM Std (column degradation evaluation)
- Daily initial CCV(s)

- Method Blank (MB) or Instrument Blank with surrogate (CCB)
- Samples up to 12 hours from the PEM or 20 samples whichever is less.
- PEM (only necessary if running more samples after the following CCVs that will be outside the 12 hour clock from the opening PEM)
- CCV(s) + *CCB (only necessary if running more samples)*
- This can be followed by another bracket of samples and CCVs.

11.6.4 The following is a typical **DoD QSM** or LaMP analytical sequence:

- Primer
- Hexane blank (with surrogates)
- PEM Std (column degradation evaluation)
- Daily initial CCV(s)
- Method Blank (MB) or Instrument Blank with surrogate (CCB)
- 10 injections including samples and QC
- CCV(s)
- Method Blank (MB) or Instrument Blank with surrogate (CCB)
- Followed by cycles of 10 injections (including samples and QC) and CCVs & Blanks as needed totaling less than 12 hours of analysis time from injection of Eval B Std.
- Closing CCV(s)
- Closing CCB

11.7 Daily Retention Time Windows

The centers of the retention time (RT) windows determined in Section 10.11 are adjusted to the RT of each analyte as determined in the 12-hour calibration verification. The centers of the RT windows must be updated at the beginning of each analytical sequence and with each 12-hour calibration, but not for any other calibration verification standards.

11.8 Upon completion of the analytical sequence:

11.8.1 Create a worklist on Chrom that reflects the machine run sequence. The Chrom worklist will serve as the instrument sequence logbook. Add the solvent *used to dilute samples* to the sample *run* reagent tab. This will serve as the record of the solvent lot used to dilute the samples.

11.8.2 Review chromatograms online and determine whether manual data manipulations are necessary.

11.8.3 All manual integrations must be justified and documented. See Corporate SOP CA-Q-S-002 for requirements for manual integration.

11.8.4 Manual integrations are processed using the Chrom software. Before and after chromatograms, reason for the change and the analyst's electronic signature are stored electronically.

11.9 Compile the raw data for all the samples and QC samples in *an analytical* batch.

11.9.1 Perform a level 1 data review, *acknowledge any Data Review Checker (DRC) findings,* and document the review on the data review checklist.

11.9.2 Submit the review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

11.10 Instrument Maintenance & Troubleshooting

11.10.1 Injection Port Maintenance

11.10.1.1 Injection port maintenance is routinely required after injecting and analyzing any number of dirty field samples. The best indicator that an instrument will require maintenance is by processing the closing CCV standard from the previous day's run. Maintenance will be required if Endrin, 4,4'-DDT and Methoxychlor fail the lower %D limits. Other analytes may fail to meet the lower %D limits as well, but these three analytes are the main indicators that maintenance is needed.

11.10.1.2 The injection port liner is changed whenever the system performance deteriorates, (i.e., DDT breakdown exceeds acceptance limits). The inlet seal may also need to be replaced. For more severe cases, the retention gap column is typically clipped by trimming approximately 10 – 20 cm, or up to ½ - 1 full loop of column.

11.10.1.3 Injector septa are changed as needed since the septa particles can cause endrin breakdown to exceed acceptance limits, or whenever baseline instability is present, or a leak is found to exist at the septum.

11.10.2 Column Maintenance

11.10.2.1 If routine injection port maintenance procedures do not bring the system back into control, the Y-splitter is replaced.

11.10.2.1.1. When the retention gap column becomes too short, it may be replaced with the Y-splitter. The analytical columns typically do not need to be replaced if they have not been in service for more than 4 – 6 months.

Note: For newer analysts, a supervisor/manager should be consulted prior to replacing any columns.

11.10.2.2 Columns are replaced every six months or as needed. The following symptoms are indicators that a new column is needed:

- Excessive baseline rise.
- Calibration curves are not linear, or fail shortly after analysis.
- Poor peak shape.
- Poor peak separation.

11.10.3 Column Replacement

11.10.3.1 **Turn off the injector and detector temperature and set the oven to 30°C. Allow the instrument to cool before performing the column change**

11.10.3.2 Remove the old column from the GC oven by loosening the injector and detector nuts with the appropriate wrench.

11.10.3.3 For ease of access and handling of the new columns, it is recommended that the two new analytical column cages, guard column and Y-splitter are assembled outside of the GC oven.

11.10.3.4 Clip approximately 10-15 cm of the column ends that will connect to the Y-splitter. Fill the Y-splitter cavity with clean methanol solvent. Prior to connecting each column end into the Y-splitter, wet the column ends with clean methanol. The methanol solvent helps to create a complete seal between the column ends and the Y-splitter.

Note: Double check your work to ensure that you have the correct column ends connected to the Y-splitter. Ensure that you did not inadvertently connect the injection port end and the detector side end of a column to the Y-splitter connection.

11.10.3.5 After assembling all three columns to the Y-splitter, the injection port end of the new guard column is installed first. Slide the column nut over the guard column end (aka retention gap).

11.10.3.6 Install the appropriate ferrule onto the guard column. The flat end of the ferrule is placed towards the column nut, where the tapered/pointed end points toward the end of the column.

11.10.3.7 Cut 1 to 2 cm from the end of the column. This is done to remove any potential graphite particles that may have entered the column end.

Note: At this point, it is recommended to pre-crush the graphite ferrule in place in order to better hold the column from slipping out during installation. To do so, perform a partial installation of the column end with an old FID adapter fitting (see the area supervisor/manager for assistance with this).

11.10.3.8 Uncoil approximately 20 cm of column and set the column in the cage so that there is enough slack to reach the injection port connection. Weave the column through the column cage in order to prevent any part of the column from touching the walls or the door of the oven. If any part of the columns touch the oven walls or door, this will create an active site on your column and the chromatography will not be ideal (i.e. excessive peak tailing will be present).

11.10.3.9 Check that the column end is approximately 3-4 mm past the graphite ferrule end and install the column into the injection port connection.

11.10.3.10 Tighten the column nut 1/4 to 1/2 turn or until column cannot be pulled out of the column nut.

11.10.3.11 Turn on the carrier gas flow. The gas flows are set to manufacturer or method recommended levels and are checked prior to each initial calibration:

11.10.3.12 Column flow: Approximately 2.5 – 3.0 mL/min (The resulting linear velocity should be approximately 70-75 cm/sec)

11.10.3.13 Make-up gas at the detector (Nitrogen): Column flow + X mL/min. = to 30 mL/min. Conditions may very between instruments.

11.10.3.14 At this point, check to see that the previous work has been installed correctly. To do so, take the detector-side column ends of each column and individually insert the column ends into a vial of methanol or hexane solvent. If the injection port and Y-splitter connections were done successfully, you will observe a stream of air bubbles form in the

solvent from the column ends.

Note: The stream of gas bubbles should be consistent with one another. If not, then the Y-splitter connections will need to be remade by replacing the Y-splitter and re-clipping approximately one inch of the columns ends that attach to the Y-splitter.

11.10.3.15 Prior to installing the columns to the detectors, utilize a long piece of extra column that was clipped from any column end to verify the type of ECD mixing liner that is currently installed in each detector. There are two types of mixing liners that could be installed: A) Siltek-treated straight mixing liner, or B) clear indented mixing liner. If mixing liner B is installed, the excess piece of column will stop moving up the detector after approximately 45-50 mm. If mixing liner A is installed, the column end will continue moving up the ECD well past the 45-50 mm length.

11.10.3.16 Clip approximately 10-15 cm off of the detector side columns. Install a column nut and graphite ferrule and clip approximately 1-2 cm of column to remove any potential graphite particles that may have entered the column end.

11.10.3.17 If mixing liner A is installed, utilize the Restek measuring tool (Cat. No. 21034) to measure and pre-crush the graphite ferrule so that the column end is approximately 49 mm. If mixing liner B is installed, simply install the column nut (without pre-crushing the graphite ferrule) by finger-tightening the nut loosely enough so that the column still has free range of movement. Carefully insert the column end into the mixing liner until it stops on its own (i.e. the column end will stop at the indented area of the mixing liner).

11.10.3.18 After both the column ends have been installed into both detectors, close the GC oven door and allow the system to sit for a minute or two. This allows the ECDs time to acclimate to the new setup by flushing out any air/moisture that may have accumulated in the system during the installation procedures.

11.10.3.19 Condition the column by heating the oven at its maximum operating temperature for approximately two hours, or until the detector signal drops to its normal operating level. Typically the column is conditioned at 320°C overnight for best results. After the column is conditioned, the oven temperature is set at standby. At this point, the instrument is ready to be calibrated.

11.10.4 ECD Maintenance

11.10.4.1 Thermal Baking of the ECD

11.10.4.1.1. If necessary, the detector is plugged with a column plug nut and heated to 400°C for at least one hour. The detector must be stabilized at to normal operating temperature (320°C) prior to analysis of any standards.

Note: It may take anywhere between 1 hour to overnight baking to stabilize the ECD signal.

11.10.4.1.2. The ECD signal may become unstable after analyzing samples with heavy matrix interferences and/or samples with

high concentrations of target/non-target analytes. In this case, while performing the routine injection port maintenance, thermal baking of the ECD(s) may be done simultaneously.

11.10.4.2 The detector is wipe tested and the wipes are sent in to TestAmerica Richland periodically for leak checks in accordance with SOP TA-QA-0409. If the detector is causing excessive baseline noise, is no longer providing a linear response, or will not produce a linear calibration curve, the detector should be sent in for repair. NOTE: ECDs contain radioactive Ni63, and should **never** be opened or maintained by untrained personnel.

11.10.5 Autosampler Maintenance

11.10.5.1 Fill the rinse reservoir daily, or more often if needed. Use the appropriate solvent for the analysis.

11.10.5.2 Check the injector syringe weekly:

11.10.5.3 Check for smooth plunger movement

11.10.5.4 Ensure that the needle tip is not bent, as this will cause septum pieces to be introduced into the injection port, and result in endrin breakdown.

11.10.6 Spare Parts

11.10.6.1 Septa, Restek Merlin Microseal

11.10.6.2 Injection Port Liners

11.10.6.3 Column nut

11.10.6.4 Ferrules: 1/4 in. graphite/vespel, 0.4 mm. ID graphite

11.10.6.5 Syringes, Hamilton 701 or equivalent

11.10.6.6 Solvent and waste vials and septa

11.10.6.7 Y-Splitter

11.10.6.8 Inlet Seal

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., GC, autosampler, columns) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone non-routine maintenance or repairs, the system is evaluated using a tune, CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL or MB, etc as may be the case).

If columns were replaced during maintenance procedures the specific make, model and serial numbers of the columns installed need to be entered in the instruments maintenance logbook.

12.0 Calculations / Data Reduction

12.1 Qualitative Identification

12.1.1 Tentative identification of an analyte occurs when a peak is found on the primary column within the RT window for that analyte, at a concentration above the

reporting limit, or above the MDL if qualified data (J flags) are to be reported. Identification is confirmed if a peak is also present in the RT window for that analyte on the second (confirmatory) column and if the analyte concentration is greater than the MDL. When confirmation is made using a second column, the analysis on the second column must meet all of the QC criteria for continuing calibration verification and RTs.

12.1.2 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2 Dual-Column Quantitation and Reporting

12.2.1 Each sample is analyzed on two different columns at the same time.

12.2.2 For DoD reporting, the laboratory designates a primary column based on optimal separation of the compounds of interest and other desirable chromatographic characteristics. The result from the primary column is normally reported. The result from the secondary (confirmatory) column is reported if any of the following is true:

- There is obvious chromatographic interference on the primary column.
- The difference between the result for the primary column and the result for the secondary column is > 40% and chromatographic interference is evident.
- The continuing calibration verification, bracketing standard, or surrogate recovery fails on the primary column, but is acceptable on the secondary column. However, if the difference between the primary column result and the secondary column result is > 40% and the primary column calibration fails, then the sample must be evaluated for reanalysis.
- For BP Lamp projects the lower of the two results is reported provided all QC criteria are satisfied.

12.2.3 When the RPD between the primary and secondary column is >40%, the lower of the two results is reported unless there is obvious interference documented on the chromatogram. See SOP CA-Q-QM-006.

12.2.3.1 If there is visible positive or negative interference, e.g., failing internal standard, co-eluting peaks, elevated baseline, etc., for one column and not the other, then report the results from the column without the interference with the appropriate data qualifier flag, footnote, and/or narrative comment in the final report.

12.2.3.2 The RPD between two results is calculated using the following equation:

$$\%RPD = \frac{\left|R_1 - R_2\right|}{\frac{1}{2}\left(R_1 + R_2\right)} \times 100\% \qquad \text{Equation 14}$$

Where R_1 is the result for the first column and R_2 is the result for the second column.

12.3 Multi-Component Analytes (Toxaphene and Technical Chlordane)

12.3.1 Qualitative Identification

Retention time windows are also used for identification of multi-component analytes, but the “fingerprint” produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3.2 Quantitation of Toxaphene

12.3.2.1 While Toxaphene contains a large number of compounds that produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. The unresolved complex mixture results in a "hump" in the chromatogram that is characteristic of the Toxaphene mixture of compounds. The resolved peaks are important for the identification of the mixture, and the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

12.3.2.2 To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the RTs of the first and last eluting Toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration of Toxaphene may be significantly underestimated.

Conversely, if a sample contains significant concentrations of certain other organochlorine pesticides that elute with the RT of Toxaphene, the sample concentration of Toxaphene may be significantly overestimated. When this occurs, the sample should be quantitated using the procedure described in 12.3.2.3 or an NCM should be initiated that describes the coeluting-interferences and their impact on the Toxaphene result.

12.3.2.3 Toxaphene may also be quantitated on the basis of 3 to 5 major peaks. Using a subset of 3 to 5 peaks for quantitation provides results that agree well with the total peak approach and may avoid difficulties when interferences with Toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT.

12.3.2.4 When Toxaphene is determined using the 3 to 5 peaks approach, care must be taken to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms.

12.3.2.5 The chosen peaks must be within the established retention time. If there is an interference that affects the accuracy of results, the analyst may use as few as 3 major peaks. The same peaks that are used for sample quantitation must be used for calibration.

12.3.2.6 The heights or areas of the chosen peaks should be summed together to determine the Toxaphene concentration.

12.3.2.7 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the

multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: USACE projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

12.3.3 Quantitation of Technical Chlordane

12.3.3.1 Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. Trans-Chlordane (or α-Chlordane) and cis-Chlordane (or γ-Chlordane) are the two most prevalent major components of Technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

12.3.3.2 When the GC pattern of the sample resembles that of Technical Chlordane, Chlordane may be quantitated by comparing the total area of the Chlordane chromatogram using 3 to 5 major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area.

NOTE: Octachlor epoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.

12.3.3.3 The presence of alpha and gamma chlordane in a sample in approximately the correct proportion is sufficient evidence to call the sample positive for the presence of technical chlordane. In this case, only 2 peaks may be available to quantify the result. See SOP CA-Q-QM-003. The following is an example of a NCM narrative for the issue.

Example NCM: The following sample(s) has clear evidence of the presence of chlordane based on the presence of alpha and gamma chlordane; however, the chlordane peaks in the sample do not closely match the laboratory's Technical Chlordane standard. As a result, there is increased quantitative uncertainty associated with this result.

12.3.3.4 To measure the total area of the Chlordane chromatogram, construct the baseline of Technical Chlordane in each calibration chromatogram between the RTs of the first and last eluting Technical Chlordane components. Use this area and the mass or concentration of Technical Chlordane in each calibration standard to establish the calibration function (Section 10.7). Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration function to calculate the concentration in the sample extract.

12.3.3.5 When the GC pattern of Chlordane in a sample differs considerably from that of the Technical Chlordane standard, it may not be practical to relate a sample chromatogram back to the Technical Chlordane standard chromatogram. In these cases, all identifiable Chlordane components may be summed and reported as "Chlordane (not otherwise specified, CAS number 57-74-9)."

12.3.3.6 A third option for quantitating Technical Chlordane is to quantitate the peaks for α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers.

12.3.3.7 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: USACE projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

12.4 Surrogate recovery results are calculated and reported for DCB. TCMX may also be added, however if the two surrogate compounds are analyzed, and recoveries are calculated, and either surrogate fails to meet control limits, corrective actions are required (this also applies to programs that require the use of only one surrogate). (LaMP: if surrogates fail acceptance criteria they must be re-extracted unless the samples are high ND or demonstrate matrix interference and client is notified. See Section 9.6)

12.5 Calibration Range and Sample Dilutions

12.5.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for the analyte(s) that were found to be over the calibration range in the high sample, they must be reanalyzed to rule out carryover. It may also be necessary to dilute samples because of matrix interferences.

12.5.2 If the initial diluted run has no hits or hits below 20% if the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.5.3 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

12.5.4 Reporting Dilutions

Some programs (e.g., South Carolina and AFCEE) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported.

12.6 Interferences Observed in Samples

12.6.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can

produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

12.6.2 Aroclor Interference Check Standards for EPA Region 10

If the samples being analyzed are for EPA Region 10 and the laboratory has agreed to perform this option, Aroclor interference check standards must be analyzed following the initial calibration to assure that a PCB congener was not mistaken for the pesticide in question or that a pesticide may be present but was not reported as non-detected.

12.6.3 GC/MS Confirmation of Samples for EPA Region 10

If the samples being analyzed are for EPA Region 10 and the laboratory has agreed to perform this option, then all analyte identifications of positive concentrations that are of sufficient concentration for that purpose must be confirmed by GC/MS analysis. For multi-component analytes, the confirmation is for the presence of chlorinated biphenyls in PCB and the presence of chlorinated camphenes in Toxaphene. See Appendix 1 for detailed instructions for performing GC/MS confirmation for EPA Region 10 work.

12.6.4 Suspected Negative Interferences

If peak detection is prevented by interferences, further cleanup should be attempted (see SOP TA-OP-0353). Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.6.5 Suspected Positive Interferences

If no further cleanup is reasonable and interferences are evident that are suspected of causing false positive results, consult with the laboratory Project Manager to determine if analysis using additional confirmation techniques is appropriate for the project. Use of additional confirmation columns is another possible option. At a minimum, the Data Review Template prepared by the analyst should include the following comment for inclusion in the case narrative:

" Based on review of the chromatograms for samples _____, it is my opinion that the evident interferences may be causing false results.

Date _____ Analyst _____"

12.7 Calculations

12.7.1 LCS and Surrogate Spike Recovery Calculation

LCS and surrogate spike recoveries are calculated using the following equation:

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100\% \qquad \text{Equation 15}$$

12.7.2 MS and MSD Recovery Calculation

Matrix spike recoveries are calculated as follows:

$$\text{MS or MSD}\ \%\text{Recovery} = \left(\frac{SSR - SR}{SA}\right) \times 100\% \qquad \text{Equation 16}$$

Where:

SSR = Measured concentration in spiked sample.

SR = Measured concentration in unspiked sample.

SA = Concentration of spike added to sample.

12.7.3 MS/MSD RPD Calculation

The relative percent difference between the MS and MSD is calculated as follows:

$$\%RPD = \frac{\left|R_1 - R_2\right|}{\frac{1}{2}\left(R_1 + R_2\right)} \times 100\% \qquad \text{Equation 17}$$

Where R1 is the result for the MS and R2 is the result for the MSD.

12.7.4 Concentration of Analyte in the Sample Extract

Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10.7 for details on establishing the calibration function):

Average Calibration Factor: $C_e = \frac{A_s}{CF}$ Equation 18

Linear Regression: $C_e = \frac{\left[A_s - b\right]}{a}$ Equation 19

Non-Linear Regression: $C_e = f\left(A_s\right)$ Equation 20

Where:

C_e = Concentration of the analyte in the sample extract (ng/mL).

A_s = Peak area for the analyte in the sample extract injection.

B = y-intercept of the calibration fit.

A = Slope of the calibration fit.

$f(A_s)$ = Mathematical function established by the non-linear regression.

12.7.5 Concentration of Analyte in Original Sample

$$C_{sample} = \frac{C_e}{1000\ \frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF$$ Equation 21

Where:

C_{sample} = Concentration of analyte in original sample (µg/L or µg/kg).

C_e = Concentration of analyte in sample extract injected in GC (ng/mL).

$1000\ \frac{ng}{\mu g}$ = Factor to convert ng/mL to µg/mL.

V_e = Volume of sample extract (mL).

V_s = Volume (or weight) of original sample (L or kg).

DF = Dilution Factor (post extraction dilutions)

12.8 All data are subject to two levels of review, which is documented on a checklist, as described in SOP TA-QA-0635.

13.0 Method Performance

13.1 Initial Demonstration of Capability

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

13.2 Method Detection Limit (MDL)
The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

13.2.1 Instrumentation software must have each target limit set to the lowest MDL. CHROM (LOD)

13.3 Analyst Training and Qualification

See SOP TA-QA-0608 for detailed training requirements.

14.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.0 Waste Management

15.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

15.2 The following waste streams are produced when this method is carried out:

15.2.1 Expired Chemicals/Reagents/Standards – are discarded into satellite waste buckets labeled "Hazardous Waste" located underneath the bench top. Once the buckets are full, they are bulked into the vial waste barrel located in the waste room and sent out for incineration.

15.2.2 Vialed extract waste. Sample extracts that have been placed into autosampler vials for analysis are discarded into satellite waste buckets labeled "Hazardous Waste" located underneath the bench top. Once the buckets are full, the vials are bulked into the vial waste barrel located in the waste room and sent out for incineration.

15.2.3 Solvent waste. Any waste solvent is collected in beakers and then poured into the $MeCl_2$ /solvent satellite waste barrel located next to the neutralization tank in lab hood #17. The funnel lid on the drum must be closed after each use. At or before the satellite waste reaches 55 gallons, the barrel is transferred to the waste disposal room from where it is sent out for recycling or fuel blending.

16.0 References

16.1 Method 8081A, Organochlorine Pesticides by Gas Chromatography, Revision 1, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.2 Method 8081B, Organochlorine Pesticides by Gas Chromatography, Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, February 2007

16.3 Method 8000B, Determinative Chromatographic Separations, Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

17.0 Method Modifications:

Item	Method xx	Modification
1	8081A	Section 7.4.1.1, allows the use of a single-point calibration for the multi-component pesticides. In this SOP an initial single-point calibration is used, but a five-point calibration followed by reanalysis of associated samples is required when one of the multi-component pesticides is detected.
2	8081A	Method 8081A references 8000B, which allows the use of third-order calibration curves. TestAmerica Seattle does not allow third-order curves.

18.0 Tables

Table 1: Analyte List and Standard Reporting Limits
Table 2: Typical Instrument Conditions
Table 3: Calibration Levels ((μg/mL)
Table 4: Column Degradation Evaluation Mix
Table 5: LCS/Matrix Spike and Surrogate Spike Levels
Table 6: Summary of QC Requirements

Attachment 1: Example Retention Time Study Spreadsheet
Attachment 2: Example Pesticide Breakdown Custom Report
Attachment 3: DoD QC Tables

Appendix 1: GCMS Confirmation of Pesticides and PCBs for EPA Region 10

19.0 Revision History

- Revision 25, dated 30 June 2017
    - Updated scope of application, section 1.4
    - Edited summary of test method, section 2.1.1, 2.1.3, and 2.2.2
    - Updated procedure, sections 9.3 and 9.4
    - Edited sections 10.10.1, 10.10.3, 11.3.4, 11.3.5, 11.6.3, 11.8.1, and 11.9
    - Updated Table 6
    - Updated approvers

- Revision 24, dated 26 July 2016
    - Added reference to sulfur cleanup SOP, section 4.3
    - Added reference to florisil cleanup SOP, section 4.4
    - Added the option of screw tops for auto sampler vials, section 6.3
    - Updated calibration stock standards information, section 7.7
    - Updated calibration intermediate standards information, section 7.8
    - Changed terminology of PIBLK to CCB throughout
    - Change %D to % Breakdown, section 10.2.3
    - Added septa replacement to section 10.2.4
    - Updated section 10.10.1 for clarification
    - Updated criteria for bracketing CCVs using internal standard, section 10.10.3.2
    - Added retention time criteria, section 10.11
    - Updated sequence, sections 11.6.3 and 11.6.4
    - Updated procedures in section 11.8
    - Updated maintenance procedures, section 11.10
    - Updated section 11.6.3 on quantitation and reporting
    - Added additional guidance on reporting technical chlordane, section 12.3.3.3
    - Updated Table 2
    - Updated Attachment 2

- Revision 23, dated 06 March 2015
    - Removed the 3520 preparation procedure SOP reference in section 1.3
    - Added/updated LVI water preparation SOP and Microwave extraction SOP references in section 2.1
    - Added use of internal standard calibration in section 2.2.2
    - Added a note about copper cleanup in section 4.3
    - Added/updated guard column and analytical columns information in section 6.2

- Added Software, section 6.5
- Added IS stock standard information in section 7.7
- Added IS standard preparation instructions in section 7.9
- Updated ICAL levels information in sections 7.10.1 and 7.10.2
- Added Extended list pesticides calibration standards information in sections 7.10.4, 7.10.5 and 7.10.6
- Added CCB standard preparation information in section 7.11.2.1
- Updated ICV standard preparation information in sections 7.11.4, 7.11.7 and 7.11.10
- Updated LVI spiking and surrogate solutions preparation information in section 7.14.1, 7.14.2, 7.14.3, 7.15 and 7.16
- Added IS criteria and corrective action information in section 9.3
- Added IS calibration information in section 10.7
- Updated opening CCV criteria in section 10.10.3
- Removed non-linear calibration evaluation information in section 10.8.6
- Removed 3520 preparation reference in section 11.3.1
- Added 3546 preparation reference in section 11.3.2
- Added CCB/MB to example run sequences in sections 11.6.5 and 11.6.6
- Updated column installation procedures throughout section 11.10.3 (and subsections)

- Revision 22, dated 12 August 2013
  - Added LVI sample size to section 2.1.1
  - Added LVI final volume and delete GPC use in section 2.1.3
  - Added more detail to sulfur interference in section 4.3
  - Delete GPC clean up option in section 4.4
  - Updated CCV level standard in section 7.11
  - Added LVI spiking standards information in sections 7.13.1, 7.14.1.1.1 ,7.14.1.2, 7.14.1.3, 7.14.2.1.1, 7.14.2.2, 7.14.2.3, 7.15.2.1 and 7.15.3
  - Updated note sections for DoD requirements in sections 10.9.3.1 and 10.9.3.2
  - Add more detailed information for troubleshooting instrument maintenance procedures throughout sections 11.10.1, 11.10.2 and 11.10.4

- Revision 21, dated 6 July 2012
  - Updated cleanup procedures, sections 2.1.3, 4.3, 4.4 and 11.3.4
  - Updated reporting procedures, section 12.2.
  - Updated waste streams, section 15.2

- Revision 20, dated 31 May 2011
  - Incorporated ROMDs 00019 and 00026 in sections 6.2 and 11.10
  - Added toxaphene and technical chlordane ICV standards in sections 7.10.5 – 7.10.10.
  - Added technical chlordane LCS spike solutions in section 7.14.2
  - Incorporated ROMD 00025 in section 9.4
  - Incorporated ROMD 00020 in sections 10.1.1 and 11.4
  - Incorporated ROMD 00022 in section 10.7.6.
  - Incorporated ROMD 00024 in section 10.9.3.2.
  - Incorporated ROMD 00033 in section 11.6.3.
  - Added information about coeluting interferences impact on Toxaphene quantitiation Section 12.3.2.2
  - Changed water RL for technical chlordane in Table 1 from 0.01 to 0.1 ug/L.

- Added an additional calibration level standard to Table 3.

- Revision 19, dated 26 March 2010
  - Added recording of lot numbers for reagents used in clean-up Section 4.2
  - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
  - Added removal of expired standards Section 7.19.
  - Added requirements for PIBLK Instrument blank Section 9.2
  - Addressed corrective action after a second CCV failure, Section 10.9.3
  - Added maintenance documentation and return to service requirements, end of section 11
  - Removed Table 7 (Evaluation & Corrective Actions for CCVs)

- Revision 18, dated 12 August 2009
  - Added Table 6: Summary of QC Requirements.
  - Updated DoD QC Tables in Attachment 3.
- Revision 17, dated 03 March 2009
  - Correct standards information in Sections 7.4 through 7.16.
  - Added Appendix 1. GC/MS Confirmation of Pesticides and PCBs for EPA Region 10
- Revision 16, dated 12 March 2008
  - Integration for TestAmerica and STL operations.
  - This revision is a complete rewrite and an expansion of scope.

Table 1

Analyte List and Standard Reporting Limits

Compound	Water Reporting Limit (µg/L)	Soil Reporting Limit (µg/kg)
Aldrin	0.01	1.0
α-BHC	0.01	1.0
β-BHC	0.02	1.0
δ-BHC	0.01	1.0
γ-BHC (Lindane)	0.01	1.0
α-Chlordane	0.01	1.0
γ-Chlordane	0.01	1.0
Chlordane (technical)	0.1	10.0
4,4'-DDD	0.02	2.0
4,4'-DDE	0.02	2.0
4,4'-DDT	0.02	2.0
Dieldrin	0.02	2.0
Endosulfan I	0.02	1.0
Endosulfan II	0.02	2.0
Endosulfan Sulfate	0.02	2.0
Endrin	0.02	2.0
Endrin Aldehyde	0.05	2.0
Endrin ketone	0.02	2.0
Heptachlor	0.01	1.0
Heptachlor Epoxide	0.01	1.0
Methoxychlor	0.1	10.0
Toxaphene	1.0	100

Table 2

Typical Instrument Operating Conditions

Parameter	Recommended Conditions*
Injection port temperature	280 °C
Detector temperature	320 °C
Guard Column	Phenomenex Zebron HT Deactivated Guard Column (5m x 0.25 mm ID) or Restek Siltek Guard Column (5m x 0.25 mmID) or equivalent
Column 1 (HP6890 GC)	ZB-CLPesticides-1: 30 m x 0.25 mm ID x 0.25 µm
Column 2 (HP6890 GC)	ZB-CLPesticides-2: 30 m x 0.25 mm ID x 0.20 µm
HP6890 GC Temperature program and inlet pressure	70 °C for 0.5 minute 40 °C/min to 200 °C and hold for 0.5 minute 25 °C/min to 330 °C and hold for 1.5 minutes
Injection	1 or 2 µL
Carrier gas	Hydrogen
Make up gas	Nitrogen, 30 mL/min
Y splitter	Restek glass tee (Siltek)

* Variations in instrument conditions may exist in order to facilitate compound separation or to accommodate matrix effects from sample analysis. See maintenance log for current instrument conditions.

Table 3
Calibration Levels (µg/L)

	Level 1	Level 2	Level 3	Level 5	Level 6	Level 7	Level 8
Individual Mix AB							
Aldrin	1.0	2.0	5.0	20.0	50.0	100.0	200.0
α-BHC	1.0	2.0	5.0	20.0	50.0	100.0	200.0
β-BHC	1.0	2.0	5.0	20.0	50.0	100.0	200.0
δ-BHC	1.0	2.0	5.0	20.0	50.0	100.0	200.0
g-BHC (Lindane)	1.0	2.0	5.0	20.0	50.0	100.0	200.0
α-Chlordane	1.0	2.0	5.0	20.0	50.0	100.0	200.0
γ-Chlordane	1.0	2.0	5.0	20.0	50.0	100.0	200.0
4,4'-DDD	1.0	2.0	5.0	20.0	50.0	100.0	200.0
4,4'-DDE	1.0	2.0	5.0	20.0	50.0	100.0	200.0
4,4'-DDT	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Dieldrin	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Endosulfan I	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Endosulfan II	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Endrin	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Endrin Aldehyde	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Endrin ketone	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Heptachlor	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Heptachlor epoxide	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Hexachlorobenzene	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Methoxychlor	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Endosulfan Sulfate	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Appendix IX Standards							
2,4'-DDD	1.0	2.0	5.0	20.0	50.0	100.0	200.0
2,4'-DDE	1.0	2.0	5.0	20.0	50.0	100.0	200.0
2,4'-DDT	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Multicomponent Standards							
Chlordane (Technical)	10	20	50	100	200	400	N/A
Toxaphene	100	200	500	1000	2000	N/A	N/A
Surrogates are included the AB Mix calibration mix at the following levels:							
Tetrachloro-m-xylene	1.0	2.0	5.0	20.0	50.0	100.0	200.0
Decachlorobiphenyl	1.0	2.0	5.0	20.0	50.0	100.0	200.0

Individual Mix AB also has a 10ug/L level 4 and a 500ug/L level 9 that could not be accommodated in this table.

Table 4

Column Degradation Evaluation Mix

Component	Concentration (µg/L)
4,4'-DDT	100
Endrin	50

Table 5

LCS/Matrix Spike and Surrogate Spike Levels

Compound	(µg/L)	(µg/kg)
Aldrin	0.2	20
α-BHC	0.2	20
β-BHC	0.2	20
δ-BHC	0.2	20
γ-BHC (Lindane)	0.2	20
α-Chlordane	0.2	20
γ-Chlordane	0.2	20
4,4'-DDD	0.2	20
4,4'-DDE	0.2	20
4,4'-DDT	0.2	20
Dieldrin	0.2	20
Endosulfan I	0.2	20
Endosulfan II	0.2	20
Endosulfan Sulfate	0.2	20
Endrin	0.2	20
Endrin Aldehyde	0.2	20
Endrin Ketone	0.2	20
Heptachlor	0.2	20
Heptachlor Epoxide	0.2	20
Methoxychlor	0.2	20
Toxaphene (when required)	5	500
Surrogates		
Decachlorobiphenyl	0.2	20
Tetrachlor-m-xylene (TCMX)	0.2	20

Table 6 Summary of QC Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Minimum 5-point Initial Calibration	Initial calibration prior to sample analysis	One of the options below: For avg. calibration factor: RSD ≤ 20%. Linear least squares regression: r ≥ 0.990 **Linear least squares regression for DoD: r ≥ 0.995** For quadratic regression: r^2 ≥ 0.990.	Terminate analysis; correct the problem; recalibrate. Problem must be corrected. No samples may be run until ICAL has passed.
ICV	Following initial calibration.	80-120% recovery.	Terminate analysis; correct the problem; recalibrate.
CCV	Beginning and minimum every 12 hours *or 20 samples, whichever is less.* *DOD and* BP LaMP - prior to sample analysis, after every ten injections, and at the end of the sequence.	80-120% recovery.	Correct problem, then rerun CCV. If that fails, then repeat ICAL. Reanalyze all sample since the last successful CCV.
Retention time (RT) window width determination	At method set-up and after major maintenance (e.g. column change)	NA	See Section 10.10 for additional requirements.
Endrin/DDT Breakdown Check	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation ≤ 15% for both DDT and Endrin.	Correct problem then repeat breakdown check. No samples shall be run until degradation is ≤ 15% for both DDT and Endrin.
Method Blank	One per lot of 20 field samples or fewer.	The result must be < RL or < 1/10 the amount measured in any sample or 1/10 the regulatory limit. **For DoD and BP LaMP:** No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit.	Re-extract and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
LCS	One per batch of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must contain all analytes to be reported. Must be within acceptance criteria specified by DOD, if available. Otherwise, use in-house control limits.	See Section 9.4 for additional requirements.
CCB(Instrument blank with surrogates)	**For DoD and BP LaMP:** analyzed after each CCV (unless the CCV is followed by a Method Blank)	**For DoD and BP LaMP:** No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit.	
Surrogate	All field and QC samples.	Must be within laboratory control limits. **For DoD:** Must be within acceptance criteria specified by DOD, if available. Otherwise, use in-house control limits.	See Section 9.6 for additional requirements.
Matrix Spike and Matrix Spike Duplicate	One pair per lot of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Use LCS control limits.	See Section 9.5 for additional requirements.
Confirmation of Positive Results	All positive results must be confirmed except toxaphene and technical chlordane.	Results between primary and confirmation column RPD ≤ 40%.	Apply f if RPD ≥ 40% RPD if sample is not confirmed.

Attachment 1 Example Retention Time Study Spreadsheet

Instrument ID: SEA035

	2/20/08	2/21/08	2/22/08			
	ECD31001	ECD31003	ECD31020			
Name	Column #1	Serial # 7HM-G017-11		Mean R.T.	R. T. Std. Dev.	3X(SD)
Hexachlorobutadiene	3.348	3.348	3.347	3.348	0.000577	0.001732
Tetrachloro-m-xylene (S)	5.634	5.635	5.634	5.634	0.000577	0.001732
alpha-BHC	6.209	6.210	6.210	6.210	0.000577	0.001732
Hexachlorobenzene	6.137	6.138	6.138	6.138	0.000577	0.001732
gamma-BHC (Lindane)	6.622	6.624	6.623	6.623	0.001	0.003
beta-BHC	6.987	6.989	6.989	6.988	0.001155	0.003464
delta-BHC	7.277	7.279	7.278	7.278	0.001	0.003
Heptachlor	7.046	7.048	7.047	7.047	0.001	0.003
Aldrin	7.392	7.394	7.392	7.393	0.001155	0.003464
Heptachlor Epoxide	8.003	8.005	8.004	8.004	0.001	0.003
gamma-Chlordane	8.297	8.299	8.298	8.298	0.001	0.003
alpha-Chlordane	8.374	8.377	8.376	8.376	0.001528	0.004583
Endosulfan I	8.438	8.440	8.439	8.439	0.001	0.003
4,4'-DDE	8.602	8.605	8.603	8.603	0.001528	0.004583
Dieldrin	8.746	8.748	8.747	8.747	0.001	0.003
Endrin	9.059	9.061	9.060	9.060	0.001	0.003
4,4'-DDD	9.231	9.234	9.232	9.232	0.001528	0.004583
Endosulfan II	9.385	9.388	9.387	9.387	0.001528	0.004583
4,4'-DDT	9.509	9.512	9.510	9.510	0.001528	0.004583
Endrin Aldehyde	9.588	9.590	9.589	9.589	0.001	0.003
Endosulfan Sulfate	9.828	9.830	9.829	9.829	0.001	0.003
Methoxychlor	10.141	10.144	10.141	10.142	0.001732	0.005196
Endrin Ketone	10.363	10.367	10.365	10.365	0.002	0.006
Decachlorobiphenyl (S)	11.388	11.394	11.386	11.389	0.004163	0.01249
Name	Column #2	Seriail # 7HM-G016-17				
Hexachlorobutadiene	3.990	3.988	3.990	3.989	0.001155	0.003464
Tetrachloro-m-xylene (S)	6.095	6.094	6.096	6.095	0.001	0.003
alpha-BHC	6.625	6.624	6.626	6.625	0.001	0.003
Hexachlorobenzene	6.675	6.675	6.677	6.676	0.001155	0.003464
gamma-BHC (Lindane)	7.024	7.023	7.025	7.024	0.001	0.003
beta-BHC	7.273	7.273	7.274	7.273	0.000577	0.001732
delta-BHC	7.559	7.559	7.561	7.560	0.001155	0.003464
Heptachlor	7.721	7.721	7.723	7.722	0.001155	0.003464
Aldrin	8.112	8.112	8.114	8.113	0.001155	0.003464
Heptachlor Epoxide	8.598	8.599	8.600	8.599	0.001	0.003
gamma-Chlordane	8.884	8.884	8.885	8.884	0.000577	0.001732
alpha-Chlordane	8.970	8.971	8.971	8.971	0.000577	0.001732
Endosulfan I	9.020	9.021	9.021	9.021	0.000577	0.001732
4,4'-DDE	9.177	9.178	9.178	9.178	0.000577	0.001732
Dieldrin	9.320	9.321	9.322	9.321	0.001	0.003
Endrin	9.562	9.563	9.564	9.563	0.001	0.003
4,4'-DDD	9.731	9.733	9.732	9.732	0.001	0.003
Endosulfan II	9.801	9.802	9.802	9.802	0.000577	0.001732
4,4'-DDT	10.061	10.062	10.062	10.062	0.000577	0.001732
Endrin Aldehyde	9.939	9.940	9.939	9.939	0.000577	0.001732
Endosulfan Sulfate	10.183	10.184	10.185	10.184	0.001	0.003
Methoxychlor	10.543	10.545	10.544	10.544	0.001	0.003
Endrin Ketone	10.649	10.651	10.650	10.650	0.001	0.003
Decachlorobiphenyl (S)	11.936	11.943	11.935	11.938	0.004359	0.013077

Attachment 2 Example Pesticide Breakdown Custom Report

Report Date: 25-Jul-2016 16:35:56 Chrom Revision: 2.2 20-Apr-2016 13:59:46

Preliminary Report

Breakdown Report

TestAmerica Seattle

Data File: \\ChromNA\Seattle\ChromData\TAC034\20160721-48487.b\34G21013.D
Injection Date: 21-Jul-2016 15:12:38 Instrument ID: TAC034
Lims ID: PEM
Client ID:
Operator ID: dcv ALS Bottle#: 1 Worklist Smp#: 13
Injection Vol: 1.0 ul Dil. Factor: 1.0000
Method: 8182ISTD_TAC034 Limit Group: 8081A_B, DOD ISTD Pesticides

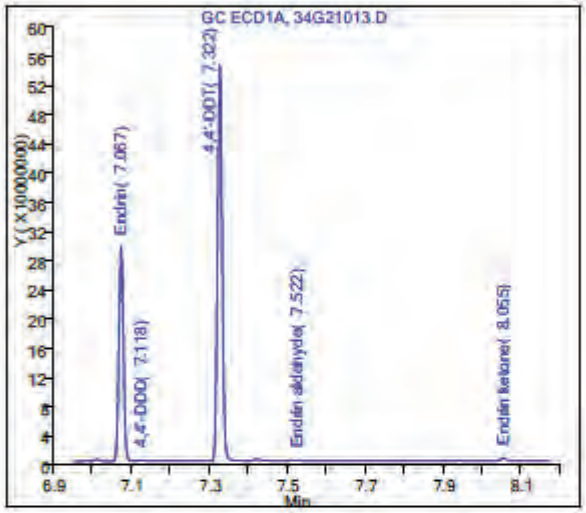
33 Endrin, Detector: GC ECD1A

SW-846 Method

%Breakdown =
(Area Breakdown Cpnds/
Total Area Breakdown Cpnds) * 100

33 Endrin, Area = 241094840
39 Endrin aldehyde, Area = 1256167
43 Endrin ketone, Area = 3870380

%Breakdown: 2.08%, Max Limit: 15.00%
Passed



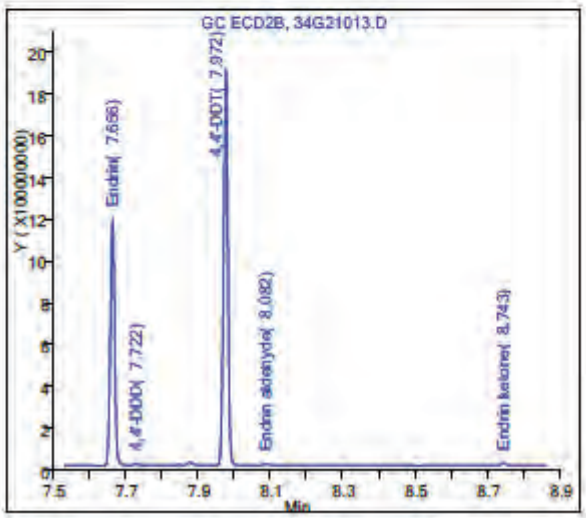
33 Endrin, Detector: GC ECD2B

SW-846 Method

%Breakdown =
(Area Breakdown Cpnds/
Total Area Breakdown Cpnds) * 100

33 Endrin, Area = 990899165
39 Endrin aldehyde, Area = 9154385
43 Endrin ketone, Area = 10428539

%Breakdown: 1.94%, Max Limit: 15.00%
Passed



Attachment 3 DoD QC Tables

Table G-3 Surrogates

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
8081 Water:				
Decachlorobiphenyl	83	17	30	135
8081 Solid:				
Decachlorobiphenyl	94	13	55	130

Table G-14. LCS Control Limits for Organochlorine Pesticides SW-846 Method 8081 Water Matrix[15]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
4,4'-DDD	88	20	25	150	10	170
4,4'-DDE	87	18	35	140	15	160
4,4'-DDT	92	15	45	140	30	155
Aldrin	83	19	25	140	10	155
alpha-BHC	94	11	60	130	50	140
alpha-Chlordane	93	10	65	125	55	135
beta-BHC	96	10	65	125	55	135
delta-BHC	91	15	45	135	30	150
Dieldrin	95	11	60	130	50	140
Endosulfan I	80	10	50	110	40	120
Endosulfan II	79	17	30	130	10	150
Endosulfan sulfate	96	14	55	135	40	150
Endrin	95	13	55	135	45	145
Endrin aldehyde	96	14	55	135	40	150
Endrin ketone	102	8	75	125	70	135
gamma-BHC	82	18	25	135	10	155
gamma-Chlordane	94	11	60	125	50	135
Heptachlor	87	15	40	130	30	145
Heptachlor epoxide	96	11	60	130	50	140
Methoxychlor	103	16	55	150	40	165

[15]A number of sporadic marginal exceedances of the control limits is allowed depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Hexachlorobenzene and Toxaphene. Sufficient data to perform statistically significant analyses were not received for those analytes during the

LCS study. Additional limits for poor performing compounds can be found in section G.6

Table G-15 LCS Control Limits for Organochlorine Pesticides SW-846 Method 8081 Solid Matrix[17]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
4,4'-DDD	81	18	30	135	10	155
4,4'-DDE	97	10	70	125	60	135
4,4'-DDT	92	16	45	140	30	155
Aldrin	93	16	45	140	30	155
alpha-BHC	93	10	60	125	50	135
alpha-Chlordane	92	10	65	120	55	130
beta-BHC	95	11	60	125	50	135
delta-BHC	94	12	55	130	45	145
Dieldrin	96	10	65	125	55	135
Endosulfan I	74	20	15	135	10	155
Endosulfan II	89	17	35	140	20	160
Endosulfan sulfate	99	12	60	135	50	145
Endrin	97	12	60	135	50	145
Endrin aldehyde	92	18	35	145	20	165
Endrin ketone	100	11	65	135	55	145
gamma-BHC	91	11	60	125	50	135
gamma-Chlordane	96	10	65	125	55	135
Heptachlor	96	15	50	140	35	155
Heptachlor epoxide	98	11	65	130	55	140
Methoxychlor	100	14	55	145	45	155

[17]A number of sporadic marginal exceedances of the control limits is allowed depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Hexachlorobenzene, Hexachlorocyclopentadiene, and Toxaphene. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for poor performing compounds can be found in section G.6.

Appendix 1 GC/MS Confirmation of Pesticides and PCBs for EPA Region 10

The Requirement

The purpose of the GC/MS analysis for the single component pesticides is for confirmation of the identification. The purpose of the GC/MS analysis for the multi-component analytes is to confirm the presence of chlorinated biphenyls in PCB and the presence of chlorinated camphenes in Toxaphene. The GC/MS analytical results for the pesticides/PCBs shall not be used for quantitation. If the identification of the analyte cannot be confirmed by any of the recommended GC/MS procedures and the concentration calculated from the GC/ECD analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit to a sample concentration equivalent to the concentration of the GC/MS reference standard, qualify the results, and note the data qualification in the Laboratory Case Narrative.

Any pesticide or PCB analyte for which a concentration is reported from a GC/ECD analysis must have the identification confirmed by GC/MS if the concentration is sufficient for that purpose. If the laboratory fails to perform GC/MS confirmation as appropriate, the EPA Region 10 will require re-analysis of any effected samples at no additional cost to EPA Region 10.

The Guidance in Performing GC/MS Confirmation

A. The GC/MS confirmation may be accomplished by one of three general means:
   - If there was an SVOC full scan GC/MS analysis (such as SW-846 Method 8270) performed on the sample in question, then examination of the tentatively identified compound library search results can be used or,
   - An analysis of the pesticide/PCB extract, following any necessary solvent exchange and concentration steps (preferred) or
   - Analysis of another aliquot of the SVOC sample extract after further concentration

B. Full-scan GC/MS will normally require a concentration of approximately 10-ng/uL in the final extract for each single component compound, 50-ng/uL for PCBs, and 125-ng/uL for multi-component pesticide (Toxaphene).

C. In order to confirm the identification of the target pesticide or PCB, the laboratory must also analyze a reference standard for the analyte. In order to demonstrate the ability of the GC/MS system to identify the analyte in question, the concentration of the standard should be less than or equal to 10-ng/uL for single component pesticides, 50-ng/uL for PCBs, and 125-ng/uL for multi-component pesticides.

D. The laboratory mass spectral interpretation specialist is advised to compare the CAS Registry numbers for the pesticides or PCBs to those from the library search routine.

E. Regardless of which of the three approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the SVOC extract, then the SVOC method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the pesticide or PCB extract prepared for the GC/EC analysis, the pesticide or PCB method blank extracted with the sample must be analyzed.

F. For GC/MS confirmation of single component analytes, the required deliverables are copies of the library search results (best tentatively identified compound matches) or analyte spectrum and the spectrum of the reference standard. For multi-component analytes, spectra of three characteristic peaks are required for both the sample component and the reference standard.

Title: PCBs
[Methods 8082 and 8082A]

Approvals

Signatures on File	
Joan Protasio Date	Manjit Nijjar Date
Semivolatile Organic Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 This SOP describes the procedure for the determination of concentrations of polychlorinated biphenyls (PCB) as Aroclors using the methodology prescribed in EPA SW-846 Method 8082. Table 1 lists the specific Aroclors that are determined using this procedure and their associated reporting limits (RLs).

1.2 This procedure is applicable to the analysis of extracts of aqueous, solid, and oil samples. When utilized for the analysis of oils, additional cleanup procedures may be required.

1.3 This SOP does not include the procedures for extracting environmental samples. Refer to TestAmerica Seattle SOPs TA-OP-0301 (Method 3510), TA-OP-0367 (Method 3546), TA-OP-0314 (Method 3580A),and TA-OP-0302 (Method 3550) for sample preparation procedures.

1.4 This SOP does not include the determination of the concentration of PCB congeners.

1.5 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 Preparation

2.1.1 Aqueous Samples

PCBs are extracted from a one-liter aqueous sample with methylene chloride using a separatory funnel (SW-846 Method 3510). The extract is evaporated to near dryness and exchanged to hexane. The final extract volume is 10 mL for medium level and 1 mL for low level.

LVI samples are extracted from *250* mL of aqueous sample using method 3510. The extract is evaporated to near dryness and exchanged to hexane. The final extract volume is *2.5* mL.

The extraction procedure is detailed in SOP TA-OP-0301.

2.1.2 Solid Samples

PCBs are extracted from solid materials using methylene chloride and ultrasonic agitation (Method 3550) *or* Microwave (Method 3546). The extract is evaporated to near dryness and exchanged to hexane. The final extract volume is 10 mL. The extraction procedure is detailed in SOP TA-OP-0302 *and TA-OP-0367.*

2.1.3 Oil Samples

Oil samples are typically prepared by diluting 0.2 gram of sample to a final volume of 10 mL with hexane. The extraction procedure is detailed in SOP TA-OP-314.

2.1.4 Solid Sample Cleanup Procedures

Cleanup options are discussed in Section 4 below. Instructions for performing various cleanup procedures are detailed in - TA-OP-0366 (Florisil Cleanup 3620) and TA-OP-0383 (Acid Cleanup 3665). Sulfur clean-up (TA-OP-0353) using copper is performed if necessary.

2.2 Analysis

Samples are analyzed using a gas chromatograph with dual electron capture detectors (ECDs). Specific Aroclor mixtures are identified by the pattern of peaks compared to

chromatograms of reference standards. The concentrations of Aroclors in the sample extract are determined using an external standard calibration or internal standard calibration.

3.0 Definitions

3.1 Polychlorinated biphenyls (PCBs): PCBs are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl, with a general chemical formula of $C_{12}H_{10-x}Cl_x$. There are 209 possible congeners.

3.2 Aroclor: PCBs were produced as technical mixtures by the chlorination of biphenyl. Production processes were designed to produce mixtures with characteristic chlorine contents. In the United States, most of the PCBs in the environment are in the form of Aroclors, which were produced by Monsanto from the 1930s through 1977. Each Aroclor mixture is identified by a four-digit number, the first two digits of which indicate the number of carbons in the biphenyl ring, i.e., 12, and the second two of which indicate the weight percent of chlorine. For example, Aroclor 1254 has 12 carbons and 54% by weight chlorine. The exception is Aroclor 1016, which has 12 carbons and 42% by weight chlorine.

NOTE: Each specific Aroclor produces a characteristic gas chromatographic pattern that represents the relative amounts of PCB congeners in the formulation. The formulation of the mixtures from batch to batch was fairly consistent, but never exactly the same. In almost all cases, the gas chromatogram can be used as a fingerprint to identify the specific Aroclor. Exceptions occurred for Aroclors 1254 and 1221. In each case, at least one batch was produced under different conditions, which resulted in an Aroclor mixture with the same approximate chlorine content, but with a significantly different distribution of congeners. These odd batches of 1254 and 1221 produce chromatographic patterns that are very different from the typical formulations. Standards for these odd batch Aroclors can be used to aid in the qualitative identification of Aroclors in environmental samples.

3.3 AR1660: Laboratory designation for the mixture of Aroclors 1016 and 1260.

3.4 AR2154: Laboratory designation for the mixture of Aroclors 1221 and 1254.

3.5 AR3262: Laboratory designation for the mixture of Aroclors 1232 and 1262.

3.6 AR4268: Laboratory designation for the mixture of Aroclors 1242 and 1268.

3.7 AR1248: Laboratory designation for Aroclor 1248.

4.0 Interferences

4.1 Hydrocarbons can co-elute and thereby mask the Aroclor pattern. The laboratory uses acid cleanup with concentrated sulfuric acid to remove hydrocarbons for all PCB samples. Acid cleanup removes low-to-medium molecular weight polar organic interferences from sample extracts. Detailed instructions for performing acid cleanup are provided in SOP TA-OP-0383. The Lot# of the reagent used to perform the cleanup will be documented in the prep batch sheets.

4.2 Sulfur will interfere, and when observed is removed using copper granules or Mercury. See Figure 2 for an example chromatogram showing sulfur interference. See SOP TA-OP-0353 for Sulfur Cleanup instructions. The Lot# of the reagent used to perform the cleanup will be documented in an NCM.

4.3 Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Any affected samples are re-analyzed.

4.4 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.5 Samples that may have interference, colored extract after acid clean-up or a history of interference problems may require an additional silica gel clean-up. Refer to SOP TA-OP-0364.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum. Cut resistant gloves must be worn when using sharp tools or when washing glassware.

5.1 Specific Safety Concerns or Requirements

5.1.1 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.2 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.3 All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the EH&S Coordinator shall be immediately notified.

5.1.4 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. As a safety precaution, all standards, samples, and extracts are handled in an approved fume hood.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydrogen gas	Explosive	None	The main hazard is flammability. Exposure to moderate concentrations may cause dizziness, headache, nausea, and unconsciousness. Exposures to atmospheres less than 8 to 10% oxygen will bring about sudden unconsciousness, leaving individuals unable to protect themselves. Lack of sufficient oxygen may cause serious injury or death.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

A gas chromatography system with dual columns and dual ECD (^{63}Ni) detectors, and a data system capable of measuring peak area and/or height.

6.1.1 Data acquisition system: Agilent's ChemStation, is used for data acquisition and storage on machine-readable media. Since no processing is done by ChemStation and since there are no audit trail functions associated with data acquisition, the audit trail feature for ChemStation may be either enabled or disabled. The other component, Chrom, is used for data processing such as the measurement of peak area or peak height. By design, the audit trail feature for Chrom is always enabled.

6.1.2 Data processing: Chrom version *2.2* or higher

6.1.3 TestAmerica LIMS (TALS), current version

6.2 Columns

- Primary Column: Phenomenex ZB-CLPesticides-1 30 m x 0.25 mm ID x 0.25 um film thickness; or equivalent.
- Secondary Column: Phenomenex ZB-CLPesticides-2 30 m x 0.25 mm ID x 0.20 um film thickness; or equivalent.
- Guard column: Agilent FS, Deactivated (Part number 160-2255-5): 5 m x 0.25 mm ID, Siltek Guard Column 5 m, 0.25 mm ID (Restek 10026), or equivalent.

NOTE: The columns listed were the ones in place when SOP was prepared.

6.3 Supplies

- Autosampler vials, crimp caps with PTFE-faced septa or equivalent.
- Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Standards

7.2.1 Stock Standards

7.2.1.1 All standards are subject to verification using a second-source standard before they are used for sample analysis. This process is described in SOP TA-QA-0619.

7.2.1.2 All standards must be stored at manufacturer's specifications. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.2.1.3 Stock standards are monitored for signs of degradation or evaporation.

7.2.1.4 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. The standards must be replaced at least once a year or sooner if comparison with check standards indicates a problem.

7.2.2 PCB and Surrogate Stock Calibration Standards

7.2.2.1 Stock A

For each of the Aroclors listed in Table 1, a commercially prepared stock standard solution is obtained. Each stock standard contains the specific Aroclor in pesticide-grade hexane (or in some cases, isooctane) at a concentration of 1,000 µg/mL.

7.2.2.2 Surrogate Stock B

A commercially prepared stock standard solution is obtained that contains the surrogate compounds tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) in acetone, each at a concentration of 200 µg/mL.

7.2.2.3 Internal Standard

A commercially prepared stock standard solution is obtained that contains the 1-Bromo-2-nitrobenzene internal standard analyte in Acetone at a concentration of 1,000 ug/mL.

7.2.3 Intermediate and Working Level Calibration Standard Solutions

7.2.3.1 Stock C Standard Solutions

A Stock C standard solution is prepared for the various Aroclors or combination of Aroclors as summarized in the following table.

Stock C	Recipe	Conc (µg/mL)	Final Vol (mL)	Final Concentrations (µg/mL)	
AR1660	100 µL of Aroclor 1016 Stock A	1000	10	Aroclor 1016	10
	100 µL of Aroclor 1260 Stock A	1000		Aroclor 1260	10
	50 µL of surrogate Stock B	200		TCMX	1.0
				DCB	1.0
AR2154	100 µL of Aroclor 1221 Stock A	1000	10	Aroclor 1221	10
	100 µL of Aroclor 1254 Stock A	1000		Aroclor 1254	10
AR1242	100 µL of Aroclor 1242 Stock A	1000	10	Aroclor 1242	10
AR3262	100 µL of Aroclor 1232 Stock A	1000	10	Aroclor 1232	10
	100 µL of Aroclor 1262 Stock A	1000		Aroclor 1262	10
AR4868	100 µL of Aroclor 1248 Stock A	1000	10	Aroclor 1248	10
	100 µL of Aroclor 1268 Stock A	1000		Aroclor 1268	10

7.2.3.2 AR1660 Calibration Levels

A total of 7 calibration standards are prepared for AR1660 as summarized in the following table. As needed, the following table can be used to prepare calibration standards for any of the Aroclors, but only the AR1660 calibration standards include the surrogates. In all cases, measured volumes of the Stock C standard are diluted using pesticide-grade hexane to the final volume indicated in the following table.

Level	Vol of Stock C Used (µL)	Final Volume (mL)	Final PCB Conc (µg/L)	Final Surrogate Conc (µg/L)*
1	10	10	10	1.0
2	20	10	20	2.0
3	50	10	50	5.0
4 (CCV)	100	10	100	10.0
5	500	10	500	50
6	1000	10	1000	100
7**	1000	5	2000	200

* Surrogates are in the AR1660 calibration solutions only. None of the other Aroclor calibration solutions contain the surrogate compounds.

** Level 7 calibration standard is used for the AR1660 and AR2154 calibrations, since they are the most common Aroclors observed in client samples.

7.2.3.3 Working Internal Standard (IS) solution

The working internal standard solution is prepared by diluting 1.0 mL of the stock standard into a 100 mL volumetric flask of hexane. The final concentration is 10,000 ug/L.

Note: The IS analyte is photosensitive. Therefore, extra care must be taken to avoid exposure to light as much as possible while handling the standard.

7.2.3.3.1 Add 100 uL of the IS to each calibration standard level prior to bringing the final volume up to 10 mL. This will result in an on-column concentration of 100 ug/L of the IS analyte.

7.2.3.3.2 For the analysis of sample extracts, add exactly 1.0 mL of extract to an autosampler vial and add 10 uL of the working IS solution to each sample. Cap each vial and mix/shake each vial prior to loading on the instrument autosampler tray for analysis. The final, on-column concentration of the IS will be 100 ug/L.

7.2.3.4 Working Single-Point PCB Calibration Standards

The Level 4 standard in the table above is used for single-point calibrations of the individual Aroclors. These standards are also used as pattern recognition standards.

7.2.4 Second-Source Standards for Initial Calibration Verification (ICV)

These standards are purchased from a vendor different from the one that supplied the stock calibration standards.

7.2.5 Second-Source Stock A' Aroclor Standard Solutions

Commercially prepared solutions in pesticide-grade hexane (or isooctane) are routinely obtained for Aroclors 1016 and 1260. The Aroclor concentration in each solution is 1000 µg/mL. A second source may be obtained for the other Aroclors, if necessary.

7.2.6 Second-Source Surrogate Stock B' Standard Solution

A commercially prepared solution is obtained containing TCMX and DCB, **each at a concentration of 200 µg/mL.**

7.2.7 Second-Source Working Level Standards

The working level second-source ICV standard is prepared by combining 1.0 mL of Aroclor 1016/ 1260 Stock A' and 0.50 mL of surrogate Stock B', and diluting to a final volume of 100 mL with pesticide-grade hexane. This results in a concentration of 10.0 µg/mL for each of the Aroclors and 1.0 µg/mL for each of the surrogates. If a second source verification standard is prepared for any of the Aroclors other than the AR1660 mixture, the surrogates are not added.

7.2.8 Continuing Calibration Verification Standard (CCV), 0.1 µg/mL

The working CCV solution is the same as the Level 4 initial calibration standard, as shown in the table in Section 7.2.3.2.

7.2.9 RL Standard

The lowest concentration calibration standard (i.e., Level 1) is used as the RL Standard.

7.2.10 Laboratory Control Standard (LCS) Spiking Solution (AR1660)

NOTE: The LCS/MS spiking solution is prepared and used as part of the scope of the organic preparation SOPs TA-OP-0301 and TAN-OP-0302. The following information is provided for reference only.

The soil working LCS spike solution is prepared in a 10 mL volumetric flask by combining 1 mL of the Aroclor 1016/ 1260 Stock A' standard, and diluting to volume with acetone.

The water working LCS spike solution is prepared in a 10 mL volumetric flask by combining 100 µL of the Aroclor 1016 Stock A standard and 100 µL of the Aroclor 1260 Stock A standard, and diluting to volume with acetone.

The LVI water working LCS spike solution is prepared in a 10 mL volumetric flask by adding 2.5 mL of the water working LCS spike solution, described above, and diluting to 10 mL with acetone.

The LCS for a batch of aqueous samples is prepared by adding 100 µL of the water working LCS spiking solution to one liter of water, or 100 uL of the LVI water LCS spiking solution to 250 mL of water. The LCS for a batch of soil samples is prepared by adding 100 µL of the soil working LCS spiking solution to 10 grams of Ottawa sand.

7.2.11 Matrix Spike (MS) Spiking Solution:

The working matrix spike solution and LVI working matrix spike solution is the same as the LCS spike solution. Matrix spike samples are prepared by adding 100 uL of the working solution to a second one-liter aliquot of the selected aqueous sample, or to a 10-gram subsample of the selected soil sample. For LVI samples, 100 uL of the LVI working solution is added to a ~~125~~ 250 mL aliquot of the selected aqueous sample. The MS duplicate (MSD) is prepared in the same way using a third aliquot of the selected sample.

7.2.12 Surrogate Spike Solution

7.2.12.1 Stock Surrogate Spike Solution:

A commercially prepared solution containing 200 µg/mL each of decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX) in acetone is purchased.

7.2.12.2 Working Surrogate Spike Solution

NOTE: Samples are spiked with the surrogate compounds during sample preparation, which is described in the organic preparation SOPs TA-OP-0301 and TA-OP-0302. The following information is provided for reference only.

The soil and water working surrogate spike solution is prepared in a 50 mL volumetric flask by adding 500 uL of the stock surrogate spike solution and diluting to 50 mL volume with acetone. The LVI water surrogate spike solution is prepared by adding 2.5 mL of the aforementioned soil and water working surrogate spike solution to a 10

mL volumetric flask and diluting to volume with acetone. The surrogate compounds are added to all field and QC samples as follows:

Sample	Sample Volume (L) or Mass (grams)	Vol. of Surrogate Spike Solution Added (µL)
LCS (aqueous)	1 L reagent water	100
LCS (solid)	10 g reagent free sand	100
MS/MSD (aqueous)	1 L sample aliquot	100
MS/MSD (solid)	10 g reagent free sand	100
Aqueous Sample	1 L sample aliquot	100
Solid Sample	10 g reagent free sand	100
All LVI sample aliquots (aqueous)	125 mL reagent water or sample aliquot	100 uL of LVI solution

7.2.13 Primer Mix

The primer mix typically consists of a mixture of CCV standards and/or old calibration standards. The concentrations of the components of the primer mix are not critical. The primer mix is injected one or more times prior to analyzing standards and samples to ensure that the chromatographic system is stable, i.e., that retention times are reproducible.

7.3 Reagents

7.3.1 Acetone, 99.4% for organic residue analysis. Each lot is tested for purity prior to use per SOP S-T-001.

7.3.2 Hexane, pesticide grade. Each lot is tested for purity prior to use per SOP S-T-001.

7.3.3 Carrier Gas: ≥ 99.99999% pure hydrogen

7.3.4 Make-up Gas: ≥ 99.99980% pure nitrogen

7.4 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned amber glass bottles fitted with a Teflon-lined caps. To achieve routine reporting limits, a full one liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Soil samples are collected in 8-ounce, wide-mouth jars with a Teflon-lined lid.

8.3 Samples are stored at 0-6℃.

8.4 Water samples must be extracted within 7 days of collection, and soil samples must be extracted within 14 days of collection.

8.5 Sample extracts are refrigerated at 0-6℃ and analy zed within 40 days from extraction.

Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	1 Liter	Cool 0-6°C	7 Days	40 Days from extraction	40 CFR Part 136.3
Soils	Glass	30 grams	Cool 0-6°C	14 Days	40 Days from extraction	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Seattle SOP TA-QA-0620, Quality Control Program.

9.1.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument. See SOP TA-QA-0620 for further details.

CCB instrument blank with surrogate and IS added. Needs to be run after a CCV unless a MB is run first. If the CCB is run, it needs to be evaluated with results less than the RL for the target list and passing surrogate criteria and uploaded to TALS.

9.3 Internal Standard

The internal standard needs to be evaluated for recovery and retention time drift.

9.3.1 The recovery of the IS must be within 50-200% of the expected concentration.

Corrective Action: If the %recovery of the IS falls outside of the acceptance limits, then sample re-analysis must be performed for confirmation. If the sample chromatogram and/or sample extract indicates significant sample matrix

interference, the sample re-analysis may be performed at a dilution.

9.3.2 The retention time drift must not exceed 0.5 minutes when compared to the retention time of the IS in from the daily CCVIS standard (for non-DOD work). For DOD work, the retention time drift is compared to that of the initial calibration in the ICIS standard.

Corrective Action: If the retention time drift affects all sample injections, a new initial calibration will be required for DOD work to resume. For non-DOD work, if the retention time drift exceeds the acceptance limit of 0.5 minutes, evaluate the sample chromatogram and/or sample extract for matrix interference. If there are no apparent signs of sample matrix interference, re-analyze the extract as is. If there are signs of sample matrix interference, re-analysis at a dilution is warranted. If the re-analysis at a dilution yields no significant improvement in the retention time, report the original analysis and narrate the re-analysis efforts in an NCM.

9.4 Method blank

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water (for aqueous sample batches) or reagent free sand (for solid sample batches) to which the surrogate compounds are added. The method blank is subject to the entire extraction and analysis process.

Acceptance Criteria: The method blank must not contain any analyte of interest at or above the reporting limit (RL) or above one-tenth of the concentration found in the associated samples. Note that some programs (e.g. BP LaMP, AFCEE, Navy, and USACE) require that the maximum blank concentration must be one-half of the RL or less.

Corrective Action: If the method blank exceeds allowable levels, the source of the contamination should be investigated and all associated samples re-extracted and reanalyzed.

Correction Action for DOD batches: Re-analyze the method blank. If the method blank confirms at >1/2 the RL, then any sample with a detection greater than 10X the concentration of that found in the method blank may be reported. For all other samples, an NCM must be initiated and a client variance must be requested; however, re-extraction should commence immediately, in the event that the client does not give approval to report the qualified data.

9.5 Laboratory Control Sample (LCS)

One LCS is prepared and analyzed with each batch of samples. The LCS is prepared as described in Section 7.2.9. The LCS is subject to the entire extraction and analysis process. In cases where insufficient volume is submitted, for the analysis of an MS/MSD, an LCSD will also be prepared.

Acceptance Criteria: The LCS recovery must be within the established control limits. The laboratory's standard control limits are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. Current control limits are maintained in the LIMS.

Corrective Action: If recoveries are not within the established limits, the analytical system is out of control and corrective action must occur. All associated samples must be re-extracted and reanalyzed. Samples

which are associated with a high LCS recovery but are non-detect may be reported. This occurrence must be documented in a non-conformance memorandum and the data flagged.

Corrective Action for DOD batches: Re-analyze the LCS/LCSD for confirmation of low or high failure. If the LCS/LCSD confirms low, all samples must be re-extracted, unless there is insufficient volume for re-extraction. If the LCS/LCSD confirms high, then all non-detect samples may be reported with client approval. Initiate an NCM and email the respective project manager with the details of the %recovery failure(s). Any sample(s) with detections above the RL must be re-extracted, if extra volume is available.

9.6 Matrix Spike (MS) and Matrix Spike Duplicate Samples (MSD)

One MS/MSD pair is required with each analytical batch. Note that some programs (e.g., North Carolina and South Carolina) require preparation and analysis of an MS/MSD pair at a 10% frequency. Preparation of the MS is described in Section 7.2.11. The MSD is another aliquot of the sample selected for the MS that is spiked in the same manner as the MS.

Acceptance Criteria: The MS and MSD recoveries must fall within the established control limits, which are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. The relative percent difference (RPD) between the MS and MSD must be less than the established limit, which is based on statistical analysis of past results, unless otherwise dictated by project requirements. Current control limits are maintained in the LIMS.

Corrective Actions: If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of analytical problems, and qualified results may be reported. The situation must be described in an NCM and in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

If the recovery for any component is outside control limits for both the MS and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.

The MS must be analyzed at the same dilution level as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.7 Surrogates

Each field sample, QC sample, and each calibration standard that is used for the AR1660 initial calibration, is spiked with surrogate compounds decachlorobiphenyl (DCB) and trichloro-m-xylene (TCMX). The surrogate spike solution is prepared as described in Section 7.2.12.

Acceptance Criteria: The surrogate recoveries must be within the established control limits, which are set at ± 3 standard deviations around the historical

mean, unless project requirements dictate otherwise.

Corrective Action: If recoveries of the surrogates in blanks are outside of the control limits, check for calculation or instrument problems. High recoveries might be acceptable if the surrogate recoveries for the samples and other QC in the batch are acceptable. Low surrogate recoveries in the blank require re-preparation and reanalysis of the associated samples.

For field samples, surrogate recovery is calculated and reported for DCB only. TCMX may also be added. However, if both surrogate compounds are added, and recoveries calculated, and either surrogate fails to fall within the control limits, corrective actions are required (this also applies to programs that require the use of only one surrogate).

If matrix interference is not obvious from the initial analysis, it is only necessary to re-prepare and reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effects, as long as the extraction/instrument system is proven to be working properly.

Note: For BP samples, if the surrogate percent recovery fails, the recovery must be confirmed by re-extraction and reanalysis with the following exceptions:

- The lab has unequivocally demonstrated a sample matrix effect and informed the BP representative.
- The recovery exceeds the upper control limits and all target analytes in the sample are non-detect.

9.8 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-00610. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

10.3.1 Samples are extracted and prepared for analysis as described in SOPs TA-OP-0301 or TA-0P-0323 (aqueous samples) and TA-OP-0302 (solid samples).

10.3.2 Acid cleanups are routinely performed on sample extracts. Sulfur cleanups are performed as needed. Cleanup procedures are described in SOPs TA-OP-0364 (silica gel cleanup), TA-OP-0353 (sulfur cleanup), and TA-OP-0383 (sulfuric acid cleanup). Lot# of reagent(s) used for cleanup must be

noted where applicable in an NCM or in the prep batch sheets.

10.4 Calibration

10.4.1 TestAmerica Seattle gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

10.4.2 Use the ChemStation chromatography data system to set up GC method for calibration. See Table 2 for typical operating conditions. These methods may also be found in the maintenance log book for each instrument and may vary depending on instrument.

10.4.3 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.4.4 After processing the calibration data, the associated initial calibration verification is linked in TALS to the first set of samples analyzed after the calibration. *Review the ICAL, acknowledge any Data Review Checker (DRC) findings, document the review on the ICAL checklist,* and submit to a qualified peer or the group leader for final review.

10.4.5 A new calibration curve must be generated initially, after major changes to the system, or when continuing calibration criteria cannot be met. Major changes include installation of new columns.

10.5 Initial Calibration (ICAL)

10.5.1 An external or internal standard calibration using seven concentration levels of the AR1660 mixture is routinely performed. (At least five calibration levels are required or 6 levels if using a quadratic fit.) This provides concentration levels for Aroclor 1016, Aroclor 1260, and the surrogate compounds DCB and TCMX.

10.5.2 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.5.3 The calibration curves for Aroclors 1016 and 1260 and the surrogate compounds are modeled either as average calibration factors (CF) or as calibration curves using a systematic approach to selecting the optimum calibration function.

10.5.4 The calibration for each of the other Aroclors (see Table 1) is initially determined using one point calibrations. As needed, the laboratory may generate a multi-point calibration for other commonly detected Aroclors, such as 1221, 1254, and 1248. When additional multi-point calibrations are developed for the other Aroclors, a second-source ICV standard is also analyzed.

NOTE: Samples from sites known to be contaminated with specific Aroclors should be analyzed using a multi-point calibration curve for the identified Aroclors. This information is provided to the analyst through special instructions in the LIMS.

NOTE: Generally, it is NOT acceptable to remove points from a calibration for the purposes of meeting calibration criteria, unless the points are the

highest or lowest on the curve AND the reporting limit and/or the linear range is adjusted accordingly. The only exception is that a level may be removed from the calibration if the reason can be clearly documented, for example a broken vial. A minimum of five levels must remain in the calibration for a linear regression (or 6 levels for quadratic). The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration.

10.5.5 The high and low standard for the initial calibration of the AR1660 mixture defines the acceptable quantitation range for all of the Aroclors. If a sample extract contains any Aroclor at a concentration that exceeds the upper range of the calibration, then the extract must be diluted and reanalyzed.

10.5.6 Select 5 major peaks in each Aroclor pattern (only 3 peaks are used for Aroclor 1221). Calculate the response of each of the major peaks for each Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be co-eluting with contaminant peaks from the quantitation (i.e. peaks that are significantly larger than would be expected from the rest of the pattern).

NOTE: A minimum of three accurate peaks must be used to quantify an Aroclor.

10.6 Resolution Check

Note: The 1260 resolution peak analytes must be added to the stock standard list of analytes during the entry of the standard into the LIMS. The “calibrate” box does not need to be checked and a concentration does not need to be entered for these analytes.

In the AR1660 standard, a resolution check is evaluated on the trailing triplet peaks of the Aroclor 1260 chromatographic analyte pattern in the ICV and CCVIS standards. These three peaks are identified as 1260 Res1, 1260 Res2 and 1260 Res3. The minimum resolution requirement between peaks1 & 2 and 2&3 is <75% on the primary reporting column, using the following SW-846 formula:

$$\%\text{Resolution} = \frac{V}{(H1+H2)/2} * 100\%$$

Where: V = Valley height
H1 = Height of peak 1
H2 = Height of peak 2
H3 = Height of peak 3

For the check of peaks 2 and 3, substitute H2 for H1 and H3 for H2 in the formula above, where H3 is the height of peak 3. See Figure 12 for an example of the Chrom resolution document that is generated in Peak Review.

Note: In the example, the resolution check is performed on both columns; however, the minimum requirement is that the check passes on one column.

Corrective Action: In the event that the resolution check fails, instrument maintenance must be performed to correct the issue causing the loss of resolution. Replacing the guard and/or analytical columns may be necessary.

10.7 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors (CF), linear regression *or* non-linear regression curves, using a systematic approach to select the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until calibration acceptance criteria are met.

10.8 Average Calibration Factor

Acceptance Criteria: The RSD must be ≤ 20%.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

10.9 Evaluation of the Linear Calibration Functions

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than reporting limit (RL), and preferably less than the MDL.

Also examine the residuals, but with particular attention to the residuals at the bottom of the curve. If the intercept or the residuals are large, the calibration should be repeated.

The linear regression must have a correlation coefficient (r) ≥ 0.99. Some programs (e.g., USACE and AFCEE) require a correlation coefficient ≥ 0.995.

Corrective Action: If the correlation coefficient falls below the acceptance limit, the linear regression is unacceptable and the calibration should be repeated.

10.10 Evaluation of the non-Linear Calibration Functions

Acceptance Criteria: Non-linear calibration functions may not be used to mask instrument problems that can be corrected by maintenance. They may not be used to compensate for detector saturation. If it is suspected that the detector is being saturated at the high end of the curve, remove the higher concentration standards for the curve and try a 1st order fit or average RF.

The non-linear regression must have a correlation coefficient (r) ≥ 0.99. Some programs (e.g., USACE and AFCEE) require a correlation coefficient ≥ 0.995.

Corrective Action: If the correlation coefficient falls below the acceptance limit, the linear regression is unacceptable and the calibration should be repeated.

10.11 Polynomial regression fits of third order or higher are not allowed for this method.

10.12 See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

10.13 Second-Source Initial Calibration Verification (ICV)

The second-source ICV standard usually consists of Aroclors 1016 and 1260 only. The stock standards are obtained from a source different than that of the standards used for the calibration. The preparation of the ICV standard is described in Section 7.2.4. The concentration of each Aroclor in the ICV is 0.10 µg/mL; the concentration of each surrogate is 0.01 µg/mL. The ICV standard is analyzed immediately following the initial calibration.

If it is necessary to generate a multi-point calibration for any of the other Aroclors, then an ICV standard containing the specific Aroclor(s) is analyzed immediately following the calibration.

Acceptance Criteria: The result for the target analyte(s) in the ICV standard must be within ± 20 of the expected value.

Corrective Action: If this is not achieved, the ICV standard, calibration standards, and instrument operating conditions should be checked. Correct any problems and rerun the ICV standard. If the ICV still fails to meet acceptance criteria, then repeat the ICAL.

10.14 Calibration Verification

10.14.1 *Continuing Calibration Verification (CCV), 100 ug/L*

A mid-level calibration standard is analyzed as the continuing calibration verification (CCV) standard. The Continuing CCV is run at the beginning of an analytical sequence for every 12 hours or 20 sample injections, whichever is more frequent. If there are more than 20 samples in an analytical sequence, another CCV must run before the next bracket. Closing CCVs are not required since internal standard is used. The 1016/1260 CCV must run for all samples. If a different Aroclor is identified, the CCV for that Aroclor must be run within +/- 12 hours of the sample. **NOTE**: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration. In this case, the ICV may serve as the CCV.

NOTE: Samples are defined as field samples and batch QC (MB, LCS, MS) and do not include CCVs, CCBs, instrument blanks, etc.

For samples analyzed under DoD QSM and LAMP, CCVs are analyzed before sample analysis after every 10 injections, and at the end of the sequence.

10.14.2 RL Standard

It may also be appropriate to analyze a standard prepared at or below the reporting limit (RL) for the method at the end of the analytical sequence, as a minimum (see Section 7.2.9). This standard can be used to rule out false negatives in client samples in cases where the %D for one or more of the analytes in a bracketing CCV falls below the lower acceptance limit. The

results for the RL standard are not evaluated **unless** the previous CCV fails acceptance criteria.

10.14.3 Acceptance Criteria for Continuing Calibration Verification (CCV)

10.14.3.1 Detected Analytes (≥ RL)

For any analyte detected at or above the reporting limit (RL) in client samples, the percent difference (%D) for that analyte in the CCVs run before the sample - on the column used for quantitation, must be within ± 20%. Closing CCVs are not required since internal standard is used.

NOTE: DoD and LaMP samples require closing CCVs.

If a failing CCV is followed by a second verifying CCV and the subsequent calibration verification injection also fails, a new initial calibration curve must be processed. (i.e., no more than two consecutive injections of the calibration verification may be processed.

The %D is calculated as follows:

$$\%D = \frac{\text{Measured Conc} - \text{Theoretical Conc}}{\text{Theoretical Conc}} \times 100$$

10.14.3.2 Analytes Not Detected (< RL)

For any analyte not detected (ND) in client samples, the %D for that analyte in the bracketing CCVs should also be within ± 20%.

However, if the CCV %D exceeds +20% and the sample results are ND, it still may be possible to report sample results. In this case, the client should be consulted and an NCM written.

If the CCV % D falls below -20% and sample results are ND, but the target analytes are detected in the RL Standard, it may still be possible to report sample results, since the detection of the analyte(s) in the RL Standard indicate that there was sufficient sensitivity to detect the analyte(s) in the samples. In this case, the client should be consulted and an NCM written. **Note**: For DOD, all samples (regardless of analyte detection in the samples) must be re-analyzed, at a dilution if necessary, until all capping CCV recoveries are within control limits.

10.15 Retention Time (RT) Windows

10.15.1 Initial determination of Retention time windows.

10.15.1.1 The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV in the daily analytical sequence, whichever is more recent.

10.15.1.2 Evaluate the deviation from expected retention time for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours.

10.15.1.2.1 If three days of analytical data are not available, use a default RT window of 0.01 minutes. At the end of the

batch evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.

10.15.1.3 Calculate the mean and standard deviation of the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RT_i - \overline{RT}\right)^2}{n-1}}$$

Where:

RT_i = Retention time for the i^{th} injection.
n = Number of injections (typically 3).
SD = Standard deviation.

Note: This can be done automatically utilizing the Control Chart feature in TALS.

10.15.1.4 Multiply the maximum deviation by 1.5. This is the retention time window, unless the result is less than 0.01 min, in which case the window is set at 0.01 min . For example, if the maximum RT deviation for a specific analyte is 0.008 min, then the RT window is set at +/- 0.012 min.

10.15.1.4.1 NOTE: For the multi-component analytes, for example Aroclors, the maximum deviation must be evaluated for each of the 3 to 5 major peaks used for sample calculations.

10.15.2 Ongoing evaluation of retention time windows

10.15.2.1 Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV of the day. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the retention time window (except as discussed below).

10.15.2.1.1 Matrix spike analytes may fall outside the retention time window if there is a large non-target peak coeluting with the analyte in the matrix spike

10.15.2.2 If any analytes fall outside the retention time window in CCVs, LCS or matrix spikes (except as discussed above for matrix spikes) then the RT windows for those analytes shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

10.15.2.3 Retention time windows should be reliably narrower than +/- 0.03 minutes. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained.

10.15.3 Sample Retention Time Criteria

10.15.3.1 The surrogate should fall within the established RT window. Target analyte peaks should be within the established RT window to be reported as such. If the surrogate RT indicates an RT shift, it may be necessary to evaluate the affected sample with a wider window relative to the surrogate RT shift and report with a NCM about the retention time shift. It may be necessary to run the sample at a dilution to lower any matrix effects causing the RT shift.

10.15.3.2 Aroclors are determined through pattern recognition. Sometimes, sample matrix can cause the peaks to fall outside the RT windows but the Aroclor pattern can still be recognized. The results can still be reported with an NCM about the retention time shift.

10.16 Sample Analysis

10.17 Gas Chromatography

10.17.1 Chromatographic conditions for this method are presented in Table 2.

10.17.2 Use the Chemstation interface to establish instrument operating conditions for the GC.

10.17.3 Raw data obtained are processed using Chrom. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the software.

10.18 Sample Introduction

10.18.1 An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract. For dual-column instruments, 1 to 2 µL of sample extract are automatically injected onto two columns, depending on the response of the instrument.

10.18.2 Samples, standards, and QC samples must be introduced using the same procedure.

10.18.3 All extracts and standards are allowed to warm to room temperature before injection.

10.18.4 Use Chemstation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

10.19 Analytical Sequence

An analytical sequence starts with a minimum five-level initial calibration (ICAL) or a daily calibration verification.

10.19.1 Create a worklist on Chrom that reflects the machine run sequence. The Chrom worklist will serve as the instrument sequence logbook. *Add the solvent used to dilute samples to the sample run* reagent tab. This will serve as the record of the solvent lot used to dilute the samples.

10.19.2 Following is the typical analytical sequences:

Primer	(Injection of any standard that contains analytes to establish the stability of the chromatographic system.)

Rinse blank	Hexane
Daily initial CCVs	(Unless an ICAL is performed, which is immediately followed by the second-source initial calibration verification.) The CCVs *may i*nclude injections for AR1660. AR3262, AR1242, AR2154, and AR4868*. Only the AR1660 is required for all samples.* (DoD QSM projects require all target Aroclor compounds).
CCB or MB	*(A MB may be re-injected and used as a CCB – a CCB is not counted as a sample injection)*
Sample injections	Samples up to 12 hours from the CCVs or 20 samples whichever is less. For DoD QSM and LAMP, only 10 samples can be in the bracket.
CCV (closing) + CCB	*AR1660* only if required (DOD) or if running more samples in the sequence.
This can be followed by another bracket of sample injections and CCVs if needed.	

10.20 When a sample result exceeds the upper calibration range, then that sample extract is diluted to obtain a result in the upper half of the calibration range and reanalyzed. Any samples that were analyzed immediately following the high sample are evaluated for carryover. If the samples had target analyte detections at or above the RL, the samples must be reanalyzed to rule out carryover.

10.21 Upon completion of the analytical sequence, review chromatograms in Chrom/Peak Review (Chrom) and determine whether manual data manipulations are necessary. All manual integrations must be justified and documented. See Corporate SOP CA-Q-S-002 for requirements for manual integration. In Peak Review, a manual integration reason must first be selected in the drop down menu prior to performing a manual integration. The Chrom/Peak Review software automatically generates before and after chromatograms with sufficient scaling, including the manual integration reason, the analyst name, and the date and time stamp.

10.22 Perform a level 1 data review*, acknowledge any Data Review Checker (DRC) findings,* and document the review on the data review checklist. Submit the review checklist to a Data Reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

10.23 Instrument Maintenance

Refer to section 11.10 of TA-GS-0308 for maintenance procedures and spare parts lists.

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, model and serial number for each major component (e.g., GC, autosampler, column) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a tune, CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL or MB, etc as may be the case). If columns were replaced during maintenance, the make, model and serial number of the columns must be documented in

the maintenance log book.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification of Aroclors

Retention time windows are used for identification of Aroclors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram. See Figures 3 through 11 for chromatographic depictions of each individual aroclor.

11.2 Quantitation of Aroclors

Quantitation of Aroclors is accomplished using 5 major peaks (3 peaks for Aroclor 1221). The peaks must be within the established retention time windows. If there is an interference that affects the accuracy of results, the analyst may use as few as 3 major peaks (2 peaks for Aroclor 1221). The same peaks that are used for sample quantitation must be used for standards and QC quantitation.

11.3 Second column confirmation of Aroclors is performed only when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: USACE projects require the use of second-column confirmation of Aroclors unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

11.4 Dual Column Quantitation and Reporting

NOTE: Dual column quantitation is not routinely performed for PCB analysis. This section is included for those clients/projects that require dual column confirmation.

11.4.1 The result from a designated primary column is normally reported. The result from the secondary column is reported if any of the following is true:

11.4.1.1 There is obvious chromatographic interference on the primary column.

11.4.1.2 The difference between the result on the primary column and the result on the secondary column is > 40% and chromatographic interference is evident.

11.4.1.3 A continuing or bracketing standard fails on the primary column, but is acceptable on the secondary column. However, if the difference between the primary column and secondary column results is > 40% and the primary column calibration verification fails, then the sample must be evaluated for reanalysis.

If the relative percent difference (RPD) between the results on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. The RPD is calculated as follows:

$$\%RPD = \frac{\left|R_1 - R_2\right|}{1/2\left(R_1 + R_2\right)} \times 100\%$$

Where R_1 is the result for the primary column, and R_2 is the result for the secondary column.

11.5 Surrogate Recovery

11.5.1 Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB).

11.5.2 In cases where the addition of the surrogate tetrachloro-m-xylene (TCMX) is required, its recovery is calculated and reported. In cases where both surrogates are added, the recovery of each surrogate is evaluated and corrective action must be taken if either surrogate recovers outside of the established control limits and matrix interference is not evident. Depending on project requirements, corrective action may be necessary only if DCB and TCMX are both outside of acceptance limits. (LaMP: if surrogates fail acceptance criteria they must be re-extracted unless the samples are high ND or demonstrate matrix interference and client is notified. See Section 9.7)

11.6 Calibration Range and Sample Dilutions

If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for any analyte, they must be reanalyzed to rule out carryover. It may also be necessary to dilute samples because of matrix interferences.

11.6.1 If the initial diluted run has no hits or hits below 20% of the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.6.2 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

11.6.3 Reporting Dilutions

Some programs (e.g., South Carolina and AFCEE) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported.

For DoD projects, the over-range analyte(s) from the least diluted run is reported as secondary status. From the dilution analysis, the surrogates are reported as secondary status and the diluted analyte(s) are reported as primary status.

11.7 Interferences in Observed in Samples

11.7.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants. See CA-Q-QM-003 Technical Guidance on Reporting of Multi-Component Organochlorine Analytes.

11.7.2 GC/MS Confirmation of Samples for EPA Region 10

If the samples being analyzed are for EPA Region 10 and the laboratory has agreed to perform this option, then all analyte identifications of positive concentrations that are of sufficient concentration for that purpose must be confirmed by GC/MS analysis. For multi-component analytes, the confirmation is for the presence of chlorinated biphenyls in PCB and the presence of chlorinated camphenes in Toxaphene. See Appendix 1 for detailed instructions for performing GC/MS confirmation for EPA Region 10 work.

11.7.3 Suspected Negative Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative. If numerous PCB peaks are present but there are no good matches to any individual Aroclor fingerprint, the Aroclor or Aroclors that most closely match the sample are chosen to quantify the peaks as those Aroclors. At a minimum, the Data Review Template prepared by the analyst should include the following comment for inclusion in the case narrative:

> "Sample XXXX appears to contain PCBs based on the presence of numerous PCB peaks. However, due to weathering or other environmental processes, the PCBs in the sample do not closely match any of the Aroclor standards we use to calibrate our instruments. We quantified and reported the sample as Aroclor ZZZZ (or as a mixture of Aroclors ZZZZ and YYYY). Due to the poor match with the Aroclor standard(s), there is increased qualitative and quantitative uncertainty associated with this result. This approach is consistent with the guidance in section 7.9.3 of SW-846 method 8082A. If these results do not meet the needs of your project then we would suggest a further analysis of the sample. Depending on the objectives, this may include congener-specific analysis by 8082A; or analysis a more specific method, (e.g., method 1668 or an adaptation of method 8270) for PCB congeners or PCB homolog totals."

11.7.4 Suspected Positive Interferences

If no further cleanup is reasonable and interferences are evident that are suspected of causing false positive results, consult with the laboratory Project Manager to determine if analysis using additional confirmation techniques is appropriate for the project. Use of additional confirmation columns is another possible option. At a minimum, the Data Review Template prepared by the analyst should include the following comment for inclusion in the case narrative:

> " Based on review of the chromatograms for samples _____, it is my opinion that the evident interferences may be causing false results.
>
> Date _____ Analyst _____"

11.8 Calculations

11.8.1 Concentration of Analyte in Sample Extract

Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10.7 for details on establishing the calibration function):

Average Calibration Factor: $$C_e = \frac{A_e}{CF}$$

Linear Regression: $$C_e = \frac{[A_e - b]}{a}$$

Where:

C_e	=	Concentration of the analyte in the sample extract (ng/mL).
A_e	=	Peak area for the analyte in the sample extract injection.
b	=	y-intercept of the calibration fit.
a	=	Slope of the calibration fit.

11.8.2 Concentration of Analyte in Original Sample

The concentration of the analyte in the original sample is calculated as follows:

$$C_{sample} = \frac{C_e}{1000\frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF$$

Where:

C_{sample}	=	Concentration of analyte in original sample (µg/L or µg/kg).
C_e	=	Concentration of analyte in sample extract injected in GC (ng/mL).
$1000\frac{ng}{\mu g}$	=	Factor to convert ng/mL to µg/mL.
V_e	=	Volume of sample extract (mL).
V_s	=	Volume (or weight) of original sample (L or kg).
DF	=	Dilution Factor (post extraction dilutions)

11.8.3 Calculating the Concentration in the Extract via Internal Standard Calibration model

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

11.8.3.1 Average Response Factor Calibration

If the average of all the RSDs of the response factors in the initial calibration is ≤15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

Where:

C_{ex} = Concentration in the extract, µg/mL
R_x = Response for the analyte
R_{is} = Response for the internal standard
C_{is} = Concentration of the internal standard
$\overline{RF}$ = Average response factor

11.8.3.2 Linear Fit Calibration

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

Where:

C_{ex} = Concentration in the extract, µg/mL
R_x = Response for the analyte
R_{is} = Response for the internal standard
C_{is} = Concentration of the internal standard
A = Intercept of linear calibration line
B = Slope of linear calibration line

11.8.4 Spike Recovery Calculation

LCS, MS, and surrogate spike recoveries are calculated using the following equation:

$$\%\text{Recovery} = \frac{\text{Measured Concentration}}{\text{Spiked Concentration}} \times 100\%$$

11.8.5 MS/MSD RPD Calculation

The percent difference between the analyte concentration in the MS and the MSD is calculated as follows:

$$RPD = \frac{|MS - MSD|}{1/2(MS + MSD)} \times 100\%$$

11.9 All data are subject to two levels of review, which is documented on a checklist, as described in SOP TA-QA-0635.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory

maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

Instrumentation software must have each target limit set to the lowest MDL. CHROM (LOD).

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TC-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Waste Disposal SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Solvent/Methylene Chloride waste. Any waste solvent is collected in beakers and then poured into the $MeCl_2$/solvent satellite waste barrel located next to the neutralization tank in lab hood #17. The funnel lid on the drum must be closed after each use. At or before the satellite waste reaches 55 gallons, the barrel is transferred to the waste disposal room from where it is sent out for recycling or fuel blending.

14.1.2 Vialed extract waste. Sample extracts are transported in to the waste room and placed on the sample processing shelf. The vials are then bulked into a corrosive flammable loose pack waste stream and sent out for incineration.

14.1.3 Expired reagents and standards are discarded into satellite waste buckets located underneath the bench top and labeled as "Hazardous Waste: Contains PCB's" with an out of service date. Once the buckets are full, they are lab packed and sent out for incineration.

14.1.4 Mercury must be collected and lab packed and sent out for retort.

14.2 Samples containing polychlorinated biphenyls (PCB's) at concentrations $\geq$50 ppm are regulated under the Toxic Substance Control Act (TSCA) and must be segregated from all other waste streams. Analysts are responsible for contacting the Group Leader, Sample Control, and the Waste Coordinator immediately if a sample falls into the TSCA category. These samples are lab packed and sent out for incineration.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,

15.1.1 Method 8082, Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 0, December, 1996.

15.1.2 Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 1, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, February 2007

15.1.3 Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

15.2 EPA Handbook of Analytical Quality Control in Water and Wastewater Laboratories, Test Method EPA-600/4-81-045, September 1982.

16.0 Method Modifications:

None

17.0 Tables and Figures

Table 1: Analyte List and Standard Reporting Limits
Table 2: Typical Instrument Conditions
Table 3: Calibration Levels (µg/mL)
Table 4: Standard LCS/MS Spike and Surrogate Spike Levels (µg/L)
Table 5: Low Level LCS/MS Spike and Surrogate Spike Levels (µg/L)
Table 6: DoD QC Tables
Table 7: Summary of QC Requirements
Figure 1: Example Chromatogram with Sulfur Interference
Figure 2: Example Chromatogram of Extract with Methylene Chloride Contamination
Figure 3: Example Chromatogram of Aroclor 1221.
Figure 4: Example Chromatogram of Aroclor 1268.
Figure 5: Example Chromatogram of Aroclor 1016.
Figure 6: Example Chromatogram of Aroclor 1232.
Figure 7: Example Chromatogram of Aroclor 1242.
Figure 8: Example Chromatogram of Aroclor 1248
Figure 9: Example Chromatogram of Aroclor 1254
Figure 10: Example Chromatogram of Aroclor 1260
Figure 11: Example Chromatogram of Aroclor 1262
Figure 12: Example Chrom documentation of Resolution check
Appendix 1: GCMS Confirmation of Pesticides and PCBs for EPA Region 10

18.0 Revision History

- Revision 24, dated 05 October 2017
  - Updated summary of method, section 2.1.1
  - Edited calibration, section 10.4.4
  - Edited calibration verification, section 10.14
  - Edited analytical sequence, section 10.19 and 10.22
  - Updated chromatograms, Figure 1-11

  - Updated approvers

- Revision 23, dated 23 September 2016
  - Updated chemicals in section 5.2
  - Added number of calibration points required for quadratic curves, sections 10.5.1 and 10.5.4
  - Added non-linear regressions to sections 10.7 and 10.10
  - Removed restriction on use of 2nd order regressions from section 10.11
  - Removed curve fit calculations that are covered in the corporate SOP, referenced in section 10.12
  - Revised language in section 10.16.1, 10.16.4.1 and 10.21.2 to clarify when CCVs are to be analyzed.
  - Updated Table 7

- Revision 22, dated 26 July 2016
  - Added additional extraction SOP references to section 1.3
  - Added additional cleanup SOP references to section 2.1.4
  - Update details on interferences section 4.1 and 4.2
  - Added guard column, section 6.2
  - Updated cleanup procedures, section 10.3.2
  - Updated section 10.4.2
  - Updated information on CCV and criteria for CCV, section 10.16
  - Updated retention time criteria, section 10.17.1 and 10.17.3
  - Updated typical sequence, section 10.21
  - Added reference to technical guidance on reporting multi-component organochlorine analytes, section 11.71
  - Updated Table 2
  - Updated Table 7

- Revision 21, dated 9 February 2015
  - Add internal standard calibration option to section 2.2
  - Update the mixed Aroclor standard as 1242/1268 in section 3.6
  - Update single Aroclor standard to be 1248 in section 3.7
  - Add Florisil cleanup option for 8081/8082 combo extracts to section 4.1
  - Add Mercury cleanup option for 8081/8082 combo extracts to section 4.2
  - Updated columns used in section 6.2
  - Added IS information in section 7.2.2.3
  - Added IS preparation information in section 7.2.3.3
  - Updated LVI sample volume and standard preparation information in sections 7.2.10, 7.2.11 and 7.2.12
  - Added IS requirements in section 9.3
  - Added initial calibration by IS information in section 10.5.1
  - Added resolution check requirement and criteria in section 10.6
  - Added detailed IS calibration information in section 10.13
  - Added IS calibration data calculation formulas in section 11.8.3
  - Added a Chrom/Peak Review example document for the resolution check as Figure 12

- Revision 20, dated 14 August 2013
    - Added LVI information to section 2.1.1
    - Add LVI spiking information to sections 7.2.10 and 7.2.11
    - Add DoD corrective action for failed method blank criteria in section 9.3
    - Add DoD corrective action for failed LCS criteria in section 9.4
    - Add dilution reporting status information for DoD projects in section 11.6.3
    - Updated section 5.0, Safety
    - Updated section 13.0, Pollution Control

- Revision 19, dated 6 July 2012
    - Updated column types, section 6.2
    - Updated cleanup procedures, sections 2.1, 4.2 and 10.3.2.
    - Updated waste streams, sections 14.1 and 14.2.
    - Updated Tables 2 and 3
- Revision 18, dated 31 May 2011
    - Incorporated ROMDs 00019 and 00026 in sections 6.1 and 10.28.
    - Specified software in section 6.1.
    - Incorporated ROMD 00025 in section 9.4
    - Incorporated ROMD 00020 in section 10.7 and Table 2.
    - Incorporated ROMD 00022 in section 10.16
    - Incorporated ROMD 00024 in section 10.18.4.2.
    - Incorporated ROMD 00033 in section 10.21.3.
    - Corrected control limits in 10.18.4.2 (ROMD 00001).
    - Added Figures 3 through 11
- Revision 17, dated 26 March 2010
    - Added documentation of reagent/standards and reagent/standard preparation Section 7.1.
    - Added removal of expired standards Section 7.4.
    - Added Method PCB Instrument Blank criteria for BP LaMP Section 9.3
    - Added Method Blank criteria for BP LaMP Section 9.4
    - Added LCS Criteria for BP LaMP Section 9.5
    - Added BP LaMP Surrogate criteria, Section 9.7
    - Addressed corrective action after a second CCV failure, Section 10.18.4
    - Added recording of reagents used in clean-up Section10.5
    - Added maintenance documentation and return to service requirements, section 10.28
    - Added requirement for instrument software MDLs Section12.1
- Revision 16, dated 10 March 2009
    - Added additional column options in section 6.1.
    - Updated CCV concentrations in Section 10.18.
    - Corrected minor typographical errors.
    - DoD QSM Tables in Table 7 updated to the new QSM v.4.
- Revision 15, dated 21 March 2008
    - SOP updated to include example chromatograms for special instrument situations.
    - Example Typical Instrument Sequence updated

- Revision 14, dated 12 March 2008
    - Integration for TestAmerica and STL operations.
    - This revision is a complete rewrite and an expansion of scope.

Table 1: Analyte List and Standard Reporting Limits

Compound	Water Reporting Limit (µg/L)	Soil Reporting Limit (µg/kg)
Aroclor 1016	0.5	10
Aroclor 1221	0.5	10
Aroclor 1232	0.5	10
Aroclor 1242	0.5	10
Aroclor 1248	0.5	10
Aroclor 1254	0.5	10
Aroclor 1260	0.5	10
Aroclor 1262	0.5	10
Aroclor 1268	0.5	10

Table 2: Typical Instrument Conditions

Operating conditions can also be found in the maintenance log book for each instrument.

Parameter	Recommended Conditions
Injection Port Temperature:	280 °C
Detector Temperature:	320 °C
Temperature Program:	50 °C for 0.50 minute 35 °C/min to 220 °C 20 ℃/min to 320 ℃,
Guard Column:	Phenomenex Zebron HT Deactivated Guard Column (5m x 0.25 mm ID) or Restek Siltek Guard Column (5m x 0.25 mmID) or equivalent
Column 1:	Phenomenex Zebron ZB-CLPesticides-1 (30 m X 0.25 mm ID X 0.25 um) (primary)
Column 2:	Phenomenex Zebron ZB-CLPesticides-2(30 m X 0.25 mm ID X 0.20 um) (confirmation)
Injection:	1 µL or 2 uL
Carrier Gas:	Hydrogen
Make-up Gas:	Nitrogen
Y-splitter:	Phenomenex Zebron Glass Press-Tight Y Splitter or equivalent

Table 3: Calibration Levels (µg/L)

Aroclors	Level 1	Level 2	Level 3	Level 4	Level 6	Level 7	Level 8*
Aroclor 1016	10	20	50	100	500	1000	2000
Aroclor 1221	10	20	50	100	500	1000	2000
Aroclor 1232	10	20	50	100	500	1000	N/A
Aroclor 1242	10	20	50	100	500	1000	N/A
Aroclor 1248	10	20	50	100	500	1000	N/A
Aroclor 1254	10	20	50	100	500	1000	2000
Aroclor 1260	10	20	50	100	500	1000	2000
Aroclor 1262	10	20	50	100	500	1000	N/A
Aroclor 1268	10	20	50	100	500	1000	N/A
TCMX**	1.0	2.0	5.0	10.0	50.0	100.0	200.0
DCB**	1.0	2.0	5.0	10.0	50.0	100.0	200.0

* Level 8 Calibration is analyzed for Aroclors 1016, 1260 and 1254 only since these are the most common Aroclors.
** Surrogates are included in the AR1660 calibration mix only.

Table 4: Standard LCS/MS Spike and Surrogate Spike Levels (µg/L)

Compound(s)	Concentration (µg/L)
Aroclor 1016/Aroclor 1260 mix	100
Surrogates	
Decachlorobiphenyl (DCB)	20
Tetrachlor-m-xylene (TCMX)	20

Table 5: Low Level LCS/MS Spike and Surrogate Spike Levels (µg/L)

Compound(s)	Concentration (µg/L)
Aroclor 1016/Aroclor 1260 mix	10
Surrogates	
Decachlorobiphenyl (DCB)	2
Tetrachlor-m-xylene (TCMX)	2

Table 6 : DoD QC Tables

Table G-16. LCS Control Limits for Polychlorinated Biphenyls SW-846 Method 8082 Water Matrix[18]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
Aroclor 1016	85	20	25	145
Aroclor 1260	87	19	30	145

Table G-17. LCS Control Limits for Polychlorinated Biphenyls SW-846 Method 8082 Solid Matrix[18]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
Aroclor 1016	90	16	40	140
Aroclor 1260	96	12	60	130

[18]LCS control limits are not available for Aroclors 1221, 1232, 1242, 1248, 1262, and 1268. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for surrogate compounds can be found in section G.6.

Table G-3. Surrogates

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
8082 Water:				
Decachlorobiphenyl	88	15	40	135
8082 Solid:				
Decachlorobiphenyl	91	11	60	125

Table 7: Summary of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Minimum 5-point Initial Calibration (6 required for quadratic fit)	Initial calibration prior to sample analysis	One of the options below: For avg. calibration factor: RSD ≤ *20%*. Linear least squares regression: r ≥ 0.990 **Linear least squares regression for DoD: r ≥ 0.995** **Quadratic:** r^2 ≥ 0.990	Terminate analysis; correct the problem; recalibrate. Problem must be corrected. No samples may be run until ICAL has passed.
ICV	Following initial calibration.	80 - 120% recovery. .	Terminate analysis; correct the problem; recalibrate.
CCV	Beginning and minimum every 12 hours *(or 20 samples)* and at the end of the run or every 10 *samples f*or DoD QSM and LAMP.	80 – 120% recovery.	Correct problem, then rerun CCV. If that fails, then repeat ICAL. Reanalyze all sample since the last successful CCV.
Retention time (RT) window width determination	At method set-up and after major maintenance (e.g. column change)	NA	See Section 10.19 for additional requirements.
Method Blank	One per *prep batch o*f 20 field samples or fewer.	The result must be < RL or < 1/10 the amount measured in any sample or 1/10 the regulatory limit. **For DoD and LAMP:** No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit.	Re-extract and/*or* reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.
LCS	One per batch of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must be within QSM control limits.	See Section 9.4 for additional requirements.
*CCB (*Instrument blank with surrogates)	**For DoD and BP LaMP:** analyzed after each CCV (unless the CCV is followed by a Method Blank)	**For DoD and BP LaMP:** No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the	

		regulatory limit.	
Surrogate	All field and QC samples.	Must be within laboratory control limits. **For DoD:** must be within QSM control limits.	See Section 9.6 for additional requirements.
Matrix Spike and Matrix Spike Duplicate	One pair per lot of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must be within QSM control limits.	See Section 9.5 for additional requirements.
Confirmation of Positive Results	Required for select projects (i.e. DoD QSM).	Results between primary and confirmation column RPD ≤ 40%.	Apply f if RPD ≥ 40% RPD if sample is not confirmed.

Figure 1: Example Chromatogram of Sulfur Interference

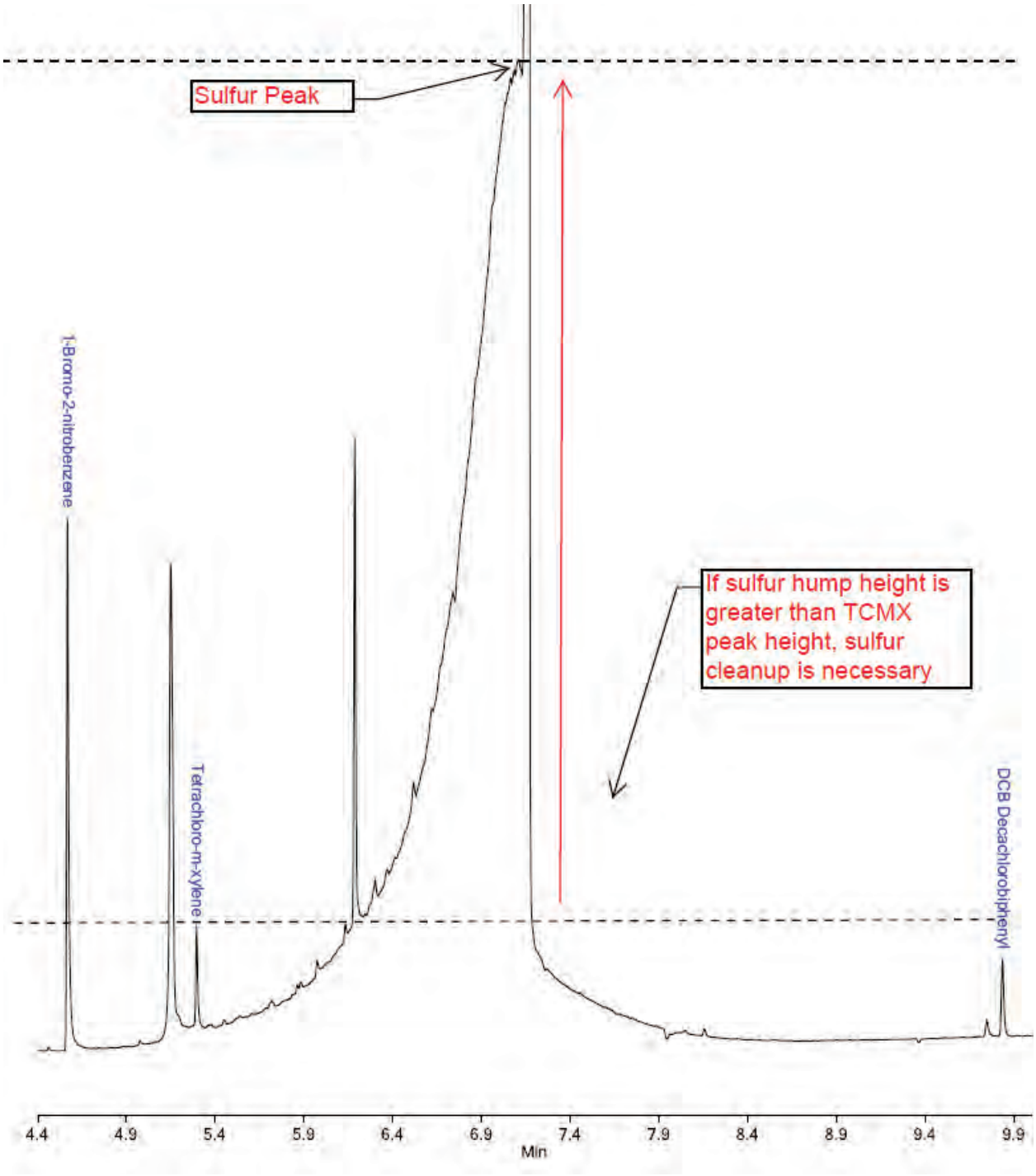


Figure 2: Example Chromatogram of Methylene Chloride Contamination

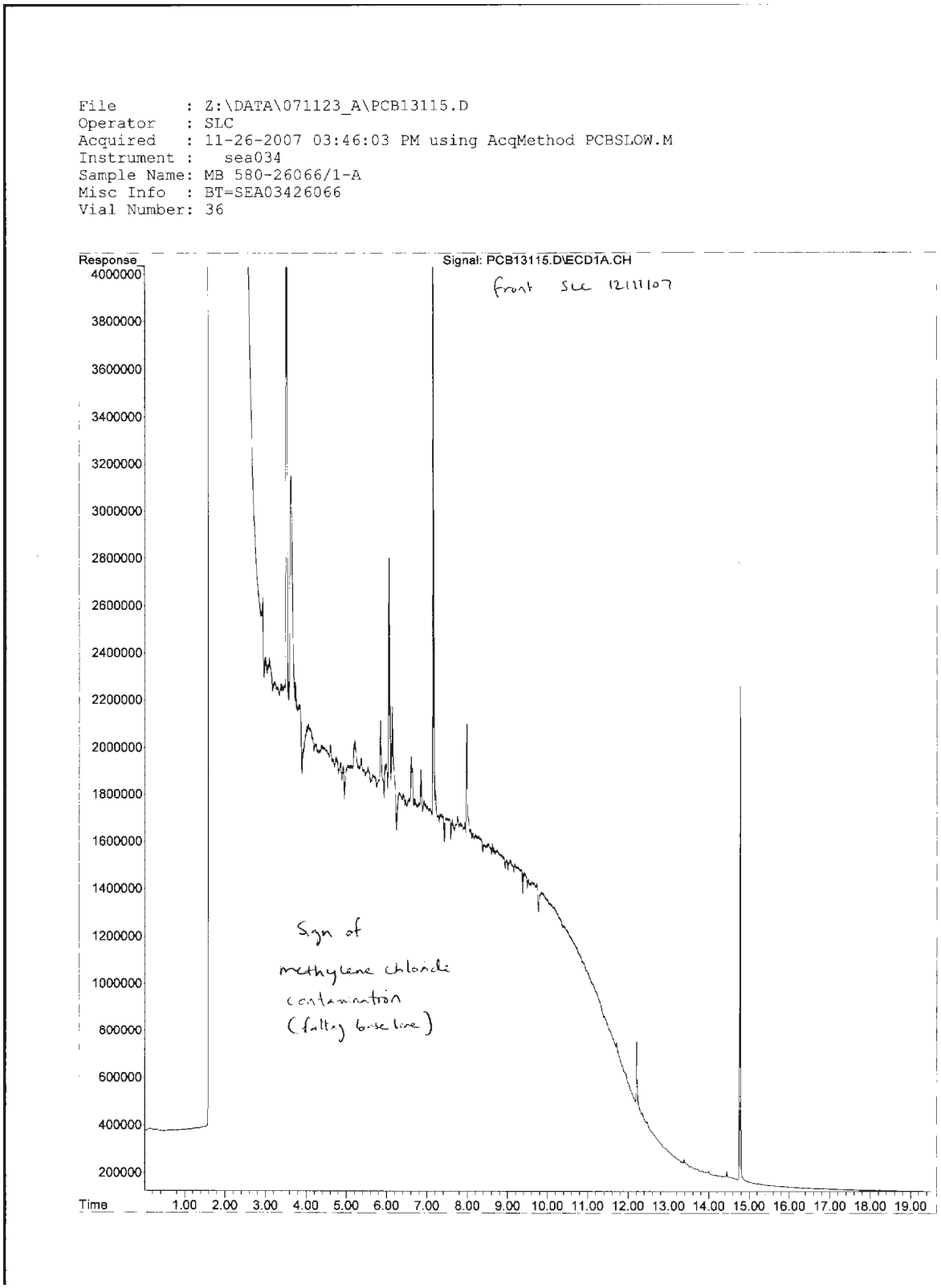
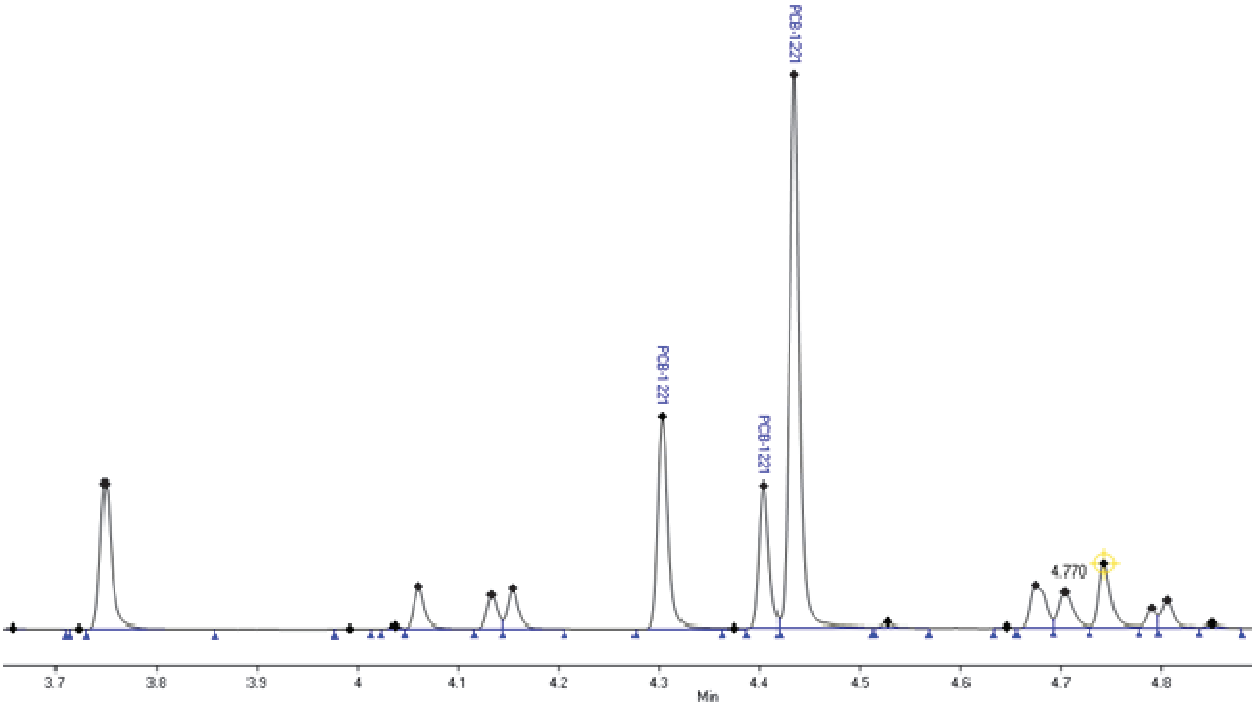


Figure 3: Aroclor 1221

(*ZB-CLPesticides-1):*



ZB-CLPesticides-2:

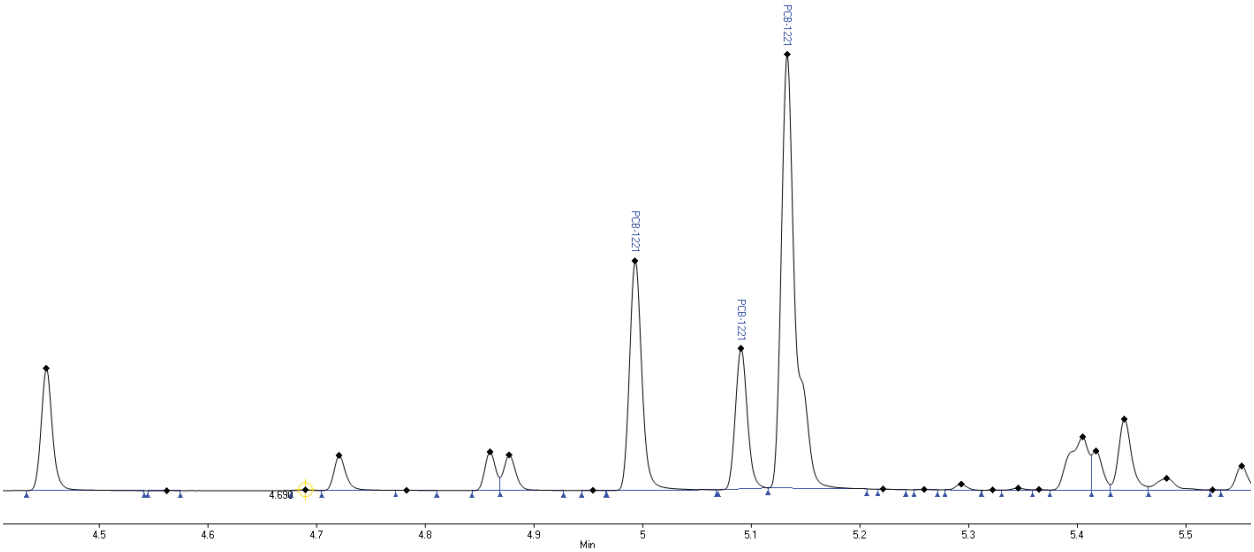
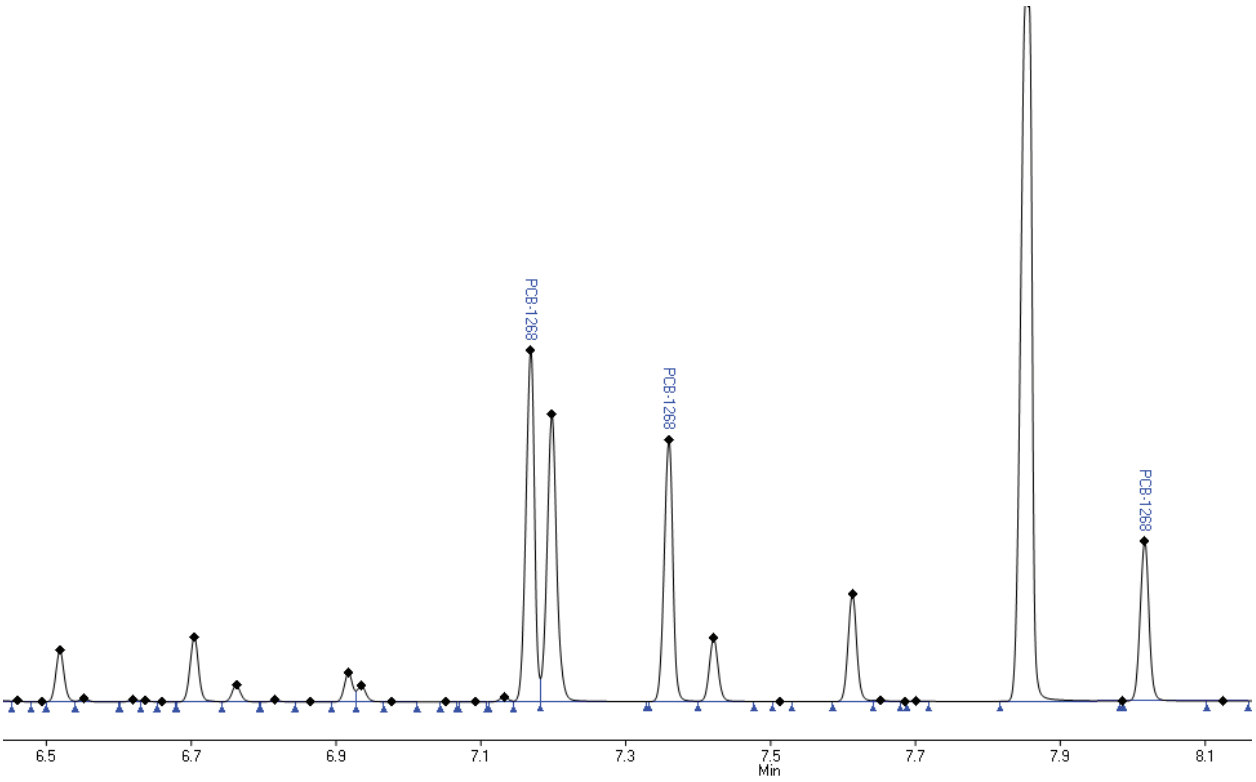


Figure 4: Aroclor 1268

ZB-CLPesticides-1:



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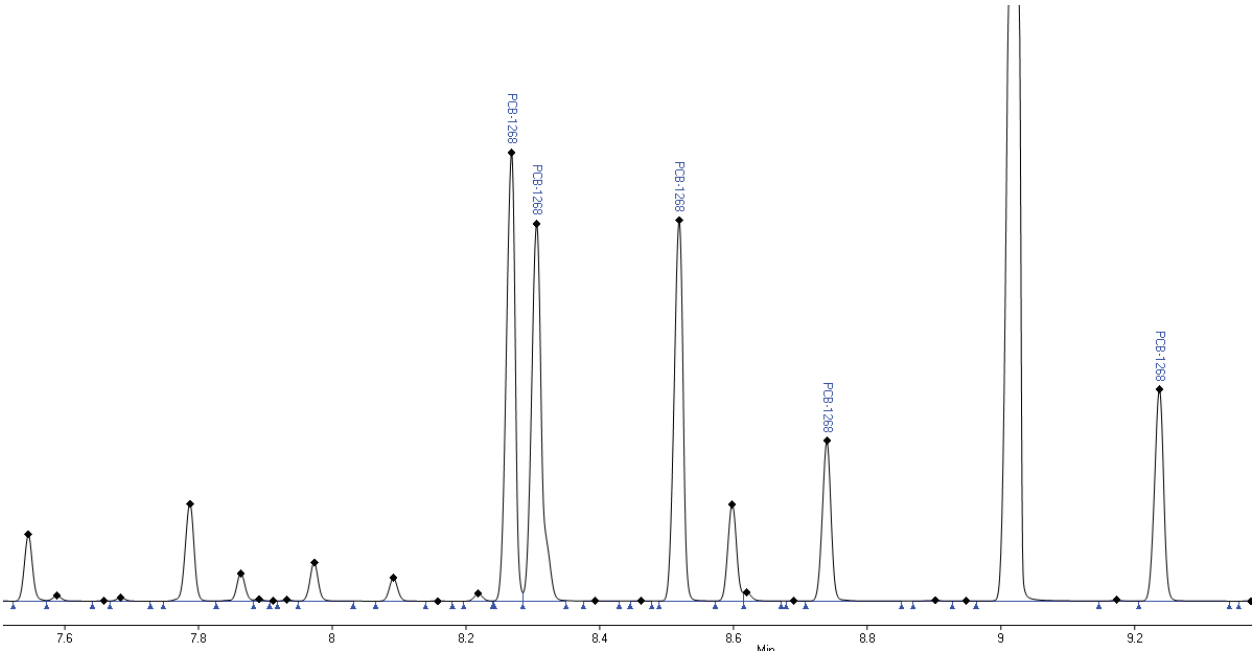
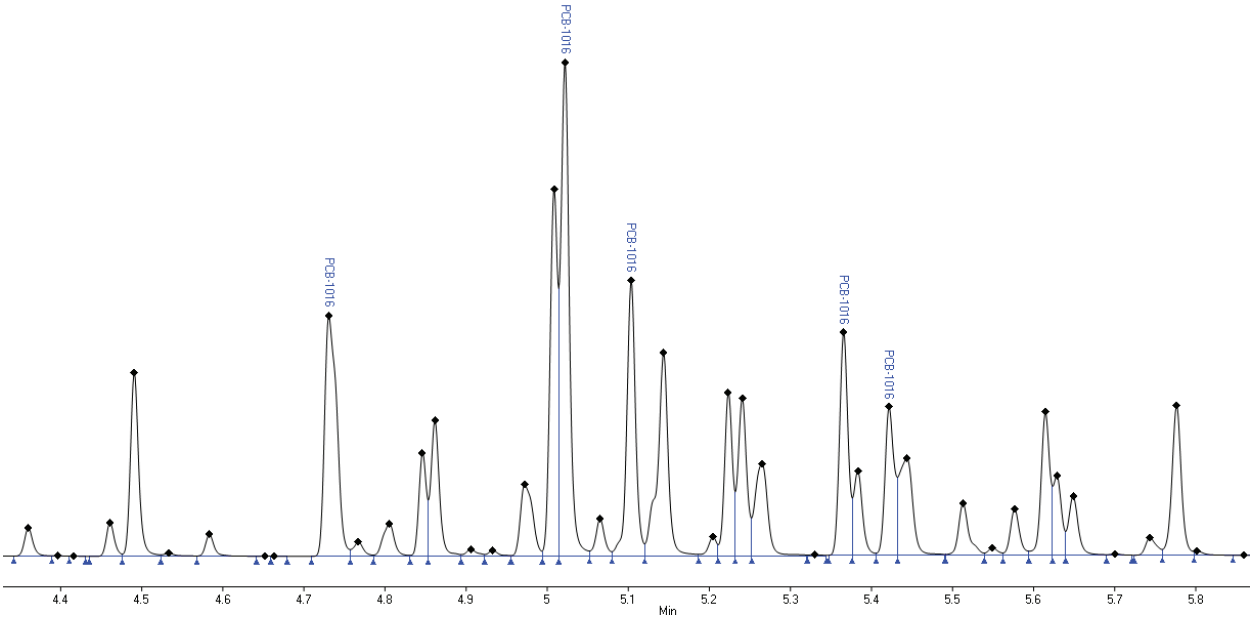


Figure 5: Aroclor 1016

ZB-CLPesticides-1:



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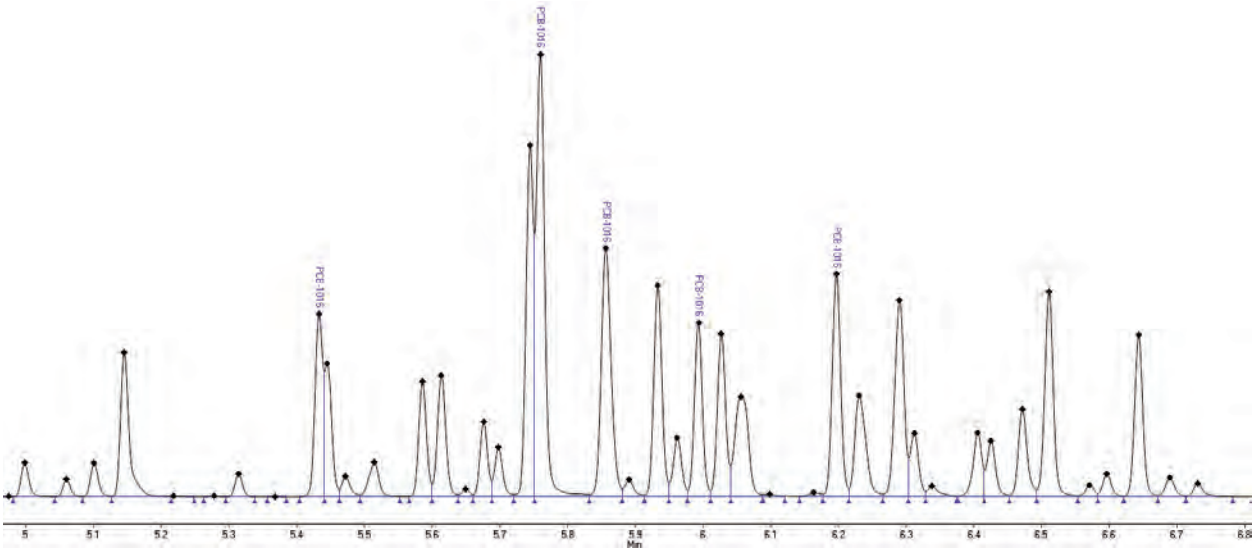
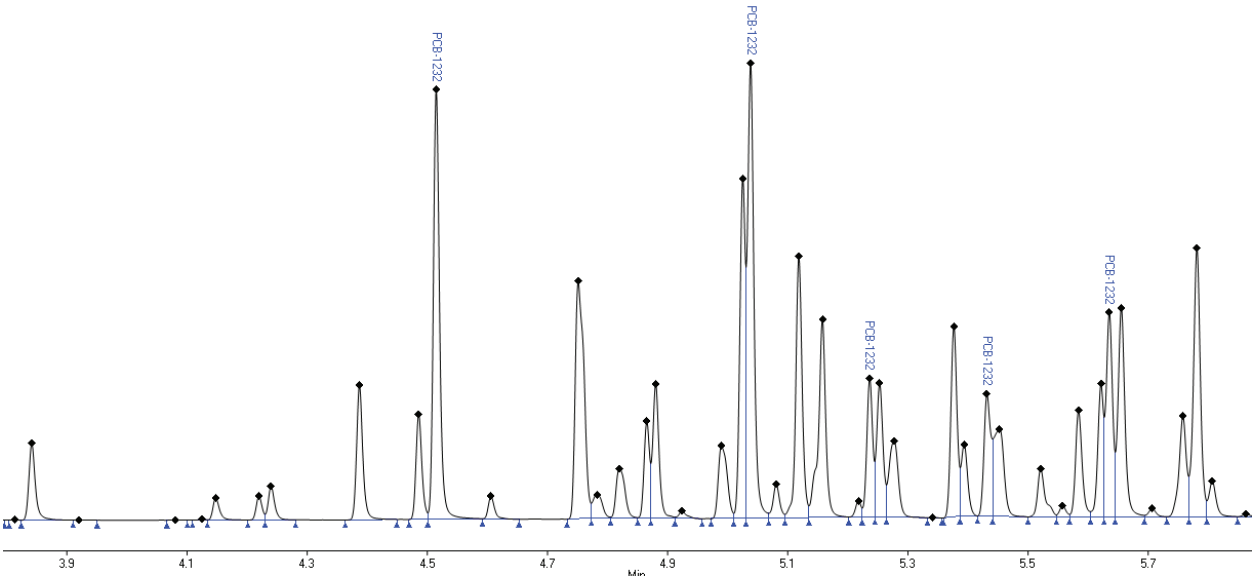


Figure 6: Aroclor 1232

ZB-CLPesticides-1:



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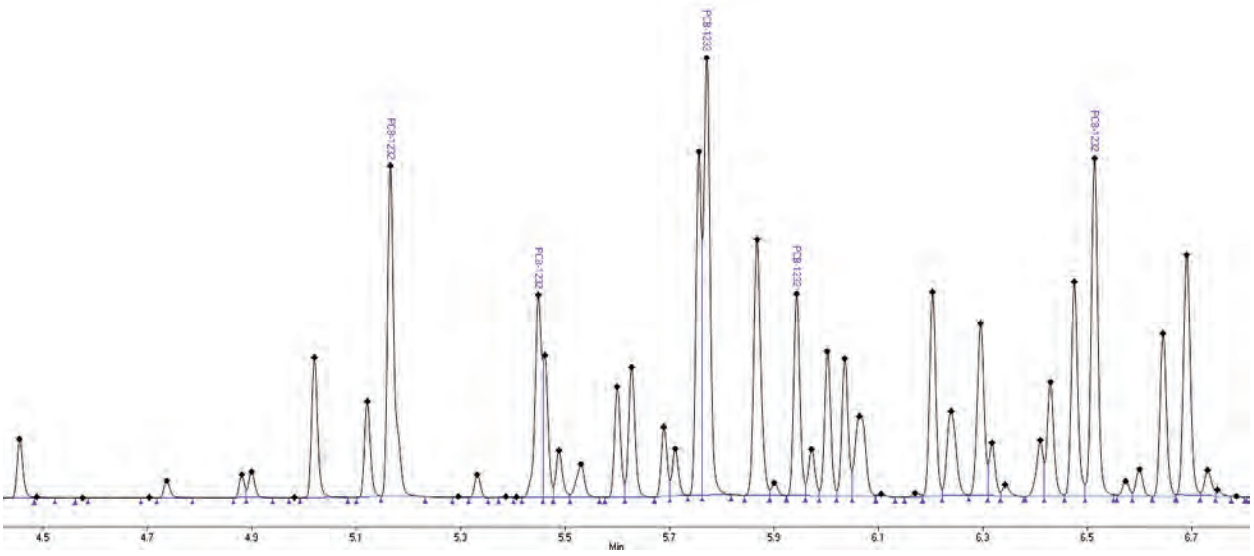
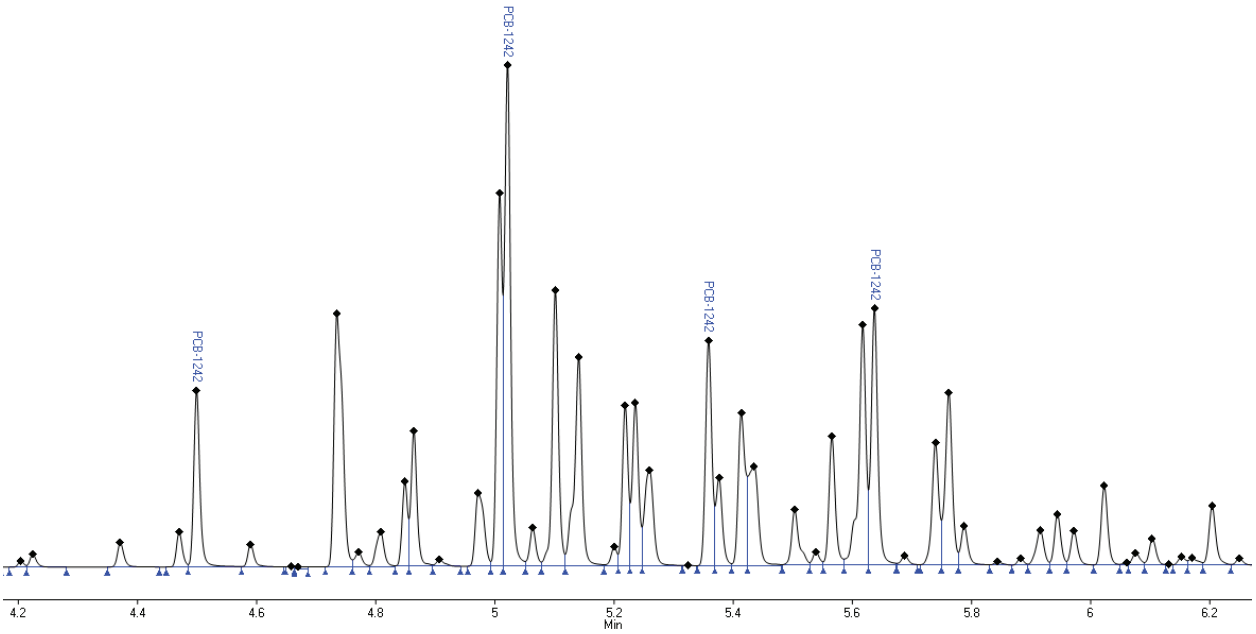


Figure 7: Aroclor 1242

ZB-CLPesticides-1:



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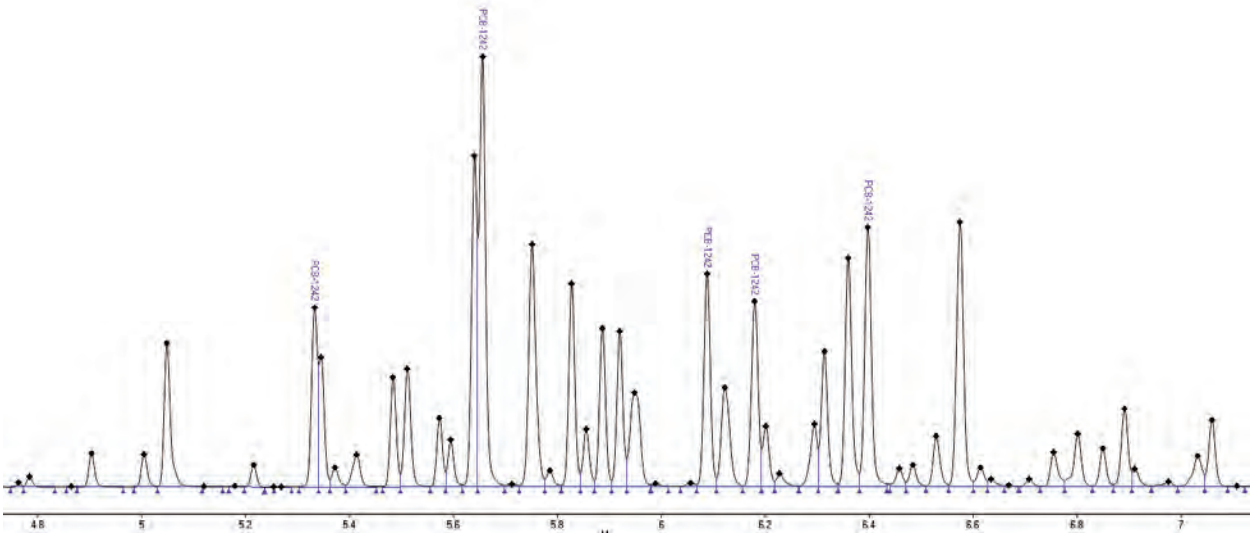

Figure 8: Aroclor 1248

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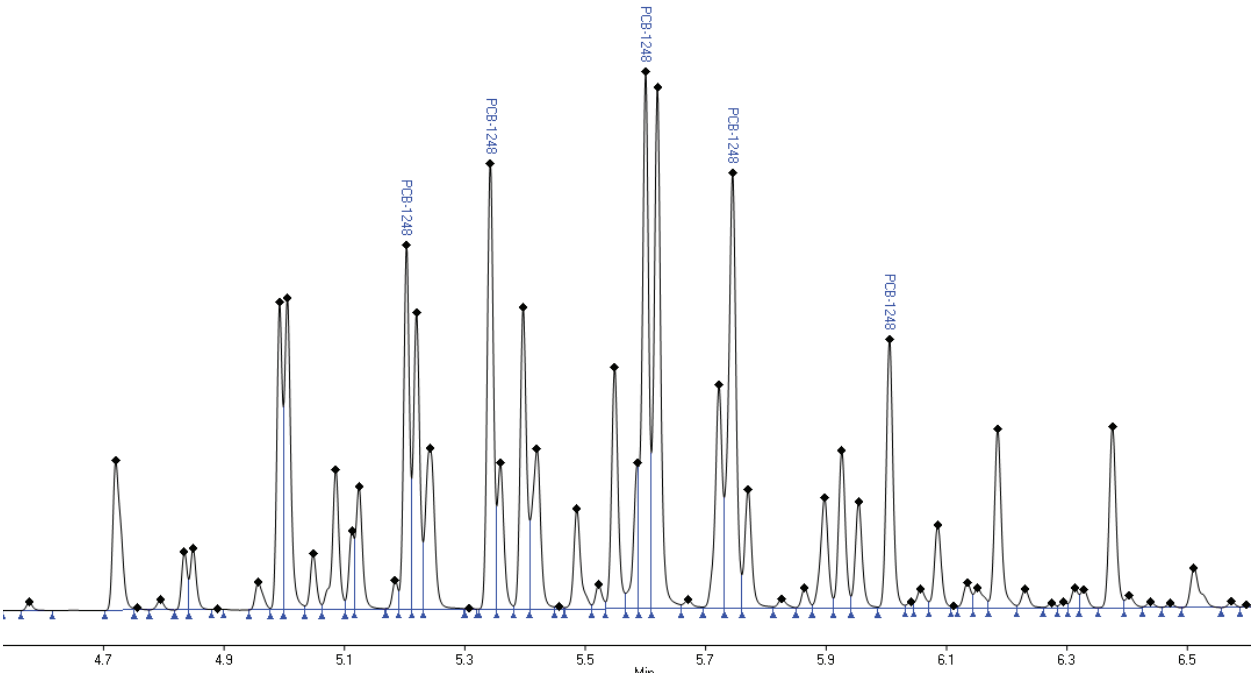

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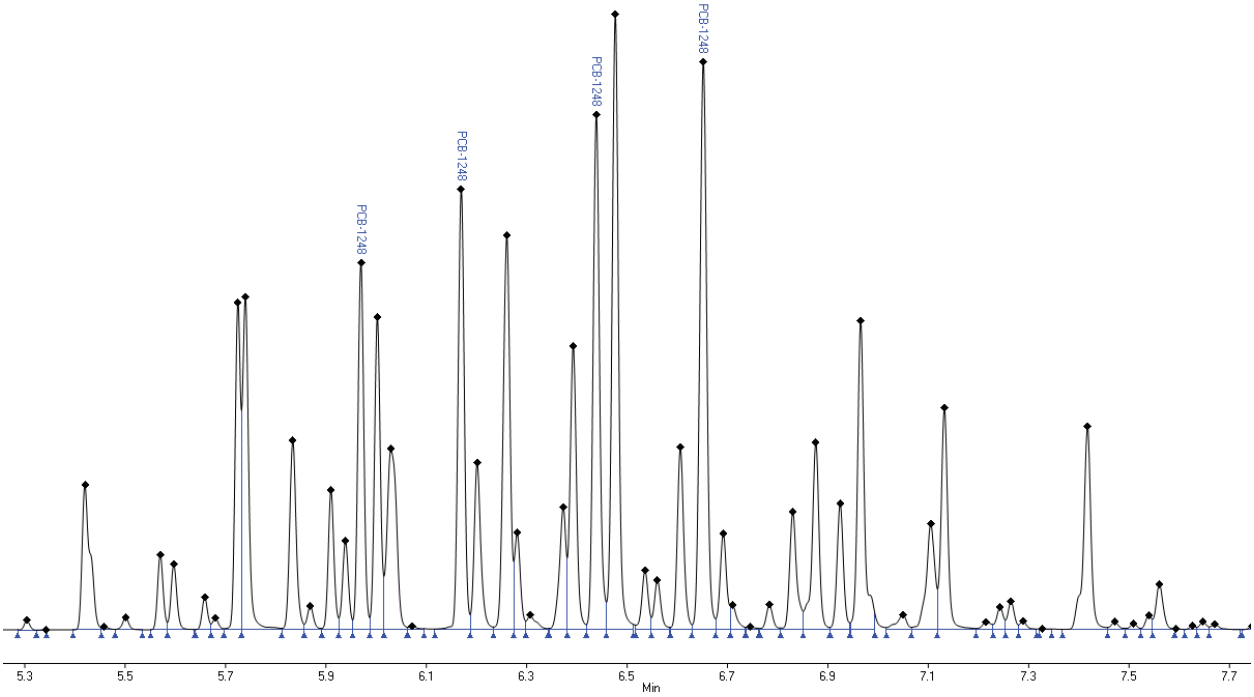
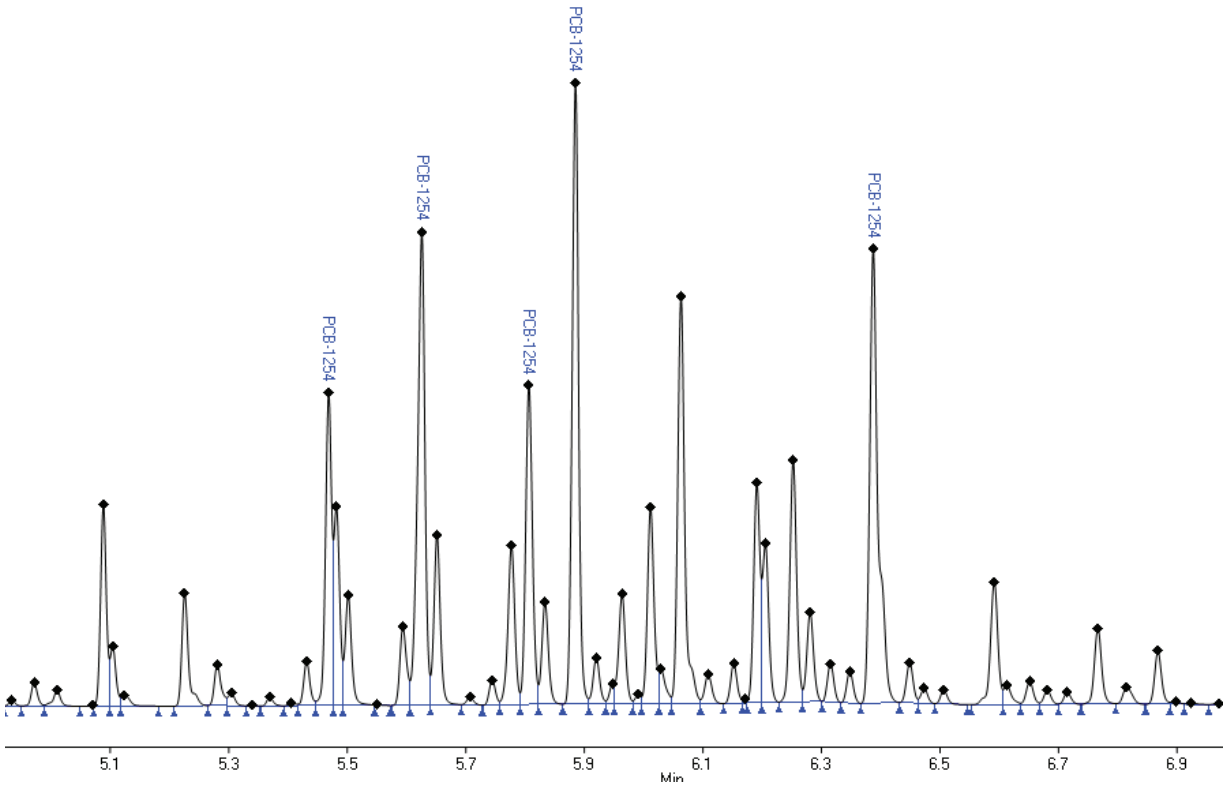


Figure 9: Aroclor 1254

ZB-CLPesticides-1:



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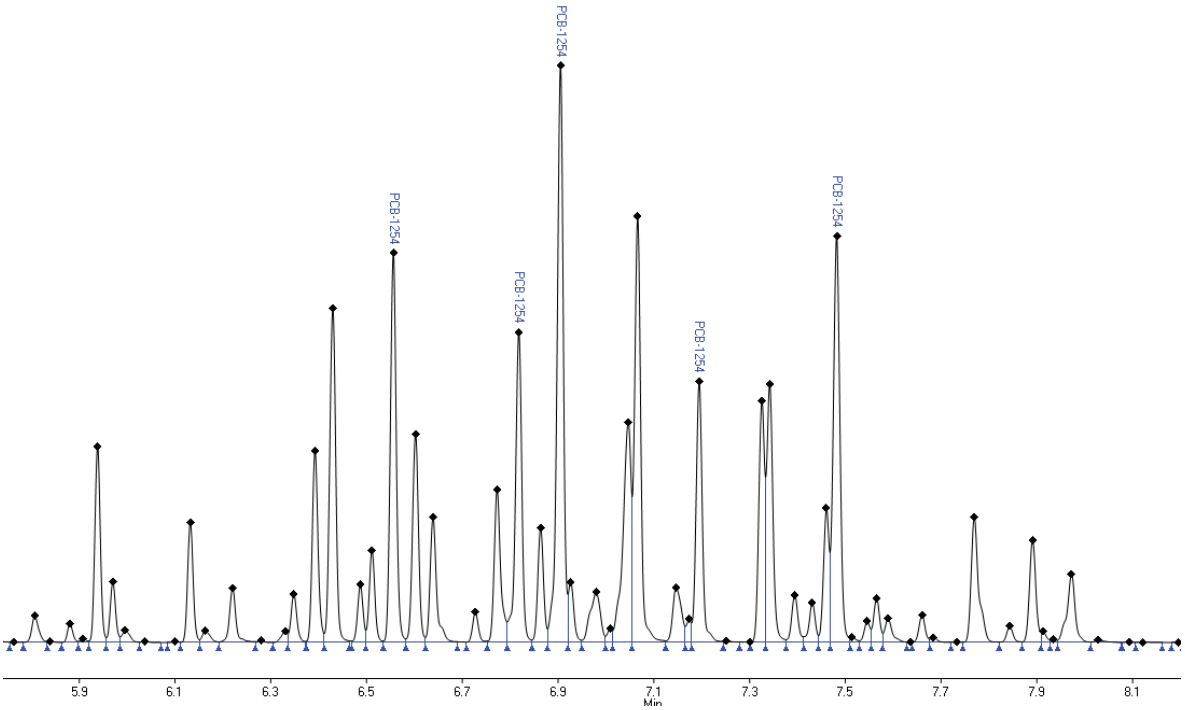
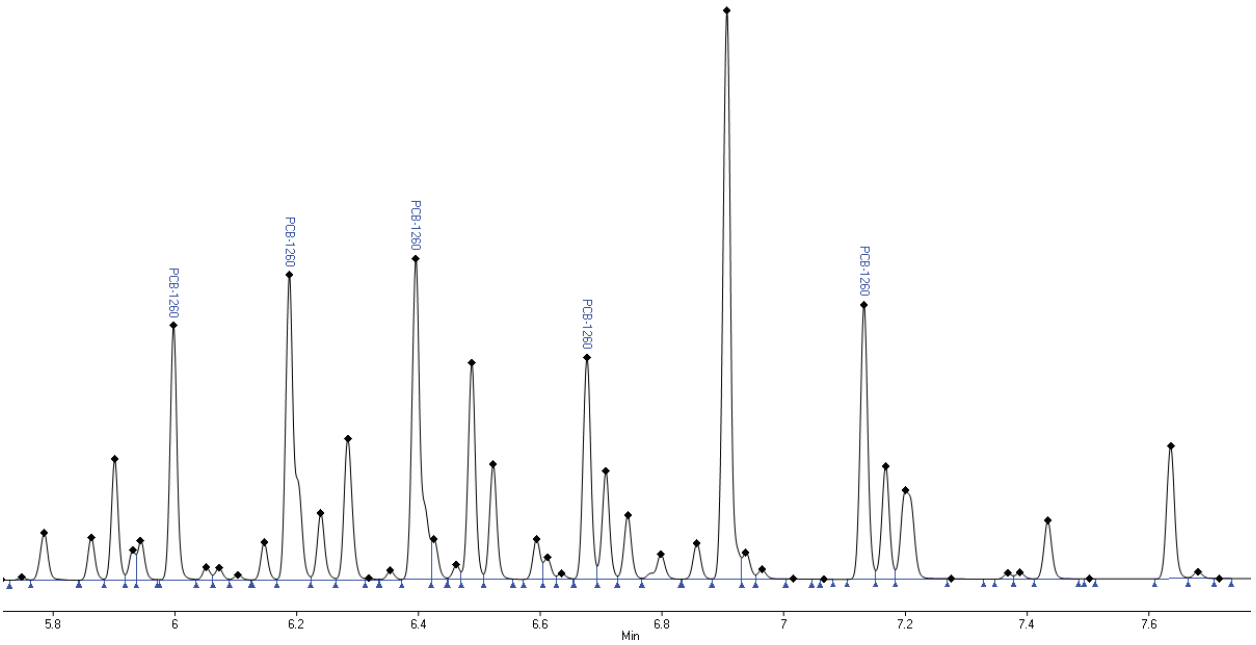


Figure 10: Aroclor 1260

ZB-CLPesticides-1:



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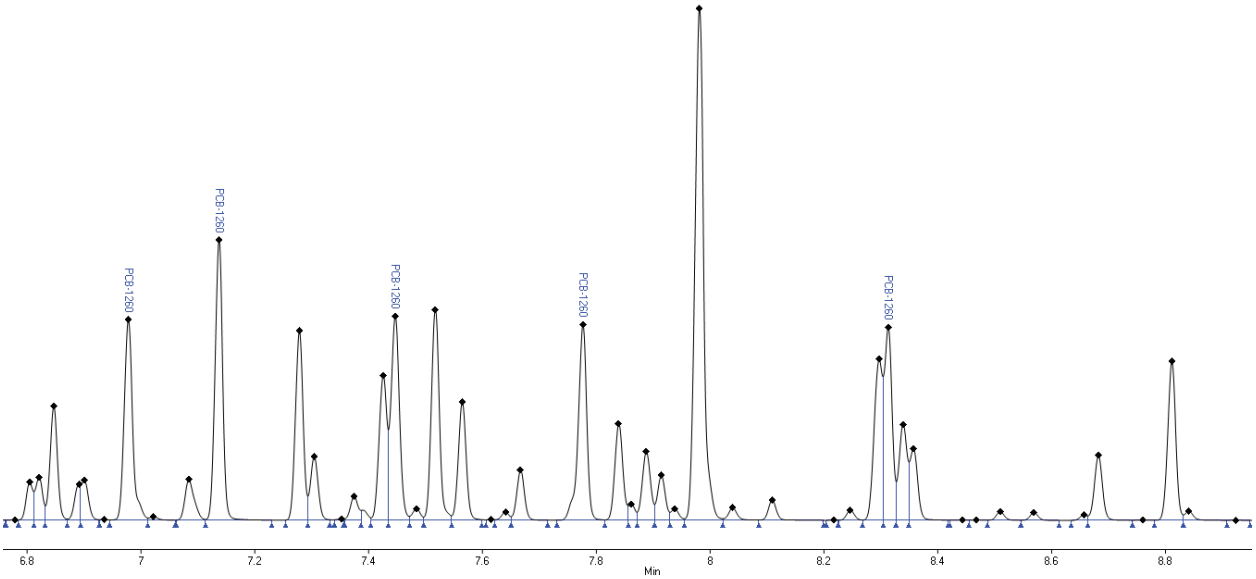
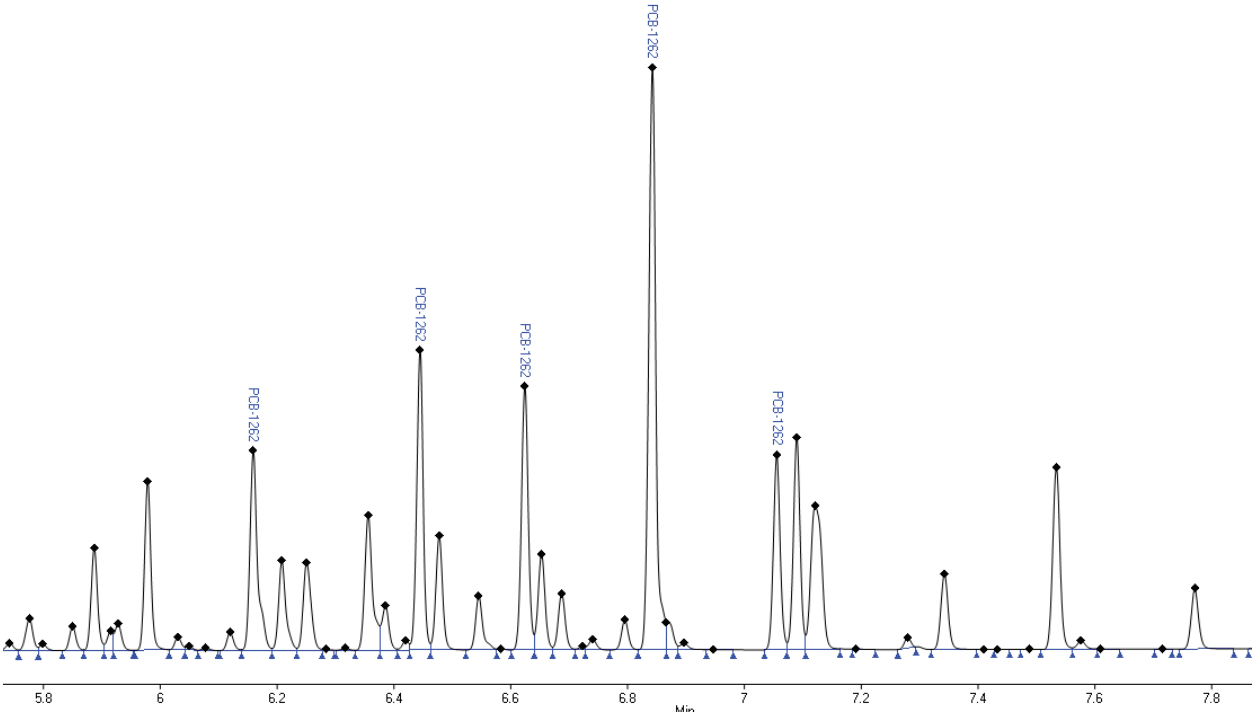


Figure 11: Aroclor 1262

ZB-CLPesticides-1:



ZB-CLPesticides-2:

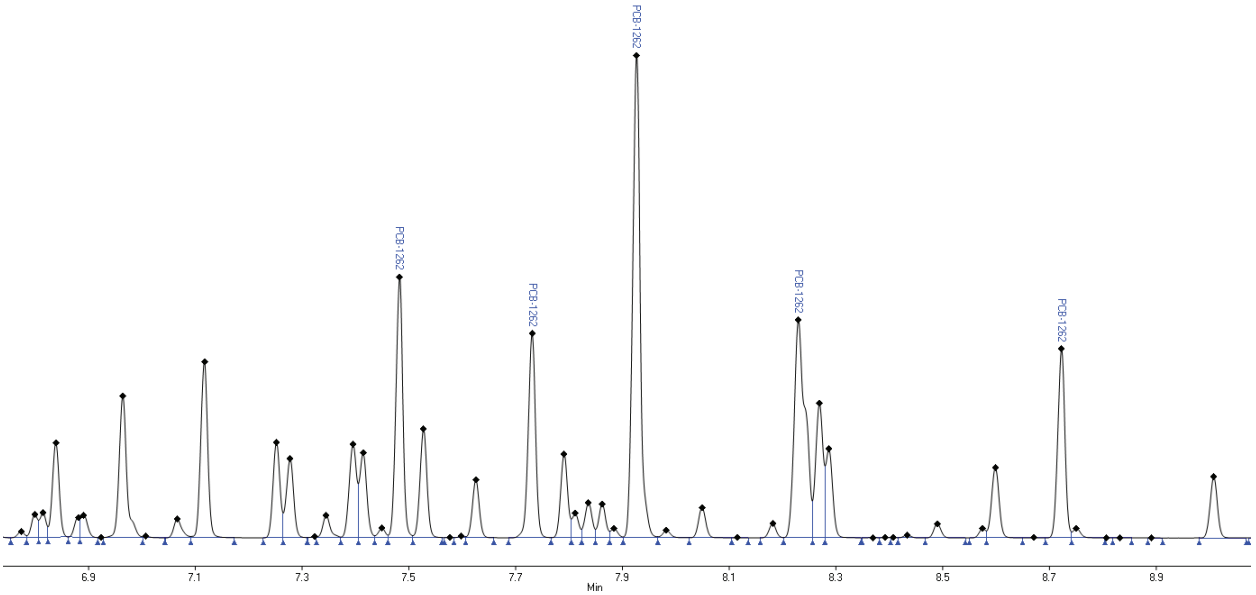


Figure 12: Example Chrom documentation of Resolution check

Report Date: 11-Feb-2015 13:32:42 Chrom Revision: 2.2 15-Jan-2015 13:05:58

Preliminary Report

Resolution Report

TestAmerica Seattle

Data File: \\tacsvr5\ChromData\TAC042\20150211-40597.b\42B11009.D
Injection Date: 11-Feb-2015 10:30:23 Instrument ID: TAC042
Lims ID: CCVIS AR1660
Client ID:
Operator ID: EKK ALS Bottle#: 1 Worklist Smp#: 1
Injection Vol: 1.0 ul Dil. Factor: 1.0000
Method: 8182ISTD_TAC042 Limit Group: 8082 and DOD ISTD PCBs

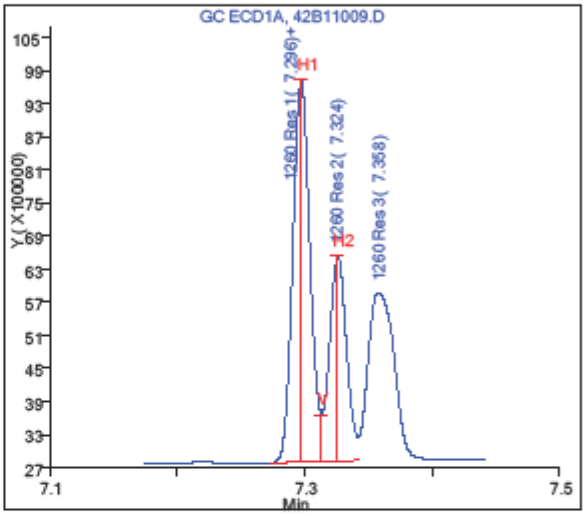
14 1260 Res 1 - 15 1260 Res 2

SW-846 Method

Version C: %R = (V / (H1 + H2)) * 100
Version D: %R = (V / ((H1 + H2)/2)) * 100

V (Valley Height) = 837641
H1(14 1260 Res 1) = 6894678
H2(15 1260 Res 2) = 3700828

Version D: %R = 15.8 <= 75.0
Passed



Report Date: 11-Feb-2015 13:32:42 Chrom Revision: 2.2 15-Jan-2015 13:05:58

Preliminary Report

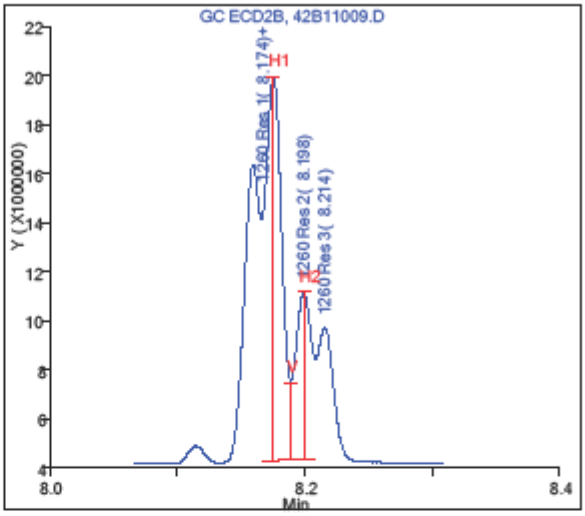
14 1260 Res 1 - 15 1260 Res 2

SW-846 Method

Version C: %R = (V / (H1 + H2)) * 100
Version D: %R = (V / ((H1 + H2)/2)) * 100

V (Valley Height) = 3031674
H1(14 1260 Res 1) = 15017227
H2(15 1260 Res 2) = 6591302

Version D: %R = 28.1 <= 75.0
Passed



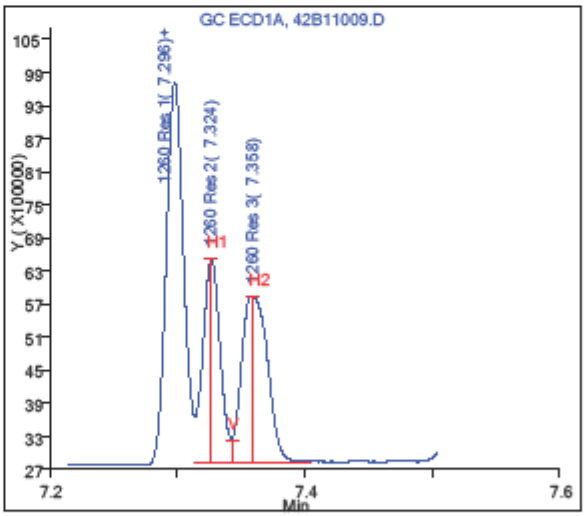
15 1260 Res 2 - 16 1260 Res 3

SW-846 Method

Version C: %R = (V / (H1 + H2)) * 100
Version D: %R = (V / ((H1 + H2)/2)) * 100

V (Valley Height) = 403008
H1(15 1260 Res 2) = 3693684
H2(16 1260 Res 3) = 3009099

Version D: %R = 12.0 <= 75.0
Passed



Report Date: 11-Feb-2015 13:32:42 Chrom Revision: 2.2 15-Jan-2015 13:05:58

Preliminary Report

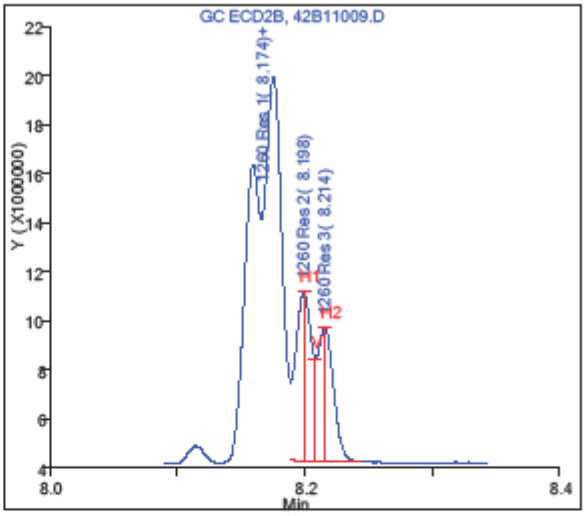
15 1260 Res 2 - 16 1260 Res 3

SW-846 Method

Version C: %R = (V / (H1 + H2)) * 100
Version D: %R = (V / ((H1 + H2)/2)) * 100

V (Valley Height) = 3988186
H1(15 1260 Res 2) = 6607811
H2(16 1260 Res 3) = 5223625

Version D: %R = 67.4 <= 75.0
Passed



Appendix 1: GC/MS Confirmation of Pesticides and PCBs for EPA Region 10

The Requirement

The purpose of the GC/MS analysis for the single component pesticides is for confirmation of the identification. The purpose of the GC/MS analysis for the multi-component analytes is to confirm the presence of chlorinated biphenyls in PCB and the presence of chlorinated camphenes in Toxaphene. The GC/MS analytical results for the pesticides/PCBs shall not be used for quantitation. If the identification of the analyte cannot be confirmed by any of the recommended GC/MS procedures and the concentration calculated from the GC/ECD analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit to a sample concentration equivalent to the concentration of the GC/MS reference standard, qualify the results, and note the data qualification in the Laboratory Case Narrative.

Any pesticide or PCB analyte for which a concentration is reported from a GC/ECD analysis must have the identification confirmed by GC/MS if the concentration is sufficient for that purpose. If the laboratory fails to perform GC/MS confirmation as appropriate, the EPA Region 10 will require re-analysis of any effected samples at no additional cost to EPA Region 10.

The Guidance in Performing GC/MS Confirmation

A. The GC/MS confirmation may be accomplished by one of three general means:
   - If there was an SVOC full scan GC/MS analysis (such as SW-846 Method 8270) performed on the sample in question, then examination of the tentatively identified compound library search results can be used or,
   - An analysis of the pesticide/PCB extract, following any necessary solvent exchange and concentration steps (preferred) or
   - Analysis of another aliquot of the SVOC sample extract after further concentration

B. Full-scan GC/MS will normally require a concentration of approximately 10-ng/uL in the final extract for each single component compound, 50-ng/uL for PCBs, and 125-ng/uL for multi-component pesticide (Toxaphene).

C. In order to confirm the identification of the target pesticide or PCB, the laboratory must also analyze a reference standard for the analyte. In order to demonstrate the ability of the GC/MS system to identify the analyte in question, the concentration of the standard should be less than or equal to 10-ng/uL for single component pesticides, 50-ng/uL for PCBs, and 125-ng/uL for multi-component pesticides.

D. The laboratory mass spectral interpretation specialist is advised to compare the CAS Registry numbers for the pesticides or PCBs to those from the library search routine.

E. Regardless of which of the three approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the SVOC extract, then the SVOC method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the pesticide or PCB extract prepared for the GC/EC analysis, the pesticide or PCB method blank extracted with the sample must be analyzed.

F. For GC/MS confirmation of single component analytes, the required deliverables are copies of the library search results (best tentatively identified compound matches) or analyte spectrum and the spectrum of the reference standard. For multi-component analytes, spectra of three characteristic peaks are required for both the sample component and the reference standard.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [Methods 6020, 6020A, 6020B, 200.8]

Approvals

Signatures on File

Stan Palmquist — Date
Metals Department Manager

Manjit Nijjar — Date
Health & Safety Manager / Coordinator

Terri Torres — Date
Quality Assurance Manager

Dennis Bean — Date
Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP/MS) based on EPA Methods 200.8 and 6020.

1.2 Method 200.8 lists twenty-one elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Se, Ag, Tl, Th, U, V, and Zn). Method 6020 lists fifteen elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, and Zn). This procedure has been developed for thirty-five elements (see Table VII), and additional elements may be included provided that the method performance criteria presented in Sections 9 and 10 are met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the promulgated methods. See Table XII for a list of elements and associated reporting limits.

1.3 The procedure is applicable to the analysis of acid digested waters, soils, and wastes. The preliminary acid digestion for aqueous samples is described in SOP TA-IP-0205, and the digestion procedure for soils is given in SOP TA-IP-0220.

1.4 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a R.F. plasma. There the sample is decomposed and desolvated.

2.2 The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution better than or equal to 0.9 amu (see Section 3.1) peak width at 10% of the peak height. For analysis by methods 200.8, the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier.

2.3 Interference must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and the constituents of the sample matrix. Recommended elemental equations, which correct for many of these interferences, are listed in Table I. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3.0 Definitions

3.1 Atomic Mass Unit (amu) – Obsolete term replaced by “unified atomic mass unit (u)” or “dalton (Da)”, which denotes a small unit of mass that is used to express atomic and molecular masses. It is defined to be 1/12 of the mass of one atom of carbon-12, or $1.66053886 \times 10^{-27}$ kg.

3.2 Dissolved Metals - Those elements which pass through a 0.45-μm membrane filter (sample is acidified after filtration).

3.3 Suspended Metals - Those elements which are retained by a 0.45-μm membrane filter.

3.4 Total Metals - The concentration determined on an unfiltered sample following vigorous acid digestion.

3.5 Total Recoverable Metals - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acids.

3.6 Instrument Detection Limit (IDL) - See Section 12.1.1.

3.7 Sensitivity - The slope of the analytical curve (i.e., the functional relationship between raw instrument signal and the concentration).

3.8 Tuning Solution - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

3.9 Initial Calibration Verification / Quality Control Standard (ICV/QCS) - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.

3.10 Continuing Calibration Verification (CCV) - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

3.11 Interference Check Standard (ICS) - A solution containing both interfering and analyte elements of know concentration that is used to verify background and interelement correction factors.

3.12 Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB) - A multi-element standard of known concentrations that is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.

3.13 Reagent Blank - High purity (> 18 megohmcm) DI water containing the same acid matrix as the calibration standards that is carried through the entire digestion process.

3.14 Calibration Blank - High purity (> 18 megohmcm) DI water acidified with the same acid concentrations present in the standards and samples. Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).

3.15 Method Detection Limit (MDL) - See section 12.1.2.

4.0 Interferences

4.1 Isobaric Interferences

4.1.1 Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.

4.2 Isobaric Molecular and Doubly Charged Ion Interferences

4.2.1 Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Table III lists isobaric interferences which might possibly affect required analytes. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied and the data flagged to indicate the presence of interferences.

4.2.2 Chloride in samples can produce low recoveries for antimony and silver. If chloride interference is a concern, 1% HCl can be added during digestion, but calibration standards must be adjusted to include 1% HCl also.

4.3 Physical Interferences

4.3.1 Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.3.2 Internal standards should be added at a level to give greater than 100,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 50 amu of the mass of the measured analyte.

4.3.3 Matrix effects are monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing method 6020, the internal standard intensities must be between 30% and 120% of the intensities in the calibration blank. For method 6020A *and 6020B,* the internal standard intensities must be ≥*30%* If they fall outside this window, a five-fold dilution (1:4) is performed on the sample to correct for matrix effects and the sample is reanalyzed. *For method 200.8,* the internal standards must be between 60% and 125% of the calibration blank. If they are outside this window, the sample is diluted by a factor of 2 (1:1) and is reanalyzed.

4.3.4 Memory effects are dependent on the relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.4 The use of hydrochloric and sulfuric acids should be minimized due to higher incidence of molecular-ion interferences with the presence of these acids. Excessive amounts of nitric acid can also lead to molecular interferences.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating.

NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.

A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Materials with Serious or Significant Hazard Rating

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm TWA 4 ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

(1) Always add acid to water to prevent violent reactions.
(2) Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

- Inductively Coupled Plasma Mass Spectrometer (ICP/MS) capable of providing resolution, less than or equal to 0.9 amu at 10% peak height from 6-253 amu and 1.0 amu at 5% peak height from 6-253 amu with a data system that allows corrections for isobaric interferences and the application of the internal standard technique
- Autosampler with autosampler tubes
- A four-channel peristaltic pump
- Vacuum pump, Recirculating Chiller, Spray Chamber Cooling Power Pack

6.2 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- Data acquisition/processing system: Agilent 7500 ICP-MS ChemStation or equivalent
- LIMS system: TALS version 1.0 or higher

6.3 Supplies

- Calibrated automatic pipettes or Class A glass volumetric pipettes
- Argon gas: High purity grade (99.99%)

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Standards

7.2.1 Storage and Shelf-Life

7.2.1.1 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Standards stored at concentrations as received from the vendor and mid-level dilutions must be replaced prior to the expiration date assigned by the vendor. If no expiration date is provided, the stocks and mid-level standards may be stored for up to one year. They must be replaced sooner if verification from an independent source indicates a problem.

7.2.1.2 Working standards, i.e., all standards at concentrations ready to analyze on the ICP/MS (all except tuning mixes, ICSA and ICSAB mixes, which are received at ready-to-use concentrations), are prepared every three months.

7.2.2 The tuning solution is purchased as a custom multi-element mix or as single element solutions. The elements and concentrations of the constituents are shown in Table VIII.

7.2.3 Initial calibration standards are purchased as custom multi-element mixes or as single element solutions. The standards are prepared every three months and diluted to working levels using a combination of 2% nitric acid and 1.5% hydrochloric acid. The concentrations are given in Table XI.

7.2.4 Initial calibration verification (ICV) standards are obtained from a source different than the source for the calibration standards. The ICV standards are prepared every three months in a solution of 2% nitric acid and 1.5% hydrochloric acid to the concentrations shown in Table XI.

7.2.5 Continuing calibration verification (CCV) standards are prepared from the same source as the calibration standards. The CCV standards are prepared every three months in a solution of 2% nitric acid and 1.5% hydrochloric acid. The concentration is different than the ICV, as shown in Table XI.

7.2.6 Reporting limit (RL), LLICV, and CCVL verification standards are prepared every three months from the same stock as the calibration standards using a solution of 2% nitric acid and 1.5% hydrochloric acid. The concentrations must be less than or equal to the reporting limits.

7.2.7 Linear dynamic range *(LDR) s*tudies are conducted *every six months. Hg at 50 µg/L; Na, Mg, Al, P, K, Ca, Fe at 250,000 µg/L; Ti, Mo, Ag, Sn, Sb, Tl at 1,000 µg/L; the remaining elements* at 10,000 µg/L

7.2.7.1 *6020B and DOD requires a LDR verification within 10% of the true value with each calibration. If a LDR verification is not analyzed for any specific element, the highest standard in the calibration becomes the LDR.*

7.2.8 Spiking solutions are CLP Sample Spike solution. Spike concentrations are listed in Table XI.

7.3 Reagents

7.3.1 DI Water

ASTM Type I or equivalent for the elements of interest, generated using an ion-exchange water polishing system capable of achieving 18.0 megohm-cm.

7.3.2 Acid Diluent, 2% HNO_3 and 1.5% HCl

Carefully dilute 220 mL of concentrated HNO_3 and 165 mL of concentrated HCl to 11 L with DI water. This solution is used to dilute samples, and it is used for calibration blanks.

7.4 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards/reagents and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Aqueous samples and digestates are stored at room temperature.

8.2 Aqueous samples are preserved with nitric acid to a pH of 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.3 Soil samples do not require preservation, but must be stored at 0-6°C until the time of preparation.

8.4 The analytical holding times for metals are six months from the time of collection.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	HDPE	50 mL	HNO_3, pH < 2;	180 Days	40 CFR Part 136.3
Soils with Hg Analysis	Glass	1 gram	≤ 6 C	180 Days	SW-846, Chapter 3 Table 3.1
Soils	Glass	1 gram	None	180 days	SW-846, Chapter 3 Table 3.1

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 Quality control requirements are also summarized in TABLE X.

9.2 Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Control limits are maintained in the laboratory LIMS system. See QC SOP TA-QA-0620 for definition of QC terms, details about establishing control limits, minimum elements of a preparation batch, and general guidelines for evaluating batch QC.

9.3 QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). Failing QC that is automatically flagged by TALS does not need a NCM as long as it is a routine failure. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate and the NCM can be included in the report narrative. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610.

9.4 Method Blank / Laboratory Reagent Blank (MB/LRB)

For aqueous and soil samples, the method blank consists of DI water that has been processed in the same manner as the samples. For soil samples analyzed under the DoD QSM, the method blank consists of polyethylene beads that have been processed in the same manner as the samples. One method blank must be processed with each preparation batch. In addition, the method blank should be analyzed at the same dilution as the associated samples.

Acceptance Criteria: Method blank results are acceptable if the concentration for each analyte of interest is less than the applicable reporting limit (RL).

NOTE: Some programs (e.g., DoD) require control of method blanks to have a concentration less than or equal to one-half of the RL. Some programs (LaMP) and method 6020A require no detections in the method blank more than 10% of the low limit calibration check solution. Method 200.8 requires no detection in the method blank greater than 2.2X the MDL. This can not be obtained in some cases. TestAmeria Seattle will only evaluate the method blank to 1/2 the RL or Project DQOs and when specific DQOs are not provided by the client the RL will be defined as the DQO.

Corrective Action: If the method blank does not meet the acceptance criteria, the source of contamination should be investigated to determine if the problem can be minimized or eliminated. Samples associated with the contaminated blank shall be reprocessed for analysis or, under the following circumstances, may be reported as qualified (qualifier flags or narrative comments):

- The same analyte was not detected in the associated samples;
- The method blank concentration is less than 1/10 of the measured concentration of any sample in the batch;
- The method blank concentration is less than 1/10 the specified regulatory limit; or
- The analyte is a common laboratory contaminant (copper, iron, lead, calcium, magnesium, potassium, sodium, or zinc) less than 2 times the RL. Note that some programs do not recognize common lab contaminants.

If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5 Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB)

The LCS consists of DI water that is spiked with the analytes of interest as summarized in Table XI. For soil samples analyzed under the DoD QSM, the LCS consists of polyethylene beads that have been spiked with the analytes of interest and processed in the same manner as the samples. One LCS must be processed for each preparation batch. However, if there is not sufficient sample volume for a matrix spike duplicate or sample duplicate, then precision information for the batch will need to be derived by processing a LCSD.

Acceptance Criteria: LCS control limits are based on three standard deviations of past laboratory results. These limits are not to exceed 85-115%

recovery for Method 200.8 or 80-120% for Method 6020. The control limits are maintained in the LIMS system.

Corrective Action: If the LCS % recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reprocessed for analysis. One possible exception is a recovery for a given element above the upper control limit with no detection for the same element in the samples. (No such allowance is permitted for BP LaMP samples).

9.6 Matrix Spike / Matrix Spike Duplicate / Laboratory Fortified Sample Matrix / Laboratory Fortified Matrix Duplicate (MS/MSD/LFM/LFMD)

An MS is prepared by taking a second aliquot of a selected sample and spiking it with the analytes of interest as summarized in Table XI. An MSD is prepared by taking a third aliquot of a selected sample and spiking it with the analytes of interest as summarized in Table XI. The MS and MSD are processed in the same manner as the samples. One MS/MSD pair must be processed for each preparation batch. If there is not sufficient sample volume for a matrix spike duplicate or sample duplicate, then precision information for the batch will need to be derived by processing a LCSD. The spike concentration should be the same level as the LCS. (For BP LaMP samples, a trip blank or field blank should not be used for MS/MSD).

Acceptance Criteria: Control limits are based on three standard deviations of past laboratory results. These limits are not to exceed 80-120% recovery *(75-125% for 6020B)*, and 20% relative percent difference (RPD). The control limits are maintained in the LIMS system.

Corrective Action: If MS/MSD results do not meet the acceptance criteria and all other quality control criteria have been met, then matrix interference is suspected. Failed matrix spikes are flagged automatically, and are discussed in the final report case narrative.

9.7 Interference Check Solutions (ICSA/ICSAB) **method 6020/*A/B* only**

NOTE: It may not be possible to obtain pure ICSA or ICSB standards*. 6020B has no ICSAB requirements.*

The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table VI. The interference check solutions must be analyzed at the beginning of every analytical run or once every 12 hours (for BP LaMP samples - prior to analytical run, every 8 hours and after analysis), whichever is more frequent. The results of solution "A" and solution "AB" should be monitored for possible interferences. See Table VI for analyte concentrations.

Acceptance Criteria: The results for the interference solution (A portion) must be $\leq$ LOD (unless they are a verified trace impurity form one of the spike analytes).

Corrective Action: If ICSA results exceed the LOD and the suspected trace impurities aren't verified, then the analysis sequence must be terminated. The problem must be investigated and fixed. The ICS and all affected samples must be re-analyzed. If the contamination can be

confirmed by another method (e.g., ICPAES), acceptance criteria will be applied at that level and the data accepted.

Acceptance Criteria: The results for the trace elements (AB portion) must be within ± 20% of the expected value.

Corrective Action: If the ICSAB results exceed the 20% limit, then the analysis sequence must be terminated. The problem must be investigated and fixed. The ICS and all affected samples must be re-analyzed.

9.8 Internal Standards Evaluation for Samples

9.8.1 Method 6020

The IS recovery in samples must be between 30% and 120% of the intensity of the calibration blank. For 6020A*/B,* IS recovery must be greater or equal to *30%*. If sample IS recoveries fall outside of this criterion, a five-fold (1:4) dilution must be performed, the dilution analyzed, and the same acceptance criteria applied.

9.8.2 Method 200.8

The internal standards in samples must be between 60% and 125% of the intensity in the calibration blank. If the sample intensities fall outside this range, the sample is diluted by a factor of 2 (1:1) and reanalyzed.

9.8.3 IS limits and corrective actions for standards and blanks are described in Section 10.

9.9 Serial Dilution **method 6020/*A/B*only**

One serial five-fold dilution should be analyzed per batch. If the analyte concentration is within the linear range of the instrument and sufficiently high (generally, a factor of *25* times above the RL or for BNSF and BP LaMP a factor of 5 times above the RL), the serial dilution must agree to within 10% *(20% 6020B) o*f the original analysis. If not, an interference effect is suspected, which must be described in an anomaly report and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

9.10 Post-Digestion Spike Addition (PDS) **method 6020/*A/B*only**

A PDS is performed for each batch. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference should be suspected. For 6020A, PDS recoveries are 80 - 120%.

9.11 For analytical sequences that include BNSF and/or BP LAMP samples, the RSD between multiple instrument integrations must be <20% if the analyte is greater than the reporting limit. If the RSD is above 20% then the laboratory must reanalyze the sample.

9.12 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above. Corrective action for a failing PDS is a Serial Dilution Test. This test is run as standard practice in all analytical batches.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the

laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.1 Sample Preparation

Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs TA-IP-0204 and TA-IP-0205).

10.2 Instrument Start Up

Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning. The current operating conditions of each instrument must be either written, or printed out and attached to the corresponding instrument maintenance logbook.

10.3 Instrument Tuning / Mass Calibration

10.3.1 Tune the instrument with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of 4 times. For method 200.8, the tuning solution must be analyzed 5 times with a relative standard deviation less than 5%.

10.3.2 Mass calibration and resolution checks using the tuning solution must be completed at the beginning of every day.

10.3.2.1 Mass Calibration Check - The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.3.2.2 Mass Resolution Check - The resolution must be verified to be less than 0.9 amu full width at 10% peak height. Due to a limitation of the instrument software, the resolution requirement for method 200.8 of 1.0 amu full width at 5% peak height cannot be verified automatically. If the mass resolution requirement of 0.9 amu at 10% peak height is met, the 200.8 requirement is also satisfied.

10.4 Initial Calibration

10.4.1 The calibration curve is established on each day of operation using a blank and five standards. The preparation of the ICAL standards is described in Section 7. The final concentrations of the ICAL standards are presented in Table XI. Report the average of at least three integrations. An r value of 0.995 or better is required for analysis to continue for any element. If an element does not meet the requirement, it must be recalibrated. If an element does not meet this requirement it may not be reported during that days run. For details regarding calibration models and algorithms, refer to corporate SOP CA-Q-S-005.

10.4.2 The validity of the calibration is determined by the subsequent calibration verifications, which are performed at concentrations as described in the next sections.

10.4.3 The internal standard recoveries for 6020 must fall between 30% and 120% of true values, 6020A/*B* must be ≥*30%*, and for 200.8 must fall between 60% and 125% of true values.

10.5 Second-Source Initial Calibration Verification (ICV)

An ICV standard (see Section 7.2.4) is analyzed immediately after the initial calibration. This is a standard obtained from a different vendor than the standard used for calibration. This analysis also satisfies the Method 200.8 requirement for a Quality Check Standard (QCS).

Acceptance Criteria: The ICV recovery must be within 90-110%. The ICV can be reanalyzed, but must be successful twice in succession or corrective action must be taken.

Corrective Action: If the ICV results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.6 Calibration Blank

An initial calibration blank (ICB) is analyzed after the ICV. Continuing calibration blanks (CCBs) are analyzed after each continuing calibration verification.

Acceptance Criteria: Results for the calibration blanks must be less than the RL.

Note: All projects that are under the DoD QSM will evaluate the calibration blanks to ensure the criteria of no analytes being detected above the LOD. Any analyte above the LOD will be qualified B on all associated samples.

BP LAMP requires control of calibration blanks to a concentration less than 1/ 2 RL.

Corrective Action: If the calibration blank exceeds acceptance limits, then the possibility of instrument contamination should be examined, particularly the possibility of carry-over from high level samples. The blank can be reanalyzed, and if successful, analysis can continue. However, samples tested after high-level samples should be retested. If the reanalysis is not successful, then the analysis should be terminated. After the problem is corrected, recalibrate and reanalyze all samples tested since the last acceptable CCB.

10.7 Reporting Limit (RL) Verification Standard, LLICV, CCVL

An independent standard is analyzed after the ICV to monitor the lab's ability to produce reliable results at RL level concentrations. The RL verification standard (see Section 7.2.6) is analyzed after the daily ICB. (For BP LaMP the RL verification standard is run prior to analysis, every 8 hours and after analysis. The standard must be within 2 times the RL concentration.)

Acceptance Criteria: For project reporting limits at or above two times the MDL, the results should be within 50% of the expected value. Note that the DoD QSM requires control of the low-level calibration check standard to ± 20% of the expected value, in which case the RLs will need to be three or more times the MDL concentration. For DoD QSM 5.0, the acceptance limit is ± 20% for LLICV. *For*

*6020B, the acceptance limit is ± 35% for LLICV and RSD should be < 20%. F*or 6020A, the acceptance limit is ± 30% for *LLICV/C*CVL. For BP LAMP, the acceptance limit is ± 30% for LLICV and CCVL.

Corrective Action: If the RL verification fails to meet acceptance limits, data for the associated samples must be assessed. For example, if the results are high, consider blank contamination, and if the results are low, consider MDL verifications. At a minimum, sample results must be qualified in the final report.

10.8 Continuing Calibration Verification (CCV) Standard

A 50 µg/L CCV standard is analyzed after every set of ten samples and at the end of the analytical sequence.

Acceptance Criteria: The CCV recovery must be within 90-110%. If CCV results are not within these limits, the CCV can be reanalyzed, but it must be successful twice in succession or further corrective action must be taken.

Corrective Action: If the CCV fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCB.

Calibration Controls	Sequence	Control Limit
Calibration Standards	5-point (minimum) linearity	r≥ 0.995 *(LaMP 0.998)*
Cont. Cal. Verif. (CCV)	Prior to / after every 10 injections	Recovery 90-110 %
Cont. Cal. Blank (CCB)	Following ICV/CCB	<2X MDL

10.9 Sample Analysis

10.9.1 Report the average of at least three integrations for all field and QC samples analyzed.

10.9.1.1 For analytical sequences that include BNSF and/or BP LAMP samples the RSD between multiple instrument integrations must be <20% if the analyte is greater than the reporting limit. If the RSD is above 20% then the laboratory must reanalyze the sample.

10.9.2 Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

10.9.3 Masses, which would affect the data quality, must be monitored during the analytical run to determine the potential effects of matrix on a given element.

10.9.4 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the IDL. (The sample should be diluted to the approximate midrange of the analytical curve.)

10.9.5 The analytical run sequence should be performed as follows to meet all quality control criteria:

Instrument initialization
Warm-up
Tune instrument
Perform mass calibration
Perform resolution check
Validate tuning criteria
Calibration blank
Calibration standards
ICV
ICB
RL verification standard / LLICV
ICSA
ICSAB
LDR Check (6020B/DOD)
CCV
CCVL (6020A)
CCB
10 Samples (which can include all sample types)
CCV
CCVL (6020A)
CCB
10 samples
CCV
CCVL (6020A)
CCB

10.10 Data Reduction and Review

10.10.1 Upon completion of the analytical sequence, review the raw data to determine if dilutions are necessary and then perform a level 1 data review and document the review on the data review checklist.

10.10.2 Submit the data package and review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635. All data is calculated using the formulas in Section 11.

10.10.3 Update instrument sequence logbook.

10.11 Instrument Maintenance

10.11.1 All instrument maintenance must be documented in the instrument maintenance logbook.

- Routine Maintenance (which includes, but is not limited to daily, weekly, and semiannual maintenance) is completed periodically and does not necessary indicate the instrument is out of control. It is noted in the logbook with the notation “RM”. **RM maintenance might include weekly cleaning of cones and changing tubing.**
- The logbook must include the instrument name, serial number for each major component (e.g., AA, autosampler) and the date of start-up.
- When an instrument is not capable of analyzing samples, it needs to be tagged “Out of Service”.

- For non-routine maintenance or repairs, logbook entries must include a description of the problem and what actions were taken to address the problem.
- When non-routine maintenance or repairs are complete, the instruments return to control is noted in the logbook with the notation “RTC”.

10.11.2 Daily Use and Maintenance

- For both the P.E. and Agilent instruments, the daily tune and daily mass calibration will be printed, monitored for changes and included in the instrument sequence logbook.

10.11.3 Weekly Maintenance (or more frequently if needed)

- Change the pump tubing as needed.
- Check pump and pump rollers.

10.11.4 Monthly Maintenance (or more frequently if needed)

- Clean the nebulizer as needed when instrument reading are inconsistent.
- Clean the torch as needed. Sonicate the nebulizer in mild soap for 10 minutes to clean.
- Clean the spray chamber if dirty.
- Check the air filters on the power supply and spectrometer, and clean if dirty.

10.11.5 Annual and Semiannual Maintenance (or more frequently if needed)

- Clean the chiller.
- Change the oil in the rough pump
- Change the Lens as needed
- Change the cell annually or as needed

10.11.6 Spare Parts

10.11.6.1 Instrument supplies

- Purge windows.
- Injector tip.
- Lens
- Cell

10.11.6.2 Plasma Torch Assembly.

- Quartz torch.
- Spray chamber.
- Nebulizer.

10.11.6.3 Tubing

- Sample tubing.
- Drain tubing.
- Internal standard tubing
- Sample capillary tubing and sample probe

10.12 Troubleshooting

10.12.1 Refer to Appendix A, Troubleshooting Guide.

11.0 Calculations / Data Reduction

For details regarding calibration models and algorithms, refer to corporate SOP CA-Q-S-005.

11.1 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Concentration

The final concentration for an aqueous sample is calculated as follows:

$$\text{Result}\,(\mu\text{g/L}) = \frac{C \times V1 \times D}{V2}$$

Where: C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

NOTE: Samples prepared for total recoverable analytes by Method 200.8 will have a preparation dilution factor of 1.25.

The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result}\,(\mu\text{g/kg}) = \frac{C \times V \times D}{W}$$

Where: C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

12.0 Method Performance

12.1 Instrument and Method Detection Limit Studies

12.1.1 Instrument Detection Limit (IDL) - IDLs are determined by analyzing seven replicates of low concentration undigested standards on each of three nonconsecutive days, calculating the standard deviation for each day's results, and calculating the average of the three standard deviations. The IDL must be performed *annually*.

12.1.2 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TC-QSM-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.1.3 Linear Dynamic Range (LDR)

Linear range standards (see Section 7.2.7 for preparation) must be analyzed semiannually.

Acceptance Criteria: The highest standard must produce a recovery within 90-110% of the expected value. Then the highest LDR is 90% of the highest successful standard.

Correction Action: Samples producing results above the LDR must be diluted reanalyzed.

12.1.3.1 Linear Range Verification

The LDR should be verified whenever, in the judgment of the analyst, a change in the analytical performance caused by either a change in instrument hardware or operating conditions would dictate the necessity to re-establish them.

Acceptance Criteria: The LDR verification standard must produce a result within 90-110% of the expected value.

Corrective Action: If this limit is not met, then a new LDR study is required.

Some programs (e.g., USACE/Navy) require verification of linear ranges in each analytical run or the samples must be diluted at the concentration of the high standard.

Acceptance Criteria: Results must be within 90-110% of the expected value.

Corrective Action: Samples producing results greater than the concentration of the daily check standard will be diluted and reanalyzed.

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TC-QSM-0617 for details.

12.3 Training Requirements

See SOP TC-QSM-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Waste Disposal SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

Metals acid waste – Acid waste consisting of sample and rinse solution: Waste in which the only hazardous constituent is its pH is neutralized and sewered. Standards and any other high metal waste are collected in satellite waste stations. The waste is then taken to the waste warehouse where it is bulked and sent out for chemical precipitation with or without treatment.

15.0 References / Cross-References

15.1 Test Methods For Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update II, Method 6020: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 0, September 1994.

15.2 Test Methods For Evaluating Solid Waste, EPA SW-846, 4th Edition, Draft Update IVA, Method 6020A: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 1, January 1998.

15.3 Environmental Monitoring Systems Laboratory, EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.4, EMMC Version.

16.0 Method Modifications:

Item	Method	Modification
1	6020/*A/B,* 200.8	Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept on file.
2	6020/*A/B*, 6020A, 200.8	The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL.
3	6020/*A/B,* 6020A	The serial dilution results are evaluated when the original result is greater than 100 times the MDL rather than 100 times the concentration in the reagent blank.
4	6020/*A/B,* 6020A	Corrective action for a PDS failure will be limited to generating an NCM indicating the failed analyte and the recovery rather than diluting and reanalyzing the sample.
5	6020/*A/B,* 6020A	Internal standard recoveries are based on the intensities of the internal standards in the most recent calibration blank rather than the intensities of the internal standards in the initial calibration

		standard.
6	6020*/A/B,* 6020A	The internal standard recovery limits for the ICV/CCV and ICB/CCB results is 30 - 120% for all analyses as stated in method 6020A rather than 80-120% as stated in method 6020.
7	200.8	Resolution criteria of the mass calibration are met if the resolution criteria for method 6020 are satisfied.
8	6020A *6020B*	Method Blank criteria of no detections in the method blank more than 10% of the low limit calibration check solution. TestAmeria Seattle will only evaluate the method blank to 1/2 the RL or Project DQOs and when specific DQOs are not provided by the client the RL will be defined as the DQO.
9	200.8	Method Blank criteria of no detections in the method blank more than 2.2 times method detection limit. TestAmeria Seattle will only evaluate the method blank to 1/2 the RL for DoD and LaMP projects and to the RL for all other projects.
10	*6020A 6020B*	*IDL Studies are being performed annually not every 3 months.*

17.0 Tables

Table I: Recommended Elemental Equations

Table II: Contributions of Contaminant Elements when Resolution and Measurement Schemes Vary

Table III: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Table IV: Changes in Isobaric Molecular-Ion Interferences with Changing Plasma Conditions

Table V: Recommended Internal Standards

Table VI: Interference Check Sample Components and Concentrations

Table VII: Suggested Mass Choices

Table VIII: Tuning Solution

Table IX: Suggested Tuning and Response Factor Criteria

Table X: Summary of Quality Control Requirements

Table XI: Calibration, Calibration Verification, and Spike Concentrations

Table XII: Reporting Limits

Appendix A: Troubleshooting guide

18.0 Revision History

- Revision 26, dated 2 May 2017
  - Incorporated Method 6020B throughout.
  - Updated Internal Standard limits, sections 4.3.3, 10.4.3 and Table X
  - Added more detail for the Linear Dynamic Range study, section 7.2.7
  - Removed dilutions for method 200.8, section 10.9.4
  - Added LDR Check sample, section 10.9.5
  - Updated Table VI and XII

- Revision 26, dated 2 March 2016
  - Incorporated ROMD 00063 in sections 12.1.1 and 16.0

- Revision 25, dated 24 September 2014
  - Changed all references of Reagent water to DI water
  - Added r value criteria to ICAL section 10.4.1
  - Updated method blank criteria, section 9.4
  - Updated section 16.0 to add modification to 200.8

- Revision 24, dated 4 January 2014
  - Updated section 4.3.3 with 6020A internal standard intensity criteria
  - Added computer hardware and software, section 6.2
  - Updated section 7.2.6 to include LLICV and CCVL
  - Updated NCM criteria, section 9.3
  - Updated method blank criteria, section 9.4
  - Updated section 9.8 with 6020A internal standard intensity criteria
  - Updated serial dilution criteria for LaMP, section 9.9
  - Updated PDS criteria fro 6020A and added corrective action, section 9.10
  - Updated section 10.4.3 with 6020A internal standard intensity criteria
  - Updated section 10.7 to include LLICV and CCVL
  - Updated section 10.9.5 to include LLICV and CCVL
  - Added troubleshooting, section 10.12
  - Updated section 16.0 to add modification to 6020A
  - Added Appendix A, section 17.0

- Revision 23, dated 6 August 2012
  - Update safety intro, section 5.0
  - Added instructions for diluting the method blank by the same factor as associated samples, section 9.4
  - Updated pollution control, section 13.0
  - Updated waste streams, section 14.1

- Revision 22, dated 25 April 2011
  - Under 4.3.2 the IS should be added at a level greater than 100,000 not 1,000,000
  - Preservation temps aligned with SW-846 chapter 3 were added in section 8.4
  - Incorporated ROMD 00025 in sections 9.5 and 9.6
  - Incorporated ROMD 00020 in section 10.2
  - Incorporated ROMD 00022 in sections 10.4.1 and 11.0
  - Added section 10.4.3 about IS limits
  - The reference under 10.7 section 7.1.6 was changed to 7.2.6
  - Made corrections to the table under 10.8
  - Section 10.10 was added about data review
  - Under 10.11.1, an explanation of what RM consists of
  - Added more complete instrument maintenance information in section 10.11
  - Incorporated ROMD 00033 in section 10.11.2
  - Table V was revised
  - Table VI was changed to reflect the dilution of this standard
  - Strontium was added to table VII
  - Suggested Mass Calibration information was updated in Table IX
  - Updated soil RLs in Table X11

- Revision 21, dated 16 April 2010
    - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
    - Updated concentrations for nitric/hydrochloric acid mixture Section 7
    - Added removal of expired standards Section 7.4.
    - Updated Method Blank criteria for BP LaMP, Section 9.4
    - Updated LCS criteria for BP LaMP, Section 9.5
    - Updated 9.7 ICS-A/AB criteria for BP LaMP, Section 9.7
    - Added criteria for additional QC, Section 9.11.
    - Updated Calibration Blank control criteria 10.6
    - Updated MRL Standard criteria for BP LaMP, Section 10.7
    - Added maintenance documentation and return to service requirements, Section 10.10.1
    - Updated TableVI with interference check sample components and concentrations

- Revision 20, dated 13 August 2009
    - Added Table XII.X. Summary of Quality Control Requirements

- Revision 19, dated 28 February 2009
    - Updated RLs in Table XII.

- Revision 18, dated 22 February 2008
    - Integration for TestAmerica and STL operations.

TABLE I: Recommended Elemental Equations

Element	Isobaric Correction	Mathematical Equation
Al	none	(1.0000)(27M)
Sb	none	(1.0000)(121M)
As	ArCl, Se	(1.0000)(75M) - (3.1278)(77M) + (1.0177)(78M)
Ba	none	(1.0000)(135M)
Be	none	(1.0000)(9M)
Cd	MoO, Sn	(1.0000)(114M) - (0.0268)(118M) - (1.0000)(135M)
Ca	none	(1.0000)(44M)
Cr	none	(1.0000)(52M)
Co	none	(1.0000)(59M)
Cu	none	(1.0000)(65M)
Fe	none	(1.0000)(57M)
Pb	none	(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)
Mg	none	(1.0000)(25M)
Mn	none	(1.0000)(55M)
Hg	none	(1.0000)(200M)
Ni	none	(1.0000)(60M)
K	none	(1.0000)(39M)
Se	Ar2	(1.0000)(78M) - (1.1869)(76M)
Ag	none	(1.0000)(107M)
Na	none	(1.0000)(23M)
Tl	none	(1.0000)(205M)
V	ClO, Cr	(1.0000)(51M) - (3.1081)(53M) + (0.3524)(52M)
Zn	none	(1.0000)(66M)
6Li	Li (natural)	(1.0000)(6M) - (0.0813)(7M)
Sc	none	(1.0000)(45M)
Y	none	(1.0000)(89M)
Rh	none	(1.0000)(103M)
In	Sn	(1.0000)(115M) - (0.0149)(118M)
Tb	none	(1.0000)(159M)
Ho	none	(1.0000)(165M)
Bi	none	(1.0000)(209M)

Where M = Total ion count rate at the specified mass.

TABLE II: Contributions of Contaminant Elements when Resolution and Measurement Schemes Vary

Concentrations listed are the approximate level (μg/L) measured when the interferent is present at 100 mg/L.

Analyte	Interferent Element	Peak Width at 10% of the Peak Height			
		1.0 amu Integration Width		0.8 amu Integration Width	
		0.9 amu	0.3 amu	0.9 amu	0.3 amu
^{121}Sb	^{120}Sn	820	5	10	1
^{121}Sb	^{122}Te	77	None	1	none
^{75}As	^{74}Se, ^{76}Se	910	4	3	none
^{9}Be	^{10}B	1,200	12	9	1
^{112}Cd	^{113}In	1,700	8	10	none
^{114}Cd	^{115}In	5,000	150	180	18
^{116}Cd	^{115}In	30	None	5	none
^{52}Cr	^{51}V	1.4	1.5	none	none
^{53}Cr	^{54}Fe	650	7	1	none
^{59}Co	^{58}Ni, ^{60}Ni	1,500	6	2	none
^{63}Cu	^{62}Ni, ^{64}Ni	190	1	none	none
^{63}Cu	^{64}Zn	4,000	14	9	none
^{65}Cu	^{64}Ni	1	1	none	none
^{65}Cu	^{64}Zn, ^{66}Zn	4,400	22	15	none
^{208}Pb	^{209}Bi	140	14	57	none
^{55}Mn	^{54}Fe, ^{56}Fe	900	8	4	none
^{58}Ni	^{59}Co	3,000	96	75	7
^{60}Ni	^{59}Co	9	4	10	5
^{62}Ni	^{63}Cu	8,500	690	4,500	16
^{107}Ag	^{106}Pd, ^{108}Pd	2,400	22	80	4
^{107}Ag	^{106}Cd, ^{108}Cd	130	3	5	2
^{109}Ag	^{108}Pd, ^{110}Pd	1,800	12	36	3
^{109}Ag	^{108}Cd, ^{110}Cd	1,600	10	37	3
^{51}V	^{52}Cr	2,100	45	410	1
^{64}Zn	^{65}Cu, ^{63}Cu	7,800	57	410	2
^{66}Zn	^{65}Cu	2	none	3	2

TABLE III: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS, SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}

TABLE III: (cont.) Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN				
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

NOTE: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Table IV: Changes in Isobaric Molecular-Ion Interferences with Changing Plasma Conditions**

	Molecular Interference	Nebulizer Flow Rate		
		High	Average	Low
Oxides	ScO/Sc	0.00326	0.00055	0.00116
	YO/Y	0.00568	0.00395	0.00353
	TbO/Tb	0.0156	0.00648	0.00614
	ClO, Cl	0.00725	0.00227	0.00233
Hydroxides	ScOH/Sc	0.00040	0.00011	0.00000
	YOH/Y	0.00078	0.00044	0.00048
	TbOH/Tb	0.00034	0.00008	0.00011
	ClOH/Cl	0.00048	0.00031	0.00029
Chlorine	ClO/Cl	0.00725	0.00227	0.00233
	ClOH/Cl	0.00048	0.00031	0.00029
	ArCl/Cl	0.00605	0.00091	0.00477

** Information for this table is being determined by the EPA.

Table V: Recommended Internal Standards

Method 6020	Method 200.8
Li 6	Li 6
Rh	Rh
Sc	Sc
Ge	Ge
Ho	Ho
Lu	Lu
Bi	Bi

Table VI: Interference Check Sample Components and Concentrations
(ICSAB minors are suggested spike levels)

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	*25*	*25*
Ca	*30*	*30*.0
Fe	*25*	*25*.0
Mg	*10*	*10*.0
Na	*25*	*25*.0
P	*10*	*10*.0
K	*10*	*10*.0
S	*10*	*10*.0
C	*20*	*20*.0
Cl	*100*	*100*.0
Mo	*0.2*	0.*2*
Ti	0.*2*	0.*2*
As	0.0	0.02
Cd	0.0	0.02
Cr	0.0	0.04
Co	0.0	0.04
Cu	0.0	0.04
Mn	0.0	0.04
Ni	0.0	0.04
Se	0.0	0.02
Ag	0.0	0.01
V	0.0	0.04
Zn	0.0	0.02

Table VII: Suggested Mass Choices

Boldface masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data. Suggested masses for method 200.8 are in "quotes."

Mass	Element of Interest
"**27**"	Aluminum
121, "**123**"	Antimony
"75"	Arsenic
138, "137", 136, **135**, 134, 132, 130	Barium
"9"	Beryllium
114, 112, "111", 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium
"**52**", **53**, **50**, 54	Chromium
"**59**"	Cobalt
"**63**", **65**	Copper
56, **54**, **57**, 58	Iron
"**208**", "**207**", "**206**", 204	Lead
24, **25**, **26**	Magnesium
"**55**"	Manganese
196, 198, 199, **200**, **201**, "**202**", 204	Mercury
58, "**60**", 62, **61**, 64	Nickel
39	Potassium
80, **78**, "**82**", **76**, **77**, 74	Selenium
"**107**", **109**	Silver
23	Sodium
88	Strontium
"**205**", 203	Thallium
"**51**", **50**	Vanadium
64, "**66**", **68**, **67**, 70	Zinc
72	Germanium
139	Lanthanum
118	Tin
35, 37	Chlorine
"98", 96, 92, **97**, 94	Molybdenum

NOTE: It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences that could affect the data quality.

Table VIII: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions that cover a typical mass calibration range.

Method 6020

Element	Concentration (µg/L)
Solution A	
Mg	10
Rh	10
Pb	10
Solution B	
Li	10
Co	10
In	10
Tl	10

Method 200.8

Element	Concentration (µg/L)
Be	10
Mg	10
Co	10
In	10
Pb	10

Table IX: Suggested Tuning and Response Factor Criteria

Minimum Response from Tuning Solution:

Be	>1,000
Mg	>2,000
Rh	>20,000
Pb	>10,000
Li	>2,000
Co	>20,000
In	>1,000
Tl	>1,000

Suggested Mass Calibration:

Be	9
Mg	24
Rh	103
Pb	208
Li	7
Co	59
In	115
Tl	203

Table X: Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
IS	Every reading.	6020 IS, 30-120% rec. 200.8 IS, 60-125% rec. 6020A/*B* IS ≥ *30*% rec.	Terminate analysis; correct the problem; recalibrate.
ICV/QCS	Beginning of every analytical run.	90 - 110% recovery. *6020B, < 20% RSD*	Terminate analysis; correct the problem; recalibrate.
ICB/CB	Immediately after each ICV	The result is < RL. **For DoD QSM, < LOD.**	Terminate analysis; correct the problem; recalibrate.
RL/LLICV	Beginning of every analytical run.	6020 & 200.8: 50 - 150% rec. 6020A: *70-130%* rec. *6020B: 65-135% rec.* DoD: 80-120% rec.	Terminate analysis; correct the problem; recalibrate.
CCV	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent. Beginning and end of each lot.	90 - 110% recovery.	Reanalyze once. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.
CCVL			
CCB	Immediately following each CCV.	The result must be < RL. For DoD QSM, < LOD.	Reanalyze once. If acceptable, continue. If unacceptable, terminate analysis; correct the problem, recalibrate the instrument, verify calibration and rerun all samples since the last acceptable CCB.
ICSA	Beginning and every 12 hours.	Monitor for possible interferences. **For DoD QSM, < LOD (unless they are a verified trace impurity form one of the spike analytes).**	See Section 9.7

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
ICSAB	Immediately following each ICSA.	Monitor for possible interferences. **For DoD QSM, ± 20%.**	See Section 9.7
Method Blank/Laboratory Reagent Blank	One per lot of 20 field samples or fewer.	The result must be < RL. Sample results greater than 10x the blank concentration or samples for which the contaminant is < RL, do not require redigestion or reanalysis. **For DoD QSM, < ½ RL.**	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	LCS must be within 80 - 120% recovery or QSM 5.0 control limits. (85-115% for 200.8) Samples for which the contaminant is < RL and the LCS results are > 120% (115% for 200.8) may not require redigestion or reanalysis (see Section 9.5).	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike (MS)	One per sample preparation batch of up to 20 samples.	75 – 125% recovery or tighter in-house control limits. **For DoD:** Use LCS control limits.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added.
Matrix Spike Duplicate (MSD)	One per sample preparation batch of up to 20 samples. 10% frequency for some programs (see **Error! Reference source not found.**)	75 – 125 % recovery; RPD ≤ 20% or tighter in-house control limits. **For DoD:** Use LCS control limits.	See Corrective Action for Matrix Spike.
Serial Dilution (6020 Only)	One per batch of 20 field samples or fewer.	90 - 110% recovery	See Section 9.9 for additional requirements.

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
Post-Digestion Spike (6020 Only)	One per batch of 20 field samples or fewer.	75-125% recovery 80-120% for 6020A	See Section 9.10.
Matrix Spike/Laboratory Fortified Matrix	One per lot of 20 field samples or fewer.	Must be within laboratory control limits	See Section 9.6 for additional requirements.

Table XI: Calibration, Calibration Verification, and Spike Concentrations

Element	Initial Calibration Levels (µg/L)					ICV (µg/L)	CCV (µg/L)	LCS (µg/L)	MS/MSD (µg/L)
	1	2	3	4	5				
Aluminum	1	10	100	500	1000	400	500	80	80
Antimony	0.1	1	10	50	100	40	50	60	60
Arsenic	0.1	1	10	50	100	40	50	80	80
Barium	0.1	1	10	50	100	40	50	80	80
Beryllium	0.1	1	10	50	100	40	50	2	2
Cadmium	0.1	1	10	50	100	40	50	2	2
Calcium	10	100	1000	5000	10,000	4000	5000	400	400
Chromium	0.1	1	10	50	100	40	50	8	8
Cobalt	0.1	1	10	50	100	40	50	20	20
Copper	0.1	1	10	50	100	40	50	10	10
Iron	10	100	1000	5000	10,000	4000	5000	440	440
Lead	0.1	1	10	50	100	40	50	20	20
Magnesium	10	100	1000	5000	10,000	4000	5000	400	400
Manganese	0.1	1	10	50	100	40	50	20	20
Mercury	0.005	0.05	0.5	2.5	5	2	2.5	1.0	1.0
Molybdenum	0.1	1	10	50	100	40	50	100	100
Nickel	0.1	1	10	50	100	40	50	20	20
Potassium	1	10	100	500	1000	4000	5000	400	400
Selenium	0.1	1	10	50	100	40	50	80	80
Silver	0.1	1	10	50	100	40	50	12	12
Strontium	0.1	1	10	50	100	40	50	40	40
Thallium	0.1	1	10	50	100	40	50	80	80
Tin	0.1	1	10	50	100	40	50	100	100
Titanium	0.1	1	10	50	100	40	50	100	100
Uranium	0.1	1	10	50	100	40	50	40	40
Zinc	0.1	1	10	50	100	40	50	20	20

This procedure has been developed for thirty-five elements (See Table VIII). Additional elements may be included in the calibration solution at the above levels. Levels may be adjusted to meet specific regulatory or client programs.

Table XII: Reporting Limits

Element	*Water Low Level (µg/L)*	Water (µg/L)	*Soil Low Level (µg/kg)*	Soil (µg/kg)
Aluminum	*100*	500	*15,000*	30,000
Antimony	*0.4*	2	*100*	200
Arsenic	*1*	5	*250*	500
Barium	*1.2*	6	*250*	*500*
Beryllium	*0.4*	2	*100*	200
Cadmium	*0.4*	2	*100*	*400*
Calcium	*10,000*	50,000	*50,000*	100,000
Chromium	*0.4*	2	*250*	*500*
Cobalt	*0.4*	2	*100*	200
Copper	*2*	*10*	*500*	*1000*
Iron	*200*	*1000*	*20,000*	40,000
Lead	*0.8*	*4*	*250*	500
Magnesium	*10,000*	50,000	*50,000*	100,000
Manganese	*2*	*10*	*500*	*2000*
Mercury	*0.25*	*1.25*	*100*	200
Molybdenum	*0.8*	4	*200*	400
Nickel	*3*	15	*250*	500
Potassium	*10,000*	50,000	*50,000*	100,000
Selenium	*8*	*40*	*500*	*1000*
Silver	*0.4*	2	*100*	200
Sodium	*10,000*	50,000	*75,000*	150,000
Strontium	*0.4*	2	*250*	500
Thallium	*1*	5	*200*	400
Tin	*10*	*50*	*1500*	3000
Titanium	*1*	5	*500*	1000
Uranium	*0.6*	*3*	*100*	200
Vanadium	*4*	*20*	*1000*	2000
Zinc	*7*	*35*	*2500*	5000

Appendix A – Troubleshooting Guide

Error Messages

The following messages can appear in the ChemStation green message bar when you operate the Agilent 7500. When an error message is displayed, the instrument runs a safety sequence.

Click on an error No., and you will jump to the error message corresponding to the error No.

NOTE:
An * (asterisk) indicates that an error number has multiple messages and contents. Please check the error message and error number to properly identify the problem.

1000	1001	1002	1003	1004	1005	1006 *
1007	1008	1009 *	1010 *	1011	1012 *	1013
1014	1015	1016 *	1017	1018	1019	1020
1021	1022	1023	1024	1025	1026	1027
1090	1099	1100	1101 *	1102 *	1103 *	1104 *
1109 *	1110 *	1111 *	1112 *	1113 *	1114	1115 *
1116 *	1117	1118 *	1119 *	1120 *	1121 *	1122
1123	1124	1125	1126	1127	1128	1129
1130	1131	1132	1133 *	1134	1135	1136
1137	1138	1139 *	1140	1141	1142	1143 *
1144	1145	1146	1147	1148	1149 *	1150
1151 *	1152	1153	1200	1201	1202	1203
1204	1205	1206	1208 *	1209	1210	1211 *
1212	1213	1214	1215 *	1216	1217	1218
1219 *	1220	1221 *	1222	1223	1226	1300
1301	1302	1303	1304	1305	1306	1307
1308	1309	1400 *	1402	1410	1411	1413
1414	1415	1416	1417	1418	1422	1430
1432	1433	1434	1435	1436	1440 *	1441
1442	1443	1445	1446	1449	1450	1451
1452	1453	1454	1455	1518	1519	1520
1521	1522	1523	1524	1525	1526	

Alarm Messages Number List

NOTE:
An * (asterisk) indicates that an error number has multiple messages and contents. Please check the error message and error number to properly identify the problem.

2150 *	2151 *	2152	2153	2400 *	2402
2403	2404	2405	2412	2413	2414
2415	2416	2433	2435	2605	2606
2607	2608	2609	2610	3000	3001
3002	3003	3004			

1000 **Execution Error: Instrument is busy- Between Transition Modes.**
Attempted to execute a command that cannot be executed during mode transition. Transitioning modes.

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber
Instrument Drift	RF not cooling properly Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors

Title: Determination of Volatile Organic Compounds and Total Purgeable Petroleum Hydrocarbons by GC/MS [Methods 8260B, 8260C, 624]

Approvals

Signatures on File	
Isaac Hooper — Date	Manjit Nijjar — Date
Volatiles Department Manager	Health & Safety Manager / Coordinator
Terri Torres — Date	Dennis Bean — Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 This method is applicable to the determination of volatile organic compounds (VOCs) in water, wastewater, soils, sludges, and other solid matrices. Standard analytes are listed in Tables 1, 2, and 3.

1.2 This SOP is applicable to Method 8260B and 8260C. Appendix A presents modifications to the procedures in the main SOP that are necessary for analysis of wastewater by Method 624 (CWA compliance testing). It is important that the differences among these methods are carefully observed.

1.3 This method can be used to quantify most volatile organic compounds that have boiling points below 200 °C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4 The method is based upon a purge-and-trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 1 to *100* µg/L for 8260B and 8260C waters, 1 to *100* µg/kg for low-level soils, and 8 to 6,000 µg/kg for *medium*-level soils. The working range for Method 624 (5 mL purge) is 1-*100* µg/L.

1.5 Reporting limits *can be located in TALS > Global Method Data > Methods (select method) > Limits View > LT Code (select "RL") > Select Matrix*.

1.6 Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates (MS/MSD), and laboratory control spike samples (LCS/*LCSD)*.

1.7 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2 Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate; sampled directly into pre-tarred VOA vials which contain 5mL reagent free water, a magnetic stir bar, and are immediately frozen; or collected in a suitable container to be transferred in total or by aliquot to a VOA vial and purged directly.

2.3 In the purge-and-trap process, an inert gas (generally *Helium*) is bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column (trap) is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components, which are detected with a mass spectrometer.

2.4 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3.0 Definitions

3.1 Both SW-846 (RCRA) and drinking water (SDWA) terminology are used in this section for cross-reference purposes. Elsewhere in the SOP, the SW-846 terminology is used exclusively.

3.2 Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each 4-bromofluorobenzene (BFB) analysis will normally start a new batch. Batches for high-level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

The Quality Control batch must contain a matrix spike/spike duplicate pair (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. If there is insufficient sample to perform the MS/MSD, a duplicate LCS is used to establish batch precision when requested by the client. Refer to SOP TA-QA-0620 for further details of the batch definition.

3.3 Method Blank (MB) or Laboratory Reagent Blank (LRB)

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data. Sparged water or water that has been boiled then cooled to ambient temperature is used as the blank medium for water batches and muffled Ottawa Sand for soil batches. Prepared (muffled at *400*C for at least *4* hours) batches of Ottawa sand are tracked using the reagent data base in the Laboratory Information Management System (known as TALS) and are at the time of the writing of this SOP named with the following convention: VoaSand_XXXXX.

3.4 Laboratory Control Sample (LCS) or Laboratory Fortified Blank (LFB)

A blank matrix (reagent water or muffled Ottawa Sand) is spiked with the analytes of interest and is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.5 Surrogates

Surrogates are organic compounds that are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but that are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

3.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD) or Laboratory Fortified Sample Matrix (LFM)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample, which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.7 Calibration Check Compound (CCC)

CCCs are a representative group of compounds that are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift (%D) for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.8 System Performance Check Compounds (SPCC)

SPCCs are compounds that are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

3.9 Initial Calibration Verification (ICV) or Quality Control Sample (QCS)

The ICV is a second-source calibration verification standard. The QCS is reagent water or an environmental sample that is fortified with target analytes at known concentrations. This too is a second-source standard, i.e., different than the source of calibration standards.

3.10 Continuing Calibration Verification (CCV) or Laboratory Performance Check Solution (LPC)

A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, boiled and cooled to ambient or sparged purified reagent water, and approved lots of purge-and-trap-grade methanol will greatly reduce introduction of contaminants. In extreme cases, the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly Methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3 Matrix interferences may be caused by non-target contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

Note: Due to the large number of analytes analyzed for in this method, some with higher boiling points are considered Semi-Volatile analytes. It may be necessary to evaluate for cross-contamination at levels above 10 ug/L for Naphthalene and 1,2,3-Trichlorobenzene; above 20 ug/L for 2-Ethyl-1-hexanol, n-Butylbenzene and Hexachlorobutadiene; above 50 ug/L for tert-Butylbenzene, sec-Butylbenzene, 4-Isopropyltoluene, 1,2,4-Trichlorobenzene and Ethylbenzene; above 100 ug/L for Methacrylonitrile, 1,3,5-Trichlorobenzene, 1,2-Dibromo-3-Chloropropane and Toluene, and all other analytes should be evaluated for potential cross-contamination above a detected concentration of 150 ug/L or more. (These concentrations are based on a carry-over study conducted by the laboratory detecting cross-contamination above ½ the RL). It may, therefore, be necessary to run an instrument rinse after laboratory spiked samples, such as high calibration levels, CCVs, LCS and MS to ensure no cross contamination occurs. **All client samples are also evaluated using the same criteria.**

4.5 Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered, an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used *and must also be added to the Method Blank (MB).*

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 The autosampler, purge and trap, gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.2 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.3 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.4 Cut resistant gloves or a protective cloth must be used when opening voa vials.

5.1.5 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol (MeOH)	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.
- Gas Chromatographic Column used for 8260:

  : 60 m X 0.25mm ID DB-VRX with 1.4 µm film thickness.

  Note: Other columns may be used. The serial number of the column used is documented in the instrument maintenance logbook.
- Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 amu every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria.
- GC/MS interface: In general glass jet separators are used but any interface (including direct introduction to the mass spectrometer) that achieves all acceptance criteria may be used.
- Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

- Sample Purger: The recommended purging chamber is designed to accept between 5 mL and 25 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.
- Trap: A variety of traps may be used, depending on the target analytes required. The O.I. #10 (Tenax/Silica gel/Carbon Molecular Sieve) is recommended. Other traps such as the Vocarb 3000 or Vocarb 4000 may be used if the Quality Control criteria are met.
- Desorber: The desorber should be capable of rapidly heating the trap up to 270 °C depending on the trap packing material. Many such devices are commercially available.
- Purge-and-trap Autosampler: An autosampler capable of sampling from a sealed vial, Varian Archon, or equivalent.

6.2 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- LIMS system: TALS version 1.0 or higher.
- Data acquisition system: Agilent (Hewlett Packard) ChemStation for Windows 95 (version G1701AA) or equivalent. Agilent's ChemStation, is used for data acquisition and storage on machine-readable media. Since no processing is done by ChemStation and since there are no audit trail functions associated with data acquisition, the audit trail feature for ChemStation may be either enabled or disabled. The other component, Chrom, is used for data processing such as the measurement of peak area or peak height. By design, the audit trail feature for Chrom is always enabled.
- Data processing: Chrom version 1.2 or higher. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. In addition, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.3 Supplies

- Microsyringes: 0.5 µL gas tight and larger, 0.006-inch ID needle
- Balance: Top-loading balance capable of weighing 0.1 g. The balance used for sample preparation is calibrated daily by a designated primary analyst (a back-up analyst is also assigned should the primary be unavailable). The analyst must perform this check according to SOP TA-QA-0014. It is also the responsibility of any analyst performing work on the balance to check the Balance logbook to determine if the daily calibration check has been completed, before beginning work.
- Scintillation Vials: 20 mL with screw caps.
- Volumetric flasks: 10 mL to *200* mL, class A with ground-glass or Teflon ® stoppers.
- Spatula: Stainless steel.
- Disposable pipettes: Pasteur.
- pH paper: Wide range (0-14) and narrow range (0-2.5).
- Helium: Ultra high purity, gr. 5, 99.999%.
- Nitrogen: Ultra high purity, from cylinders or gas generators, may be used as an alternative to helium for purge gas.

Note: The use of Nitrogen as a purge gas is not allowed for analysis of VOA contaminants in drinking waters.

- Compressed air: Used for instrument pneumatics.

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Reagents

7.2.1 Methanol: Purge and Trap Grade, High Purity

7.2.2 Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See Section 9.3.) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas for a minimum of 1 hour or boiling and cooling to ambient temperature prior to use. Other methods of preparing reagent water are acceptable.

7.3 Standards

7.3.1 If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturer's expiration date.

7.3.1.1 Purchased standards are stored at the manufacturer's specifications (i.e. ambient, freezer, refrigerator). Standards prepared from these purchased standards are stored in the freezer.

7.3.2 Calibration Stock Standard Solutions: Components of stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at $\leq$-10°C. Each *month a new standard is prepared.* Note: *Standards* may be prepared on a more frequent basis based on analyst observed signs of degradation.

7.3.3 Calibration Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20%, then corrective action is necessary. Generally, an analysis of all individual compounds meeting the method criteria will suffice, however a continual failure of CCC compounds may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem (two CCVs in a row fail), then a new initial calibration must be performed.

7.3.4 Aqueous calibration standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

Likewise, *medium l*evel methanolic calibration standards are prepared in reagent water with a matrix matched methanol concentration of one fortieth P&T methanol using the secondary dilution standards and must be prepared daily.

7.3.5 Internal standards (IS) are added to all samples, standards, and blank analyses. Refer to Table 5 for internal standard components.

7.3.6 Surrogate Standards: Refer to Table 6 for surrogate standard components and spiking levels.

7.3.7 Laboratory Control Sample Spiking Solutions: Refer to Tables 7 and 7a for LCS components and spiking levels.

7.3.8 Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Tables 7 and 7a.

7.3.9 Tuning Standard: A standard is made up that will deliver *a maximum* 50ng of 4-Bromofluorobenzene on column upon injection.

7.4 As soon as standard preparations are completed, the *working* standards must be returned to the freezer.

7.5 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards/reagents and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. The holding time for acid-preserved samples is 14 days from sample collection. For compliance with Method 624, 8260B and 8260C, unpreserved samples must be tested within 7 days of collection.

8.2 There are two exceptions to the information provided in Section 8.1 above:

8.2.1 2-Chloroethyl vinyl ether, acrolein, and acrylonitrile are hydrolyzed in the presence of acid. For samples collected for analysis of this compound, a separate vial without acid should be recommended.

8.3 Soils

8.3.1 Approved sampling containers for Method 5035 are EnCores, VOAs (with or without water and stir bar), and VOAs preserved with methanol or with sodium bisulfate

8.3.2 The holding time for sodium bisulfate and methanolic preserved samples is 14 days.

8.3.3 Soil collected using the EnCore™ sampler must be preserved in the laboratory within 48 hours of sampling. At specific client request, if the data is to be reported as 5030, the hold time for preservation and analysis is 14 days from collection. The holding time for EnCore™ samples varies based on client specifications and can be 48 hours, 7 days, or 14 days, see the table in Section 8.4.

8.3.4 The holding time for VOAs (with or without water and stir bar) varies based on client specifications and requirements and can be 48 hours, 7 days, or 14 days, see the table in Section 8.4.

8.4 Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	Three 40-mL VOA vials	40 mLs	HCl, pH < 2; Cool 0-6°C	14 Days	40 CFR Part 136.3 / 5030
Waters	Three 40-mL VOA vials	40 mLs	Cool 0-6℃	7 Days	40 CFR Part 136.3 / 5030
Soils	Three Encore Samplers	5 grams	Cool 0-6℃ or -10 to -20℃	48 Hrs for Preservation or 14 Days	5035A
Soils	Three VOA vials	5 grams	Sodium bisulfate Cool 0-6℃	14 Days	5035A
Soils	40 ml VOA vial or 4oz septa top jar	10 grams or 25 grams	Methanol Cool 0-6℃	14 Days	5035A
Soils	Three 40-mL VOA vials	5 grams	With or without DI Water -10 to -20℃	14 Days	5035A

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Soils	Glass Jar	10 grams	Cool 0-6°C	5035A:48 Hrs for Preservation 14 Days 5030: 14 Days	5035A or 5030C
Waste	Glass Jar	10 grams	Cool 0-6°C	14 Days	5030C

[1] Inclusive of preparation and analysis.

8.5 Aqueous samples are stored in three 40 ml glass VOA vials with Teflon lined septa at 0-6°C, with minimal headspace. If a bubble is present and it is less than 6 mm in diameter, analysis may continue with the appropriate NCM added. If headspace exceeds this amount, then a non-conformance memo must be written and in some cases client approval requested to continue analysis.

8.6 Soil Sample Collection for *Medium*-Level Analysis using Field Methanol Preservation

8.6.1 A pre-tared four ounce volatile soil jar with an accompanying VOA vial containing 25ml of a methanol/surrogate solution containing the surrogate TFT is sent out for each sample required when the sampling occurs in the state of Alaska. Otherwise a pre-tarred VOA vial containing 10 mls of methanol is sent out for each sample required. In addition the appropriate amount of trip blanks are also sent out. All bottles sent to the field are labeled with the tare weight and lot number of the methanol/surrogate solution or methanol.

8.6.2 Field samples are collected *in a 1:1 ratio, (grams of sample:mL of MeOH). Alaska samples are* placed in the *collection container* with septa lined lid *prior to adding* one VOA vial containing 25 mls of methanol/surrogate solution. *For all other methods* ten gram field samples are collected by adding an appropriate amount of sample to a 40 mL VOA vial *already c*ontaining 10 mL of methanol.

8.7 Soil Sample Collection for *Medium*-Level Analysis using EnCore™ or TerraCore™ samplers.

8.7.1 If the sample is collected a sample in an EnCore™ sampler a minimum of one EnCores should be provided to the lab. If the samples are collected using the TerraCore sampler a minimum of one 40-ml VOA vial with 5 grams of soil. Samples must be received prior to 48 hours from sampling in order to be frozen or extracted in methanol. Following shipment back to the laboratory, the soil is preserved in methanol.

8.8 Soil Sample Collection for *Medium*-Level Analysis *of U*npreserved *Soil*

8.8.1 When specifically requested by a client, unpreserved soils packed into glass jars or brass tubes may be accepted, subsampled and methanol preserved in the laboratory. These samples have a hold time of 48 hours from sample collection to sub-sampled and preserved if following Method 5035. Otherwise if following Method 5030 the holding time is 14 days to analysis.

8.9 Soil Sample Collection for Low-Level Procedure

8.9.1 Samples may be collected in 5g EnCore™ sampling device (it is recommended that a minimum of two 5g EnCore™ samples are collected, but three are preferred). Soil samples collected in a 5g EnCore™ sampling device and returned to the laboratory are extruded into a VOA vial with stir bar and frozen upon receipt or extruded into a scintillation vial with methanol and refrigerated upon receipt.

8.9.2 Samples may be collected in vendor purchased pre-tared VOA vials with or without 10 mL of DI Water with a magnetic stir bar. Samples collected in pre-tared VOA vials are stored at -10 to -20℃ in the volatile laboratory soils fr eezer until sample analysis.

8.9.3 Samples may be collected in vendor purchased pre-tared VOA vials containing 5 or 10 mL of 20% Sodium Bisulfate solution with a magnetic stir bar. Due to the exhibited potential of positive interferences in the purchased prepared vials (most notably ketones and BTEX

compounds). Samples collected in pre-tared Sodium Bisulfate preserved sample vials are stored at 0-6℃ in the volatile laboratory soils re frigerator until sample analysis.

8.9.3.1 Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, samples should be taken in a 5g EnCore™ sampling device, and stored at ≤–10℃ until analysis.

8.9.3.2 If client specifications require field preservation, samples may be collected in pre-tared VOA vials containing a magnetic stir bar and 5 mL of reagent water. Sample collected in this manner must be received and frozen by the laboratory within 48 hours of sampling. Samples stored in this manner **MUST** be frozen on their sides to minimize possible breakage of the sample container due to expansion of water as it freezes.

8.10 A refrigerator or freezer blank is stored in each refrigerator or freezer with the samples. This is analyzed at minimum every 14 days, but may be analyzed more frequently as needed (see SOP TA-QA-0616). The refrigerator or freezer blank should be run immediately after the method blank.

8.11 Percent Moisture Correction for Soils

A percent moisture correction may be performed on soil samples to adjust the extraction final volume of the sample in order to allow for the miscible solvents effect, as required by the client. Percent moisture must be determined if results will be reported as dry weight and percent moisture correction to be performed; refer to SOP TA-WC-0125 for determination of percent moisture. For all methanolic samples with a % moisture of greater than 10%, the following formula is used to determine the corrected final volume:

Corrected FV = ((g of sample * % Moisture/100) + mL of Methanol) * 40

(Also noted in section 12.9)

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in the TestAmerica Seattle QAM.

9.1.2 Specific QC requirements for Federal programs, e.g., USACE and Navy projects, are described in DoD QSM v5*.1* or the latest promulgated version.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS and may also come in the form of email or written notifications distributed at "project kick off" meetings.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or

in the same sequence. The method blank must be run on each instrument and in each analytical batch.

9.3 Method Blanks

For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards and before any samples. For low-level volatiles in water, the method blank consists of reagent water. For low-level volatiles in soil, the blank medium is muffled Ottawa sand. For *medium*-level volatiles, the method blank consists of 10 mL of reagent grade methanol and ten grams of muffled Ottawa sand. Surrogates are added and the method blank is carried through the entire analytical procedure.

Acceptance Criteria: For DoD/LaMP projects the method blank must not contain any analyte of interest at or above one-half the reporting limit or above 1/10 the measured concentration of the analyte in the associated samples or 1/10 the regulatory limits, whichever is greater. For DoD projects, when written approval is received (method notes will contain “2CLC” or “Std Var App” to indicate approval has been received), the method blank must not contain any common laboratory contaminants above the reporting limit. Contamination up to the reporting limit is allowed for non DoD/LaMP projects or at or above 1/10 of the measured concentration of that analyte in the associated samples, whichever is higher.

The method blank must have acceptable surrogate recoveries.

Corrective Actions: For DoD projects, if the analyte is a common laboratory contaminant (i.e., acetone, 2-butanone, carbon disulfide and methylene chloride), and written approval has been received, the data may be reported with qualifiers if the concentration of the analyte is less than the reporting limit. For non-DoD if the analyte is a common laboratory contaminant (i.e., methylene chloride, acetone, 2-butanone, ethyl ether, Acetonitrile and hexane) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit.

Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the associated samples.

If there is no target analyte greater than the RL (less than one half the RL for DoD clients) in the samples associated with an unacceptable method blank, the data may be reported with qualifiers for non-DoD clients. For DoD clients the data may only be reported if written approval has been received.

If surrogate recoveries in the blank are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all affected analytes in the associated samples are flagged as required by the project, and appropriate comments may be made in a narrative to provide further documentation.

9.4 Surrogates

Every sample, blank (including instrument blanks), and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that

recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 6.

Acceptance Criteria: Acceptance limits for surrogate recoveries are set at ± 3 standard deviations around the historical mean or as defined by project or program requirements. Surrogate recovery limits are updated at a fixed frequency by QA and stored in the LIMS.

Corrective Actions: If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Re-prepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is necessary to re-prepare/reanalyze a sample only once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and re-preparation/reanalysis is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

Re-analysis is not necessary if obvious matrix effect is shown in the chromatograms (e.g. a large co-eluting peak with the same quantitation ion, or non-target interferences) or were noted in sample prep (e.g. high percent moisture content without moisture correction). A non-conformance memo is generated stating the reason for not re-analyzing the affected sample.

NOTE: For LaMP client samples, if the surrogate percent recovery fails, the recovery must be confirmed by re-extraction and reanalysis with the following exceptions:

- The lab has unequivocally demonstrated a sample matrix effect and informed the LaMP client representative.
- The recovery exceeds control limits and all target analytes in the sample are non-detect.

9.5 Laboratory Control Samples (LCS)

An LCS is analyzed for each batch. The LCS is analyzed after the calibration standard and the method blank, and normally before any samples. The LCS contains all of the analytes of interest (see Table 7a) and must contain the same analytes as the matrix spike.

Acceptance Criteria: The LCS recovery for the control analytes must be within established control limits. Unless otherwise specified in a reference method or project requirements, the control limits are set at ± 3 standard deviations around the mean of the historical data or based on project/program limits. An LCS that is determined to be within acceptance criteria effectively demonstrates that the analytical system

is in control and validates system performance for the samples in the associated batch. Recovery limits are updated at a set frequency by QA and are stored in the LIMS.

If there are a large number of analytes in the LCS, then a specified number of results may fall beyond the LCS control limit (3 standard deviations), but within the marginal exceedance (ME) limits, which are set at ± 4 standard deviations around the mean of historical data. Marginal exceedances are recognized and allowed by NELAC. The number of marginal exceedances is based on the number of analytes in the LCS, as shown in the following table:

# of Analytes in LCS	# of Allowed Marginal Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

If more analytes exceed the LCS control limits than is allowed, or if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be random. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem. The source of the error must be identified and corrective action taken.

For non-DoD projects, if the LCS recovery is high and there are no detections in the associated samples for the affected analytes the data may be reported with qualifiers. For DoD projects the data may only be reported with qualifiers if approval has been received in writing (method notes will contain “3HR” or “Std Var App” to indicate approval has been received).

Note: For DOD projects, all exceedances of LCS Control Limits, are subject to corrective action. Therefore, all instances of LCS failures including the high bias but not detected in the associated samples scenario, must be investigated. For example and as noted above, the randomness of these failures can be evaluated or the spike solution can be re-verified. When the source of the problem is identified, corrective action is taken or variance from the QSM is requested.

Corrective Actions:

If any analyte or surrogate is outside established control limits as described above, the system is out of control and corrective action must occur. Corrective action will normally be re-preparation and reanalysis of the batch.

If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records (via NCMs and the case narrative) and in the final report. Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS. This type of justification should be reviewed and documented with the client before reporting.

If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Tables 7 and 7a. The selection of the spike solution is dependent on client program requirements. The matrix spike/duplicate must be analyzed at the same base dilution as the unspiked sample, even if the matrix spike compounds will be diluted out. Dilutions (beyond the base dilution if necessary) of MS/MSD analyses are not required unless there are specific client instructions to do so. If necessary, this requirement will be passed to the laboratory through the PM by means of the mechanisms described in section 9.1.3 of this SOP.

Acceptance Criteria: The MS/MSD recovery for the control analytes must be within established control limits. Unless otherwise specified in a reference method or project requirements, the control limits are set at ± 3 standard deviations around the mean of the historical data. The relative percent difference (RPD) between the MS and the MSD must be less than the established RPD limit, which is based on statistical analysis of historical data. MS/MSD recovery and RPD limits are updated at a regular frequency by QA and are stored in the LIMS.

Corrective Actions: If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

If the recovery for any component is outside QC limits for both the matrix spike/matrix spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch, except in cases where a high bias is indicated and no target is detected above the reporting limit in any associated sample.

If an MS/MSD is not possible due to limited sample, then a LCS duplicate (LCSD) should be analyzed. The RPD between the LCS and LCSD is compared to the established acceptance limit.

9.7 If batch QC samples or trip blanks are re-analyzed to confirm a recovery or result, and an improvement in results would cause the re-analysis to be reported, then the associated client samples must also be re-analyzed. The only exception to this protocol would be if an obvious analytical problem occurred during the initial analysis (i.e. no internal standard added, bent autosampler needle, etc).

9.8 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

10.1 Samples scheduled for EPA 624 will be analyzed separately (different ICAL and sequence) from samples scheduled for EPA 8260B or 8260C. Refer to appendix A for Modifications for Method 624.

10.2 One time procedural variations are allowed only if deemed necessary in the professional judgment of management to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance

Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.3 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.0 Calibration

11.1 Summary

Prior to the analysis of samples and blanks, the GC/MS system must be tuned and calibrated. Tuning is accomplished by analyzing 4-bromofluorobenzene (BFB) to establish that the GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations to determine the linearity of the response utilizing target calibration standards. The calibration must be verified each twelve-hour time period for each GC/MS system. The use of a separate calibration is required for low level water.

11.2 Recommended Instrument Conditions

11.2.1 General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 amu
Scan Time:	to give at least 5 scans/peak, ≤ 2 seconds/scan
Injector Temperature:	200 – 250 ˚C
Source Temperature:	According to manufacturer's specifications
Transfer Line:	Temperature: 250 – 300 ˚C
Purge Flow:	40 mL/minute (± 5 mL/min)
Carrier Gas Flow:	1-15 mL/minute, dependent upon column specifications

11.2.2 Gas Chromatograph Temperature Program

The temperature programs vary with the column type and instrumentation used. The GC run program on each instrument should be optimized so that each peak is broad enough to accommodate at least 5 scans across the peak (not counting the scans at the baseline start and end of the peak). The actual individual method parameters used are stored in each individual instrument methods folder on the network and can be referenced there.

11.3 Instrument Tuning

Each GC/MS system must be hardware-tuned to meet the abundance criteria listed below and in Table 8 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB. It is critical to accurately estimate the number of samples that can be analyzed within the 12-hour window. When a tune isn't analyzed every 12-hours (i.e., samples are analyzed outside of the 12-hour window), the event must be documented in a non-conformance memo and corrective *action m*ust be taken. Whenever feasible, samples that were analyzed outside of the 12-hour window will be re-analyzed within a new 12-hour window. When reanalysis is not feasible, results for the affected samples can only be reported if it's technically justified (e.g., subsequent tune passes), the data has been qualified, and it's been authorized and accepted by the client. The BFB may be taken from a specified BFB Tune injection or from the CCVIS. In the case of a calibration sequence, a specified BFB Tune must be injected prior to the injection of the first calibration standard. If an acceptable tune is not achieved, the autosampler prepares another tune standard by adding BFB to either the CCVIS or an instrument blank. The autotune process is repeated once. If the subsequent tune attempt fails, one or more of the corrective actions suggested in the TestAmerica, Inc. corporate tune policy, CA-Q-QM-002 are *to be* attempted.

Mass	Ion Abundance Criteria
50	15 to 40 % of Mass 95
75	30 to 60 % of Mass 95
95	Base Peak, 100 % Relative Abundance
96	5 to 9 % of Mass 95
173	Less than 2 % of Mass 174
174	50 to 120 % of Mass 95
175	5 to 9 % of Mass 174
176	Greater than 95 %, but less than 101 % of Mass 174
177	5 to 9 % of Mass 176

11.4 Initial Calibration

11.4.1 A series of five or more initial calibration standards is prepared and analyzed for the target compounds. Nominal calibration levels for a standard level water purge, low level soil purge and *medium* level methanolic extract purge are 0.2, 0.4, 1, 2, 5, 10, 20, 50, 100 and 150 µg/L. Low level waters curves are prepared at 0.02, 0.0*5*, 0.10, 0.20, 0.40, 1, 5, 10, 2*5*, *4*0, and *50* ug/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Table 4 shows the calibration levels for each analysis. The purge volume is *5 mL for standard level waters and* 1*5* mL *for low level waters*. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument or program requirements. Calibration levels may also vary based on analyst discretion in so far as the minimum number of calibration points are met for the curve type utilized (five for average response factor and first order curves, six for second order curves) and the lowest point on the curve is at or below the current TestAmerica Seattle reporting limit.

11.4.2 The same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

11.4.3 It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for some tests.

11.4.4 Rejection of Calibration Points

Calibration levels below the reporting limit may be removed provided that the minimum number of calibration points are met for the curve type utilized (five for average response factor and first order curves, six for second order curves), and the lowest standard is at or below the TestAmerica Seattle reporting limit.

High point calibration levels may also be removed so far as the minimum number of calibration points are met for the curve type utilized (five for average response factor and first order curves, six for second order curves) and the midpoint of the curve (the ICIS) is not the highest point of the calibration range.

Generally, it is NOT acceptable to remove mid-points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems must be fixed and documented in the maintenance logbook. Then the calibration standards must be reanalyzed. If, however, there is documented evidence of a problem with a calibration

point (e.g. misinjection, poorly sealed vial, etc…) then one point might be rejected, but it is recommended to re-calibrate.

Refer to Corporate SOP GA-Q-S-005, Calibration Curves, for further details.

11.4.5 Internal Standards

Internal standard calibration is used. The internal standards are listed in Table 5. Target compounds should reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See Corporate SOP CA-Q-S-005, for calculation of response factor and other related algorithms.

11.4.6 Calibration Check Compounds (CCC), 8260B

For 8260B the % RSD of the calibration check compounds (CCC) must be less than or equal to 30% even in cases where a first or second order regression is used for the calibration curve. Refer to Table 10. If the %RSD exceeds 30% for any CCC, the system must be evaluated (e.g. maintenance and accuracy of calibration standards) and the calibration re-run.

11.4.7 System Performance Check Compounds (SPCC), 8260B

The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. For 8260B the five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 9 for the SPCC compounds and required minimum response factors. If the minimum response factors are not met for any CCC, the system must be evaluated (e.g. maintenance and accuracy of calibration standards) and the calibration re-run.

11.4.8 For 8260C the most common target analytes are checked for a minimum response factor for each calibration level. See Table 14 for the compound list and minimum relative response factor criteria. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet this criterion. Compounds which commonly fail the criteria have been studied for an appropriate RF factors using data over a period of 3 months from all instruments used for 8260C analysis. These compounds have RF criteria based on their average RF over the time period and subtracting one standard deviation in order to include all acceptable data. For any analyte non-detect associated with a calibration that fails the minimum response factor criteria there must be a demonstration of adequate sensitivity at the quantitation limit. This is achieved by the successful analysis of a CCVL (CCV at the reporting limit) in the same analytical batch. The criterion for the CCVL is detection only but the standard qualitative identification criteria in the method must be met.

11.4.9 If all of the %RSD values in the calibration are ≤ 15% for 8260B, then all analytes may use average response factor for calibration. If all of the %RSD values in the calibration are ≤ 20% for 8260C, then all analytes may use average response factor for calibration. For analytes that fail the RSD criteria, use linear or quadratic curve.

11.4.10 If the software in use is capable of routinely reporting curve coefficients for data validation purposes and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD ≤ 15% (8260B or DoD) or ≤ 20% (8260C) for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve, then the appropriate curve should be used for quantitation. The correlation coefficient (r) must be ≥ 0.990 for SW-846 and must be ≥ 0.995 for DoD clients. For non-linear curves, the coefficient of determination (r^2) must be ≥ 0.990 for both SW-846 and DoD requirements.

11.4.11 If the software in use is capable of routinely reporting curve coefficients for data, then calibration on a curve must be used for all analytes with %RSD > 15% (8260B) or %RSD > 20% (8260C). The analyst should consider instrument maintenance to improve the linearity of response. Otherwise, the correlation coefficient (r) must be ≥ 0.990 for SW-846 and must be ≥ 0.995 for DoD clients. For non-linear curves, the coefficient of determination (r^2) must be ≥ 0.990 for both SW-846 and DoD requirements.

11.4.12 For 8260C no more than 10% of compounds can fail the 20% RSD/0.990 correlation coefficient requirement. Any individual analyte result that fails the 20%RSD/0.990 correlation coefficient requirement must be flagged or narrated as an estimated concentration.

11.4.13 For any analyte non-detect associated with a calibration that fails the 20%RSD/0.990 correlation criteria there must be a demonstration of adequate sensitivity at the quantitation limit. This is achieved by the successful analysis of a CCVL (CCV at the reporting limit) in the same analytical batch. The criterion for the CCVL is detection only but the standard qualitative identification criteria in the method must be met.

11.4.14 See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

11.4.15 Initial Calibration Verification (ICV)

Once the initial calibration has been evaluated and determined to be valid, the calibration must be verified with an Initial Calibration Verification (ICV) using a standard prepared from an alternate source. The ICV is generally run at 20 ug/L for standard level water, low-level soil and methanol preserved soil, and 10 ug/L for low level water curves. As the ICV concentration must not be equal to or greater than the highest calibration level, other ICV levels than those previously listed may be used or multiple levels of ICV may be needed to validate all compounds in the initial calibration curve.

For DoD and LaMP projects each target compound in the ICV must be <20% drift when compared to the initial calibration. The same criteria apply to BTEX and oxygenate compounds in the LaMP program. For 8260B non-DoD and non-LaMP projects, all compounds must be <40% drift when compared to the initial calibration, except for poorly performing compounds listed in Table 11, which must be <55% drift. For 8260C non-DoD and non-LaMP projects, all compounds must be <30% drift when compared to the initial calibration, except for poorly performing compounds listed in Table 11, which must be <55% drift.

For DoD projects analyses may continue if the drift is <30% for identified poor performing analytes with written approval from the client. (Method comment 4PP). See table 11 for the list of indentified poor performers.

For non-DoD and LaMP projects analyses may continue for those analytes that fail the criteria with approval from the client and an understanding that these results would be considered estimates and could be used for screening purposes.

Corrective Action: If the % drift falls outside acceptance criteria, assess the system for possible problems (standard degradation, etc.), re-prepare the verification standard and re-analyze. If the second ICV also fails, corrective action is required (e.g. system maintenance, re-preparing intermediate standards, etc.) and the calibration must be re-prepared and re-analyzed. An acceptable ICV must be achieved before sample analysis. No samples may be run until calibration has been verified. Analytes which do not meet the ICV % drift criteria will be removed from the calibration in the Chrom chromatography software for the method in which the analyte did not meet the method criteria to prevent the reporting of analytes using a deficient calibration curve.

11.4.16 If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration, Section 11.5.

11.5 Continuing Calibration

11.5.1 The initial calibration must be verified every twelve hours. For DoD projects the calibration must also be verified with a closing continuing calibration standard (CCVC) at the end of each analytical sequence.

11.5.2 Continuing calibration begins with analysis of BFB as described in Section 11.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 6 calibration standard is generally used as the CCV and CCVC.

11.5.3 For 8260B non-DoD projects the RF data from the standards are compared with the initial multi-point calibration to determine the percent drift of the CCC and target compounds. The % drift limits of CCC, target and surrogate compounds are summarized in Table 12.

11.5.3.1 If not all of the CCCs are required analytes, project specific calibration specifications (which may include the use of the CCCs listed in Table 10) must be agreed with the client.

11.5.3.2 Non CCC target compounds that exceed the specified limits for Drift or Difference should be flagged.

11.5.3.3 For sub lists having less then 10 target analytes, the % drift of difference should be <20% before analysis proceeds.

11.5.4 For 8260B (both DoD and non-DoD), the SPCCs are also monitored. The SPCCs must meet the criteria described in Table 9.

11.5.5 For 8260C non-DoD projects, the percent difference or drift (%D) of target and surrogate compounds must be within ± 20% for 80% of the target compounds.

11.5.6 For DoD and LaMP projects, the percent difference or drift (%D) of target and surrogate compounds must be within ± 20% for the opening CCV. The same criteria apply to BTEX, oxygenate and surrogate compounds in the LaMP program.

11.5.7 For DoD projects the percent difference or drift (%D) of target and surrogate compounds must be within ± 50% for the closing CCV (CCVC).

11.5.8 For non-DoD projects the retention time of the internal standards in the continuing calibration standard cannot change by more than 30 seconds (0.5 min) when compared to the most recent multi-point calibration. For DoD projects the retention time of the internal standards in the continuing calibration standard cannot change by more than 10 seconds when compared to the most recent multi-point calibration. The 30 second criteria may only be used for DoD projects if prior written approval is received (method notes will contain “8ISRT” or “Std Var App” to indicate approval has been received). The internal standard areas must not change by more than a factor of 2 (50 - 200 %) from the mid point standard of the most recent multi-point calibration.

11.5.9 If CCC, SPCC, target and/or surrogate compounds do not meet the criteria in Sections 11.5.3 through 11.5.8, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action, such as a different type of column, will require a new initial calibration. For non-DoD and LaMP, if two CCVs in a row fail, a new initial calibration must be performed. For DoD two additional consecutive CCVs must be run immediately. If both pass, samples may be reported without reanalysis. If either fails corrective action and re-calibration is required.

Corrective Actions:

For non-DoD projects if the CCV recoveries of the CCC, target or surrogates compounds exceed their specified limits, and there are no associated sample detections above the RL, the data may be qualified and reported as the system has shown a potentially high bias. For DoD projects, if the CCV recoveries for target compounds exceed their specified limits, and there are no associated sample detections above the RL, the data may be qualified

and reported as the system has shown a potentially high bias only if prior approval has been received in writing (method notes will contain "3HR" or "Std Var App" to indicate approval has been received). For all other cases, results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

11.5.10 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample desorbed less than or equal to 12 hours after the BFB is acceptable.)

11.6 Sample Preparation

Check the Balance logbook to determine if the daily calibration check has been completed. If it has not, the analyst must perform this check according to SOP TA-QA-0014

11.6.1 Sample extraction for *Medium*-Level Analysis using in house extraction.

11.6.1.1 When extracting the sample, extrude (for 5 g EnCore™) or weigh (for 10 g in house soil extraction) the sample into a tared 20 mL scintillation vial. EnCore samples should be extruded into methanol upon receipt. Record scintillation vial lot number, the sample weight, the methanol lot number, the preparation date and the analyst who prepared it in the 5035 preparation batch in TALS. Sample weights are calculated in the laboratory by adding the tare weight of the scintillation vial to the "Tare Weight" column and then entering the weight of the scintillation vial plus sample into the "Vial & Sample" column of the preparation batch sheet for the corresponding sample container ID. This can be done by either a direct read from the balance in the volatiles prep area (preferred method), or by manually entering the weight. If the samples were preserved in MeOH at another TALS lab the calculated initial sample weight can be manually entered into the "Initial Amount" column of the preparation batch sheet for the corresponding sample container ID.

11.6.1.2 For each batch of up to 20 samples a method blank (MB) and a Laboratory Control Sample (LCS) are also extracted. To prepare the method blank (MB); add 10-mL of methanol to 10g Ottawa sand. To prepare the blank spike (LCS)/blank spike duplicate (LCSD), add 160-uL of the 8260 - working solution and 10-mL of methanol to 10g muffled Ottawa sand. (NOTE: The same metal spatulas to weigh soil samples must be used for measuring out the Ottawa sand).

11.6.1.3 If sufficient sample is available, one matrix spike (MS)/matrix spike duplicate (MSD) pair is extracted per extraction batch of up to 20 samples. If the sample set being extracted consists of products, waste oils, or other sample matrixes which based on analyst experience and discretion would not yield acceptable spike results due to matrix effects, a matrix duplicate (MD) and/or MD/MS may be prepared in lieu of and MS/MSD. To prepare the matrix spike (MS)/matrix spike duplicate (MSD), add 160 uL of the 8260 working solution and 10 mL of methanol to 10 g pre-weighed soil samples.

11.6.1.4 Add 5 mL (for EnCore™ or TerraCore™) or 10mL (in house soil extraction) of methanol to all vials immediately after recording sample weight.

11.6.1.5 Vortex the samples for the extraction batch for approximately 10 to 30 seconds to break up any large clumps in the extraction vials. This is especially important for extruded samples as they may be compacted in the EnCore™ or TerraCore™ sampling device and come out as a pellet. If after 30 seconds a pellet still remains, vortex for an additional 30 seconds.

If pellet still remains, further vortex mixing is not recommended, proceed to next step. It should be noted that the MB and LCS must be vortex mixed the same amount of time as the longest associated sample.

11.6.1.6 After all samples have been vortex mixed, place all samples for the extraction batch into shaker box and set timer for *10* minutes. It is recommended that the caps of all vials are checked and tightened before placing in shaker box to prevent leaking. If samples are present which still contain pelletized sample after vortex mixing in step 11.6.1.5, set the timer for 10 to 15 minutes. It is not recommended to shake samples for more than 15 minutes. If a sample still contains pelletized sample after shaking for 15 minutes, vortex the sample for an additional 15 seconds and shake entire batch for additional 5 minutes. Any pelletized sample remaining after second shaking is noted in and NCM in the extraction batch.

11.6.1.7 After samples are shaken, place samples four at a time into centrifuge with inserts for scintillation vials. Spin samples for a sufficient time to create a transparent but not necessarily uncolored layer of methanol extract above the extracted material. The time will vary depending on the nature and particle size of the extracted material. Three to five minutes at 50% speed is usually sufficient. Again it should be noted that the MB and LCS must be centrifuged at the same rate and for the same time as the longest centrifuged associated sample.

11.6.1.8 *Medium*-level solid extracts are stored in the scintillation vial used for extraction and are stored at 0-6^{o}C. The extracts are removed from cold storage and are allowed to return to ambient temperature prior to analysis.

11.6.2 Sample extraction for *Medium*-Level Analysis, field preserved.

11.6.2.1 Each containers tare weight is recorded in the TALS preparation batch. Most containers will contain a bar code with the tare weight information that can be scanned for automatic entry into the tare weight entry field in the preparation batch. Sample weights are calculated in the laboratory by adding the received weight of the sample jar to the “Vial & Sample” column of the preparation batch sheet for the corresponding sample container ID. This can be done by either a direct read from the balance in the volatiles prep area (preferred method), or by manually entering the weight. If the samples received are in 4 oz jars with 25 mls of methanol (AK samples) the calculated initial weight of the sample must be adjusted to correct for the weight of the methanol which is not included in the container tare weight. TALS will perform this calculation, however the analyst must enter a “1” into the “Tare Incl MeOH” column of the preparation batch sheet for the corresponding sample container ID. The nominal amount of initial soil should be 10g for VOA vials with 10mL of methanol, or 25g with 25mL of methanol. When the calculated initial weight of the soil deviates by more than 20% of the expected value, high or low, an NCM should be written detailing that the 1:1 ratio of soil:methanol is significantly exceeded. Acceptable weights are 8g-12g for a 10g:10mL sample, and 20g-30g for 25g:25mL sample.

11.6.2.2 For each batch of up to 20 samples a method blank (MB) and a Laboratory Control Sample (LCS) are prepared by the laboratory prior to sample analysis. A MB and an LCS sample consists of 10g of muffled Ottowa Sand added to a scintillation vial followed by 10-mL of methanol.

11.6.2.3 Add the correct amount of matrix spiking solutions to all LCS samples. An aliquot of 160 uL of the 8260 working solution is added to 10mL extracts. The addition of the spike solutions introduces a slight error, which can be

neglected in the calculations. The listed volumes are halved (80 uL) for 5-mL extracts.

11.6.2.4 The MB, LCS and any received samples which appear to contain "clumps" of sample which could be broken up with agitation are vortex mixed for up to 1 minute. If no samples require agitation, only the MB and LCS are vortex mixed for approximately 15 seconds to ensure mixing of the sand and added solutions.

11.6.3 Sample preparation for Low-Level Analysis EnCore™.

11.6.3.1 VOA samples received in EnCores should be extruded into VOA vials with stir bars at time of receipt prior to storage in the freezer. Prior to analysis, low level soil samples collected or extruded to VOA vials with or without water are removed from the freezer and allowed to thaw. Samples should not be allowed to remain at room temperature for more than 30 minutes prior to extrusion into a VOA vial or analysis.

11.6.3.2 The weight of the samples is accurately recorded by either direct connection from the analytical balance to the batch record (preferred method) or by typing the balance reading into the batch record.

11.6.3.3 The extruded sample or the sample received in a VOA vial without water has 5 mls of reagent water added to it.

11.7 Sample Analysis

11.8 Preliminary Evaluation

11.8.1 Sample screening

Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories. Refer to section 11.15 for Dilutions.

11.9 Sample Analysis Procedure

11.9.1 All analysis conditions for samples must be the same as for the continuing calibration standards (including purge volume, time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.9.2 All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD (if sufficient sample volume allows), an LCS, and a method blank.

11.9.2.1 Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

11.9.2.2 It is not necessary to reanalyze batch QC (except for the method blank) with reanalysis of samples. However, any re-runs must be as part of a valid batch.

11.10 Water Samples

11.10.1 All samples and standard solutions must be at ambient temperature before analysis.

11.10.2 For low-level analysis water samples are sub sampled by the autosampler at the appropriate volume (10 mL).

11.10.3 For standard level analysis 5 mLs are sub sampled by the autosampler.

11.10.4 For both low-level and standard level analysis internal standards and surrogates are added by the autosampler. Refer to Tables 5 and 6.

11.10.5 MS/MSD samples are prepared by injecting the 8260 working solution through the VOA vial septa using a bevel tipped syringe or directly into the MS or MSD VOA vial.

11.10.6 Purge the sample at ambient temperature with a trap temperature of 25^{O}C.

11.10.7 After purging is complete, dry purge and desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.10.8 Purge Time, dry purge time, desorb time, bake time, and temperature are optimized for the type of trap in use and the analytical system. The same conditions must be used for samples and standards. Current at the time of writing this SOP, purge time for all instruments is 8 to 11 minutes, dry purge is *0-1* minutes, bake time is 6 to 9 minutes, desorb temperature is 195 to 260^{O}C, and bake temperature is 220 to 270^{O}C.

11.10.9 Immediately after analysis or immediately after opening the sealed VOA vial and obtaining the necessary aliquots for dilutions, the analyst must check the pH of aqueous samples with narrow range pH paper to ensure the pH is < 2. Record the pH of aqueous samples and the lot number of the pH paper used on the analytical batch sheets along with any dilution factors used. In those cases where the pH is > 2, initiate a non-conformance report and qualify the data, noting if the sample(s) was analyzed outside of the shortened seven-day hold time or zero-day hold time for aromatics.

11.11 TCLP Leach Samples

11.11.1 Follow the instructions for standard level water samples using a 100 times dilution for the method blank, laboratory control sample, and all samples. An MS/MSD pair must be prepared per batch by the method described in section 11.10.6.

11.12 Methanol Extract samples

11.12.1 Fill a VOA vial with reagent water, and remove 900 uL of water using a volumetric pipette.

11.12.2 Add 1075 uL of methanolic extract to the vial and immediately cap the VOA vial invert the vial to ensure that no air bubble larger than 4 mm is present. If there is an air bubble and it is greater than 4 mm, re-prepare sample.

11.12.3 The final volume of reagent water and methanolic extract used is entered into Chrome which then is uploaded into the analytical batch in TALS (43 mls).

11.12.4 As with water samples, internal standards and surrogates are added by the autosampler. Refer to Tables 5 and 6. TFT may be also be added to the field methanol (Alaska samples), thus the additional amount of TFT should be taken into account in the prep batch for AK samples.

11.12.5 Load the sample in the autosampler and proceed to analyze.

11.12.6 MS/MSD samples for in house extracts are prepared at time of extraction and are prepared for analysis as above. For field preserved samples, an in house post spike of the prepared sample is necessary, and is prepared by injecting the 8260 working solution through the VOA vial septa using a bevel tipped syringe.

11.12.7 Dilutions of methanolic extracts are made by adding proportional amounts of methanol extract to a new VOA vial. Samples of greater than 5x do not require the removal of water from the VOA vial prior to addition of methanolic extract.

11.12.8 Purge the sample at ambient temperature with a trap temperature of 25^{O}C.

11.12.9 After purging is complete, dry purge and desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.12.10 Purge Time, dry purge time, desorb time, bake time, and temperature are optimized for the type of trap in use and the analytical system. The same conditions must be used for samples and standards. Current at the time of writing this SOP, purge time for all instruments is 8 to 11 minutes, dry purge is *0-1* minutes, bake time is 6 to 9 minutes, desorb temperature is 195 to 260^{O}C, and bake temperature is 220 to 270^{O}C.

11.13 Low-Level Solids Analysis using Discrete Autosamplers

11.13.1 Sample collection and initial preparation for low level soil samples has been discussed in section 8.9 and 11.6.

11.13.2 As with water samples, internal standards and surrogates is added by the autosampler. Refer to Tables 5 and 6.

11.13.3 MS/MSD samples for low level soil samples prepared by injecting the 8260 Working Solution through the VOA vial septa using a bevel tipped syringe. Direct purge soil analyses are spiked during the preparation of the extraction batch through the septa after capping (as applicable).

11.13.4 When it is feasible to perform dilutions of low level soils, a smaller amount of sample is weighed and analyzed. When dilutions of low level soil samples are not possible, any analyte that exceeds the calibration range must be E flagged on the appropriate reporting form, NCM filled out, and must be noted in the case narrative. In addition, if sufficient volume was provided, a methanolic extract must be prepared and analyzed.

11.13.5 Purge the sample at ambient temperature with a trap temperature of 25^{O}C.

11.13.6 After purging is complete, dry purge and desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.13.7 Purge Time, dry purge time, desorb time, bake time, and temperature are optimized for the type of trap in use and the analytical system. The same conditions must be used for samples and standards. Current at the time of writing this SOP, purge time for all instruments is 8 to 11 minutes, dry purge is 1 minute or 2 minutes, bake time is 6 to 9 minutes, desorb temperature is 195 to 260^{O}C, and bake temperature is 220 to 270^{O}C.

11.14 Initial Review and Corrective Actions

11.14.1 Retention Times

For 8260B if the retention time for any internal standard in the continuing calibration changes by more than 30 seconds from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

For DoD projects of 8260C if the retention time for any internal standard in the continuing calibration changes by more than 10 seconds from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.14.2 Internal Standard Response

If the internal standard response in the daily continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

For non-DOD samples, the internal standard response in a sample is compared to the internal standard response in the daily continuing calibration. For DOD samples, the internal standard response in a sample is compared to the internal standard response of the mid point standard in the initial calibration (not the daily CCV). For this reason, separate analytical sequences need to be employed for DOD samples. Responses from

50% to 200% are acceptable. If a sample fails to meet these internal standard criteria, further investigation is necessary. If the change in sensitivity is a matrix effect confined to an individual sample, reanalysis is not necessary, though may be required to prove matrix effect. If the change in sensitivity is due to instrumental problems, all affected samples must be reanalyzed after the problem is corrected. If the ISTD response falls below 50% and the sample has no target analyte detections above the RL (1/2 the RL for DoD projects), the data may be qualified and reported. This should be done in consultation with the PM and client, an NCM must be written.

11.14.3 Surrogate Standard Recoveries

The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once to demonstrate matrix effect (this may be demonstrated by a MS/MSD analysis as well). Reanalysis at a dilution should be considered if appropriate. If a diluted analysis is necessary and surrogate recoveries are in control or less affected, this is sufficient to demonstrate matrix interference.

Re-analysis is not necessary if obvious matrix effect is shown in the chromatograms (e.g. a large co-eluting peak with the same quantitation ion, or non-target interferences) or were noted in sample prep (e.g. high percent moisture content without moisture correction). A non-conformance memo is generated stating the reason for not re-analyzing the affected sample.

11.15 Dilutions

Dilutions *for waters are made directly into a 40mL VOA vial and* should be *prepared* just prior to the GC/MS analysis of the sample. *For example, a 10X dilution is made by filling a VOA vial to slightly overfull and then removing 4.3 mL of reagent water from the vial. 4.3 mL of sample is then transferred to the vial to bring it back to full and it is immediately capped for analysis. In the worklist this is recorded at a 10.0 dilutiuon.*

Soil dilutions are prepared by adding a smaller aliquot than the standard 1.075mL or by serial dilution for aliquots smaller than 20uL or viscous samples. In the prep batch this is recorded as the amount added to 43 mL. The worklist is left as a 1.0 dilution.

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the sample/extract is prepared and analyzed. A dilution should be prepared to ensure that the majority of compounds being diluted for fall in the middle to upper part of the calibration curve (i.e. from 40-90% of their respective calibration range). All reported dilutions must be within the calibration range of the respective analytes and should be compared to other dilutions to ensure that the diluted data “makes sense” as a check for possible dilution errors. If this cannot be accomplished with a single dilution, multiple sample dilutions *may be* necessary. Dilution levels should be considered carefully and it is recommended that a “complicated” sample (one which has more than three compounds which require dilution) is discussed with another analyst or area supervisor as necessary in order to minimize the number of dilutions required. Samples may be screened to determine the appropriate dilution for the initial run or historical site data may be used to determine initial dilutions.

11.15.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment and reasonable client requirements and requests.

11.15.2 Reporting Dilutions

The most concentrated dilution will be reported as the base dilution. Other dilution levels will report only the required diluted compounds and all other compounds and surrogates in the dilution will be set to acceptable in the LIMS system and not reported. Other reporting techniques may be required by specific project requirements or client request and will be transferred to the laboratory by the PM using the mechanisms previously discussed. See Section 9.1.3.

11.15.3 Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP TA-WC-0125 for determination of percent moisture.

11.16 Instrument Maintenance

11.16.1 Agilent 5973 Inert, 5973 Network, 5975, 5975B, and 6890N

11.16.1.1 All circuit boards and peripheral attachments are dusted and vacuumed of debris and all plumbing and electrical connections inspected and adjusted; any replacement of worn parts is also done at this time.

11.16.1.2 The injection port is cleaned of debris by removing the injector and column nut and forcing clean methanol through the top of the injector into a waste container at the bottom. The inlet liner and gold seal are replaced as needed (e.g. visibly dirty or discolored, active site issues, etc.) The ion source is disassembled, cleaned, and reassembled with new filaments and insulators, if needed.

11.16.1.3 If low level soils cause recoveries for the internal standard to report low or purge flow to decrease in any consequent CCV's, the pencil filters or injector needle could be clogged. Methanol rinses of these parts may solve the issue, or replacing the part.

11.16.2 Column installation is performed when the following conditions are encountered;

- Heavy column bleed that cannot be eliminated by thermal conditioning.
- Loss of early eluting peaks due to column cutting.
- Inability to chromatographically resolve method performance compound peaks.
- Distortion of peak shapes i.e.; broadening, ghost peaks, split peaks that can't be resolved by injection port maintenance or flow control.

11.16.2.1 Turn the GC oven off and let the system cool to room temperature. Remove the column nut, liner, septum, and press tight inlet connector. Dispose of old column appropriately.

11.16.2.2 Cut approximately six inches off of the end of new columns. Install new column using appropriate sized ferrules and nuts.

11.16.2.3 Turn the GC on and set the injector temperature to 230 ℃, oven to the manufacturers recommended isotherm temperature or 10℃ below the manufacturers max temperature if an isotherm is not provided and condition for five minutes.

11.16.2.4 Perform an air water check on the system. When the air water spectrum shows acceptable levels, proceed with the mass calibration procedure. For additional information of column replacement see the manufacturer's operator's manual.

11.16.3 *OI Analytical 4560 and 4660* Purge and Trap Concentrator Units

11.16.3.1 A new *OI #10* trap is installed and conditioned by *baking at 210 degrees C for at least 30 minutes.*.An initial conditioning of overnight is recommended as time allows.

11.16.3.2 Sample lines, internal valves, sparge cells, and sparge cell mounts and fittings are rinsed with purge and trap grade methanol or replaced as necessary.

11.16.3.3 All dust and debris is removed from the circuit boards and tubing replaced where necessary.

11.16.3.4 The purge gas flow rate (40 mL/min ± 5 mL/min) should be measured at the vent and recorded in the maintenance logbook.

11.16.4 Archon 2000 or equivalent type auto sampler.

11.16.4.1 Remove debris and perform a calibration per manufacturer's instructions.

11.16.4.2 All dust and debris is removed from the circuit boards and tubing replaced where necessary.

11.16.4.3 The guide rails are wiped down with a Kim wipe and *n-propanol* to remove grease buildup and debris. *Arms, rods, and rails should be removed and all parts cleaned at least once per year, especially bearings.*

11.16.4.4 The syringe is cleaned per manufacturer's instructions to remove debris.

11.16.4.5 The *rinse* reservoir is refilled *with DI (standard level methods) or purge water (low level methods)* prior to analysis.

11.16.4.6 The Internal Standard/Surrogate Standard vial is refilled as needed and primed after filling to ensure the instrument is drawing volume.

11.16.5 Major Maintenance

A new initial calibration is necessary following certain maintenance procedures. These maintenance procedures include changing the column, cleaning the source and replacing the multiplier. In addition, a new initial calibration may be necessary if a large amount of routine maintenance occurs at once. This will be determined by evaluating the system using a CCV.

11.16.6 Maintenance Logbook

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., GC, autosampler, column) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a tune, CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, tune, etc as may be the case).

If columns were replaced during maintenance procedures, the specific make, model and serial numbers of the columns installed need to be entered in the instruments maintenance logbook.

11.17 Troubleshooting

11.17.1 QUESTIONS TO ASK YOURSELF

11.17.1.1 MECHANICAL ISSUE?

- Has the problem just started, or has it been getting worse with time?
- Has anything recently been done to the instrument that may have caused the problem to start?
- Have there been any nasty samples run on the instrument recently?

11.17.1.2 ANALYTE ISSUE?

- Are there any other compounds out or trending out?
- Did the CCV and/or LCS show similar trends?
- Is this a one time event? Or did you see similar signs yesterday?
- Is it failing on other mass specs?
- Did anything change from the last time it passed?
- Have there been any nasty samples run on the instrument recently?

11.17.1.3 INTERNAL/SURROGATE ISSUE?

- Have they been stable up until now?
- Is the gas on and are the standards fresh?
- Are the glass vials correctly positioned and tight?
- Do they look like they are trending in any direction or just fluctuating?
- Is the tune stable? Are the ratios close to the ICAL tune?

11.17.2 BEST PRACTICE

11.17.2.1 If you can – replace the most likely piece in the system, label the old one with which instrument it's from, the date out and possibly the problem you are having e.g. R1, 071010 Bromoform. Test if the problem is fixed. If not, move onto the next thing and replace until the problem is fixed. Then work backward and reinstall the old pieces which are still OK. If you no longer need a part that is still good, label it as such. If a piece is bad and not even good for testing with throw it out and tell your department manager what piece and part number.

11.17.3 TYPICAL FIRST THINGS TO LOOK AT AND TRY

11.17.3.1 CHECK YOUR FLOWS (For soil mode, purge on archon)

- Set the Archon to purge for 111mins instead of 11mins then set a vial to purge and "pause" the concentrator. This will give ample time to troubleshoot.
- Use the flow meter to check the flow out the purge vent using a small clear tube as an adapter – you should have about 40mls.
- Take the transfer line off at the entrance to the concentrator and measure the flow – you should also have about 40mls.
- Generally this would suggest you don't have a blockage or a leak, but check the following first
- Find a clear tube that has been blocked at one end, place this on the purge vent while the vial is purging and establish the following:
- Did the bubbles stop straight away <2mins?
- Yes – the leak is in the Archon
- Have the bubbles stopped over a 5 – 7 min period?
    - Yes – Most probably not a leak but could be a blockage (which includes the tube you put on the vent)
    - No – There is a leak somewhere, most likely the concentrator.

- If there is no soil valve attached then remove the transfer line inlet (to concentrator) fitting and replace with a capped fitting, Run the concentrator full leak check.
- If all of the above passes then you do not have a problem with the flows/blockage/leak.
- Remember to set Archon back to 11mins purge and bake off trap before running again.

11.17.3.2 IF YOU HAVE A LEAK

- In the Archon – purge a vial and leak check around the top of the needle, the transfer line and the pencil filter in the back of the Archon.
- In the concentrator – with a vial purging leak check around all the fittings starting with the entry from the transfer line, the 4-port valve, the 6-port valve ad around the water management and trap.
- You can also check the flows coming out of the 4-port, leaving the 6-port, there is an adapter which can be added instead of the trap to measure through the water management, from the trap. If all of these measures around 40mls and still you have less than 37 coming out the purge vent it could be leaking across the valves in the side of the concentrator.
- REMEMBER – any Archon that has been changed to Nitrogen will not be able to be checked with the leak detector.

11.17.3.3 COMMON PLACE TO LOOK IF IT'S A ANALYTE PROBLEM

- **1,1,2,2-Trichloroethane RRF** – Could be any of the lines as often an active site. Start with transfer line, lines in concentrator, water management and trap, soil valve if installed.
- **Bromoform** – Flow is not 40mls, water management, transfer line, small lines in concentrator. This can sometime be a tune issue as well if it is somewhat different from normal.
- **Chloromethane carryover** – Often the trap, replace the trap with the wire at the bottom and condition at 210^{o}C for 30min.
- **Napthalene carryover/low response** – Often water management, change this out and condition with 5 or 6 varying concentrations of an old main or 524 std. e.g. 20ppb, 80ppb, 10ppb, 50ppb etc. Could also be transfer line.
- **2-CEVE** – could be anywhere. Start with transfer line and work way through system, small lines in concentrator, purge needle as last resort. Could also be water management, soil valve if installed.
- **MTBE** – often an active site could be transfer line or trap. Sometimes the instrument just needs recalibrating.
- **Vinyl Chloride** – Usually the first compound to fail low in the standard mix – simply move up to next standard. If you are changing to a new standard every couple of days then your ICAL standards were too fresh and you need to ICAL again.
- **1,1-Dichloroethene** – Usually the first compound to fail low in the Main mix – simply move up to next standard. If you are changing to a new standard every couple of days then your ICAL standards were too fresh and you need to ICAL again.
- **Chloroform** – usually your tune is differing from the ICAL
- **Contamination** – look back at previous runs, if you have high hits for this compound then run 20 – 30 blanks to clean it up. If you still have high concentrations then the sample possibly blew back into the instrument so could be purge valves or the pencil filter in the back of the Archon.
- **Ethylbenzene** – usually your tune is differing from the ICAL.

11.17.3.4 PEAK SHAPE DIFFERENT

- If you have peak tailing on the front end compounds such as Vinyl Chloride, Chloromethane etc then it is often a result of a worn trap.

11.17.3.5 SURROGATES FAILING

- If you have 1,2-DCA failing and all the other surrogates are OK, then the likely cause is the tune. Often the ratios will have moved. Follow the surrogates, if low, then drop ratios etc
- If you have all the surrogates out and it seems to be consistently that way, it could be the following,
    - Is the gas turned on?
    - Is the surrogate vial positioned properly on the archon
    - Your concentration levels in the ICAL maybe incorrect if you have just ICALed.
    - The valve has perhaps worn a little and the nominal value in target needs to be updated, but this can only happen after an ICAL.
    - If the surrogates need to be weighted linear or linear in an ICAL and you see them trending this way for a while its possible the column has gone bad or you may have a standard valve leak.
    - You can check to see if it's the archon causing the problem by manually injecting IS/SS and turn off the IS and SS on the archon
- If two surrogates are high and two are low, sometimes this is because your Archon surrogate is not matching with the surrogate you ICAL'd with. Try swapping out the Archon surrogate and if this does not fix it, re-ICAL the Supp with the new surrogate.

11.17.3.6 INTERNALS FAILING, TRENDING OR BOUNCING

- How fresh is your internals? If they are more than say a month old, they may have gone bad. Is the vial on properly and done up tight (not too tight).
- Is the gas turned on?
- How long has the instrument been using the current filament? More than 4weeks then you may want to change to the other or change the filaments if they are both spent.
- If the internals bouncing seems to correlate with the tune then most likely you want to change filament or clean the source.
- If the internals fall to a value and sit there or raise to a value and sit there you may want to consider ICAL it at that tune setting, instruments have a kind of sweet spot.
- Internals falling off maybe a water buildup and the parameters need looking at on the concentrator. Have a look at other instruments to see how they are set up and try one or two different settings to establish if this helps. Always keep a note of where they were at and what you have changed them too. Best place to record this is on your sequence and in the white folder under daily changes.
- Split ratios can also effect internals, try increasing the ratio to more like 45:1 if not already at this level.

11.17.3.7 CONCENTRATOR STOPS

- Turn it off and on again, it is common for the concentrator to lose the plot every so often.
- Shows a temperature error – check to make sure the trap is covered and the main cover is down properly, any heat escape will cause an error.

11.17.3.8 SEQUENCE STOPS

- You have started on a file that already exists and you have not checked the overwrite file box.

- Communication problem with the GC and MS. Turn off the MS and GC and restart the computer. Restart the MS and GC.

11.17.3.9 ARCHON STOPS

- Standard home errors – syringe already home – use the maintenance menu on the archon to step you through cleaning the syringe. Before putting back together smear the inside of the syringe with 'Nose grease'.
- Standard home errors -

12.0 Calculations / Data Reduction

12.1 Qualitative Identification for Full Scan Analysis

12.1.1 An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library (same library as used for routine sample analysis). Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions.

NOTE: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.

12.1.1.1 The sample component retention time must compare to within ± 0.06 RRT units of the retention time of the standard component. For reference, the standard must be run within the same twelve hour tune as the sample.

12.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

12.1.1.3 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80%.)

12.1.2 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.1.3 All data are subject to two levels of technical review, as described in SOP TA-QA-0635.

12.2 Tentatively Identified Compounds (TICs)

12.2.1 If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. The following guidelines apply:

12.2.1.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

12.2.1.2 The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

12.2.1.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or co-eluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6 Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification. If the TIC requested is part of the list of target analytes, the TIC will not appear under the list of tentatively identified compounds.

12.2.1.7 Once tentative identifications are assigned, these results are uploaded into LIMS with the other data and the TICs are automatically reported to the client from the LIMS.

12.3 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

12.4 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

12.5 Response Factor (RF)

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard, ng.
C_x = Concentration of the compound being measured, ng.

12.6 Standard deviation (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(X_i - \overline{X}\right)^2}{n-1}}$$

Where:

X_i = Value of X at i through n.
n = Number of points.
$\overline{X}$ = Average value of Xi.

12.7 Percent relative standard deviation (%RSD)

$$\%RSD = \frac{SD}{\overline{RF}} \times 100\%$$

Where $\overline{RF}$ is the mean of RF values for the calibration.

12.8 Percent drift between the initial calibration and the continuing calibration:

$$\%Drift = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100\%$$

Where:

$C_{expected}$ = Known concentration in standard.
C_{found} = Measured concentration using selected quantitation method.

12.9 Concentration = mg/kg or L = $\frac{C \times V \times D}{W}$

Where:
C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor

W = Weight/Volume of sample aliquot extracted (grams or mLs)

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

Note: For all methanolic samples with a % Moisture of greater than 10%, it is necessary to adjust the extraction final volume of the sample in order to allow for the miscible solvents effect. This is done by the following equation:

Corrected FV = ((g of samples * % moisture/100) + ml of MeOH) * 40

In these situations, an "other observation" NCM must be generated and the correction and above formula must be noted in the case narrative.

12.10 Calculation of Results for Methanol Extracts

$$\text{Sample Conc (ug/Kg)} = [\text{On Column (ug/L)}] \times \frac{\text{Extraction Final Volume (mL)} \times \text{VOA Vial Volume (mL)}}{\text{Amount of Soil Sample (g)} \quad \text{Amt of MeOH Extract (mL)}} \times \frac{1\text{L (CF)} \times 1000\text{g (CF)}}{1000\text{mL} \quad 1\text{Kg}}$$

VOA vial volume is 43 ml and when the extract doesn't require a dilution, 1.075 mL of the methanol extract is used. So, the equation becomes:

$$\text{Sample Conc (ug/Kg)} = [\text{On Column (ug/L)}] \times \frac{\text{Extraction Final Volume (mL)}^{1} \times 43\text{ (mL)}}{\text{Amount of Soil Sample (g)}^{2} \quad 1.075\text{ (mL)}} \times \frac{1\text{L (CF)} \times 1000\text{g (CF)}}{1000\text{mL} \quad 1\text{Kg}}$$

[1]Extract Final Volume, miscible solvent corrected (mL) = ((g of samples * % moisture/100) + ml of MeOH) * 40
(used when % Moisture of the soil sample is greater than 10%).
[2]Amount of Soil, dry-weight corrected (g) = sample mass (g) * (100 - % moisture/100)

12.11 Upon completion of the analytical sequence:

12.11.1 Review chromatograms online and determine whether manual data manipulations are necessary.

12.11.2 Manual Integrations

All manual integrations must be justified and documented. See Corporate SOP CA-Q-S-002 for requirements for manual integration.

12.11.3 Manual integrations may be processed using Chrom, which stores the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature.

12.11.4 Alternatively, the manual integration may be processed manually. In the latter case, print both the both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration.

12.11.5 Confirm that run logs have printed on them the instrument ID, the analyst and the method used. If this is not printed on the run logs, this must be entered by hand prior to completing the package.

12.12 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 field samples.

12.12.1 Perform a level 1 data review and document the review on the data review checklist (GCMS Data Review Checklist).

12.12.2 Submit the data package and review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

12.13 Method Performance

12.14 Method Detection Limit Study (MDL)/Detection Limit

The method detection limit (MDL) or detection limit (DL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL/DL is determined according to the laboratory's MDL/DL procedure (see SOP TA-QA-0602). MDL/DLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL/DL studies for analyses performed; these are verified at least quarterly unless method requirements require a greater frequency.

For instruments that run samples which fall under LaMP regulations, a yearly MDL Study must be performed and MDLV starting at 1X the MDL.

12.15 Limit of Detection

The limit of detection (LOD) is determined for each analyte and matrix by spiking a quality system matrix at approximately two to four times the detection limit. This spike concentration establishes the LOD. The LOD is verified quarterly for each method and matrix on each instrument that analyzes said method/matrix. Refer to the laboratory's LOD procedure (see SOP TA-QA-0602)

12.16 Limit of Quantitation

The limit of Quantitation (LOQ) is verified quarterly for each method and matrix on each instrument that analyzed said method/matrix. Refer to the laboratory's LOQ procedure (see SOP TA-QA-0618)

12.17 Demonstration of Capabilities

Analyst initial Demonstrations of Capability (DOC) are performed after completing a read and understand memo for the SOP and before any client samples are analyzed. DOCs are updated annually (continuing DOC). See SOP TA-QA-0617 for details.

12.18 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Waste Disposal SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 VOA vials containing acidic water; VOA vials containing extracted acidic water and small amounts of methanol are collected in large plastic satellite waste bins marked "Hazardous Waste." At or before the waste reaches 55 gallons, the contents are transferred to the waste warehouse where the vials are bulked into a 55 gallon waste barrel and sent out for incineration.

14.1.2 VOA vials containing extracted soil samples, which will contain small amounts of methanol and possibly sodium bisulfate. Unused sample extracts are held for at least 40 days, in case further testing is deemed necessary. After at least 40 days have passed these sample extracts are transported to the waste room were they are bulked into the flammable liquid loose pack barrel and sent out for incineration.

14.1.3 Expired Standards. Expired standards are collected in satellite containers marked "Hazardous Waste." At or before the containers reach 55 gallons the containers are taken to the waste warehouse where they are bulked into an expired standards lab pack and sent out for incineration.

15.0 References / Cross-References

15.1 Method 8260B, Volatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.2 Method 8260C, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 3, August, 2006, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Fourth Edition, EPA Office of Solid Waste.

15.3 Method 5035A, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July, 2002, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.4 40CFR, Part 136, Appendix A (Method 624).

15.5 Department of Defense (DoD), Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories Based on ISO/IEC 17025:2005(E) and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), DoD Quality Systems Manual Version 5.1 DOE Quality Systems for Analytical Services Version 3.1, 2017.

- **Method Modifications:**

Item	Method	Modification
1	8260B	The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.
2	8260C	Storage conditions for standards are listed as <6C or as recommended by manufacturer. TestAmerica Seattle follows 8260B guidelines to store standards at -10C or as recommended by manufacturer.
3	8260C	The minimum RF values for Chloroethane, Acetone, 2-Butanone, 4-Methyl-2-pentanone and 2-Hexanone are based on a lab study and not as listed in the method.
4	624	See Appendix A
5	5035A	The aliquot of methanol extract taken for analysis is 125 uL rather than the 100 uL specified in Table 1 of the method.

- **Tables and Appendices**

Table 1 TestAmerica Primary *Analyte* List for 8260B and 8260C
Table A-1 Method 624 Analytes *5*-mL Purge
Table 2 8260B and 8260C Additional Analyte List
Table 3 Appendix IX List
Table 4 Typical Calibration Levels
Table 5 Internal Standards
Table 6 Surrogate Standards
Table 7 Short List LCS and Matrix Spike Standard
Table 7a Full List LCS and Matrix Spike Standard
Table 8 BFB Key Ion Abundance Criteria
Table 9 8260B SPCC Compounds and Minimum Response Factors
Table 10 8260B CCC Compounds
Table 11 Poorly Performing Compounds
Table 12 CCV % Drift Criteria for Non-DOD Projects
Table 13 Summary of QC Requirements
Table 14 8260C Minimum Relative Response Factor Criteria
Appendix A Modifications for Method 624
Appendix B Process Flow for Seattle VOA

- **Changes from last revision**

- Revision 28, dated 27 June 2017
  - Changed references to ‘high’ level soils to ‘medium’ level
  - Updated Approvals
  - Removed references to CA-LUFT, AK101, and NWTPH-GX by MS
  - Updated Calibration Ranges
  - Updated sand preparation method
  - Updated reagents
  - Added requirement for 1:1 ration for methanol soils
  - Clarified acceptable drift ranges of poor performing compounds
  - Updated section 11.15 Dilutions
  - Updated section 11.16 Instrument Maintenance

- Revision 27, dated 19 July 2016
    - Added requirement in section 11.4.16 to remove analyte calibrations which do not pass % drift criteria in ical to not calibrated.
    - Updated section 1.41 Calibration working ranges.
    - Removed from section 3.9 use of second source standard for LCS, MS, and MSD.
    - Updated section 6.1 to current column used.
    - Removed 10 mL glass syringe from section 6.3.
    - Updated section 8.9.3.2 to 5 mL DI water volume for stir bar vials.
    - Updated section 11.4.16 to current ICV concentrations.
    - Updated Approvals.

- Revision 26, dated 29 March 2016
    - Updated sections 8.9.1, 11.6.1.1 and 11.6.3.1 to clarify the requirement to extrude Encores upon receipt.
    - Updated section 11.11 to new standard level water procedures.
    - Updated section 11.13 to new methanol, medium-level soil, procedures.
    - Updated section 11.14 to new low-level soil procedures.
    - Updated calculation in section 12.10 to current procudures.

- Revision 25, dated 5 March 2015
    - Section 9.2 of Appendix B, added NWTPH-Gx batch criteria
    - Section 9.5.2 and 9.5.3 of Appendix B, added surrogate recovery criteria for AK101 and NWTPH-Gx
    - Section 10.1.4 and 11.9.4 of Appendix B, added CCV acceptance criteria per method.
    - Section 11.4.1 and 11.4.3 of Appendix B, added NWTPH-Gx criteria for the ICAL
    - Section 11.7.4 and 11.7.5 of Appendix B, added ICV acceptance criteria per method.
    - Section 15.5 of main body SOP and 15.1.3 of Appendix B, updated reference for the DoD QSM.

- Revision 24, dated 5 January 2015
    - Section 1.2, included gas by MS to list of methods
    - Section 5.1.1 updated heat concerns to include other instrument parts
    - Section 6.1 updated sample purger section
    - Section 7.3.3 expounded on CCC failures
    - Section 8.2.1 added analytes
    - Section 8.2.2 deleted, 0 day holding time is no longer applicable
    - Section 8.5 expounded on acceptable criteria
    - Section 9.5 removed LCS criteria to conform to DoD QSM 5.0 standards
    - Section 11.4.8 some RF values changed due to in-house investigation
    - Section 11.10.3 updated 5030 preparation method to correct audit finding
    - 11.10.10 updated recorded values of dilutions to correct audit finding
    - Added section 11.16.1.3
    - Section 12.2.1.6 updated TIC evaluation
    - Added Appendix B: Gas Analysis by GC/MS based on SW-846, CALUFT, AK101, and Northwest Methods
    - Table 14 updated RF values based on in lab study

- Revision 23, dated 5 January 2014
    - Section 2.3, updated purge gas.
    - Section 6.2, added computer hardware
    - Section 8.3, updated to clearly define different soil sample techniques
    - Section 8.5, updated container
    - Secton 8.6.2, updated container and volume of MeOH
    - Section 8.8, added section for unpreserved soils
    - Section 8.9.2, added VOA vials for low-level soils.
    - Section 9.3, added clarification for DoD and LaMP program requirements

- Sections 9.4 and 9.5, added program requirements
- Section 11.3, updated BFB criteria for mass 174
- Section 11.4 updated to current practice
- Section 11.4.4, added reference to corporate SOP on calibrations
- Sections 11.4.8, 11.4.9, 11.4.11 and 11.4.12, added the criteria for 8260C
- Section 11.4.15, added clarification for DoD and LaMP program requirements
- Sections 11.5.1 and 11.5.2, added DoD QSM 5.0 requirement for closing CCV
- Section 11.5.5, added the criteria for 8260C
- Section 11.5.7, added DoD QSM 5.0 requirement for closing CCV
- Sections 11.5.8 and 11.5.9, added clarification for DoD and LaMP program requirements
- Sections 11.6.1.1, 11.6.2.1, 11.6.3.1 and 11.6.3.3, added more detail for the procedure.
- Sections 11.10, 11.12 and 11.13, updated to new procedures
- Section 11.14.1, added the criteria for 8260C
- Section 11.15, updated to new procedures
- Section 11.17, added section for troubleshooting
- Updated and added Tables and Attachments

- Revision 22, dated 13 March 2013
  - Added section 11.7 to describe the bulk soil preparation procedures and documentation.
  - Added section 15.1 Waste Streams Produced by the Method.

- Revision 21, dated 12 October 2012.
  - Added an elaborated calculation for methanolic extracts 12.10.1.

- Revision 20, dated 20 June 2011
  - Incorporated ROMDs 00019 and 00026 in sections 6.1 and 11.16.6.
  - Added “Note” in section 4.4 addressing cross-contamination from laboratory spiked samples.
  - Addressed shelf life of gas standards in section 7.3.2.
  - Add instructions to return standards to freezer when daily prep is completed, section 7.4
  - Added hold time NCM for unpreserved aromatic compounds in Section 8.2.
  - Added clarification in section 8.5.2 that TCLP samples require a MS/MSD.
  - Added hold time for unpreserved aromatic compounds in Section 8.13.
  - Added clarification on spike solutions in sections 9.5 and 9.6.
  - Incorporated ROMD 00025 in section 9.6.
  - Incorporated ROMD 00020 in section 11.2.2.
  - Added optimization objectives for the GC run programs in section 11.2.2.
  - Incorporated ROMD 00022 in section 11.5.12.
  - Incorporated ROMD 00033 in section 11.6.3
  - Incorporated ROMD 00024 in section 11.6.8.
  - Updated corrective actions for CCV failure in section 11.6.8.
  - Defined CCV % Drift Criteria for non-DOD projects in section 11.6.6 and Table 12
  - Added section 11.11 for TCLP sample preparation/analysis.
  - Added pH check procedures for water samples in section 11.10.9.
  - Revised IS acceptance criteria in section 11.14.2.
  - Expanded list of compounds in Table 7 for compliance with NELAC.

- Revision 19, dated 16 September 2010
  - Updated corrective actions for ICV and CCV failures, sections 11.5 and 11.6.
  - Left italicized text from revision 18 since this revision occurred just days after.

- Revision 18, dated 13 September 2010
  - Added more detail to tuning procedures, section 11.
  - Updated corrective actions for ICV and CCV failures, sections 11.5 and 11.6.
  - Added qualitative identification requirements for SIM analysis, section 12.2

- Revision 17, dated 16 April 2010
    - Removed Chlorobenzen-D5 from Table 5. Added Pentafluorobenzene and 1,4-Dichlorobenzene and updated quantitation ion.
    - Added Sections on 8260_SIM. Including MS parameters and recommended ICAL and spike ranges. Updates Scope section 1.2.1. Updated Calibration 11.4.2. Added section 11.2.3.1 SIM parameters
    - Added a range of spiking amounts and added 10mL purge spiking amounts to sections 11.9
    - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
    - Added clarifications about standard storage conditions, section 7.3.1
    - Added removal of expired standards Section 7.4.
    - Added instructions for the analysis of storage blanks, section 8.11
    - Added clarification about re-analyzing batch QC and trip blanks, section 9.7
    - Added criteria for additional QC, Section 9.8.
    - Added daily balance check to Section 6.2.
    - Added LaMP client surrogate criteria, Section 9.4.
    - Added requirement for running 624 and 8260 methods on separate sequences Section 10.1.
    - Added measurement of gas flow rate, Section11.14.3.4.
    - Added maintenance logbook documentation requirements, section 11.14.5
    - Added specifications (MDLs) and clarifications (DOCs), section 13
    - Updated appendix A to include purge and desorb requirements for method 624.
    - Integration for TestAmerica Seattle and TestAmerica Tacoma operations.

- Revision 16, dated 16 September 2009
    - Description of preparation requirements for reagent water have been updated in sections 3.3 and 7.1.2 to reflect current practice of by purging with an inert gas for a minimum of 1 hour prior to use rather than for a period of overnight.

- Revision 15, dated 22 July 2009
    - Method modifications section updated to identify volume of methanol extract used for analysis.
    - References section updated to include Method 5035A.
    - Nomenclature for spiking solutions has been updated.
    - Spiking volumes have been updated.
    - Calibration levels have been updated.
    - Corrected typographical errors.
    - Updated RLs in Tables 1, 2, 3, and A-1.
    - Added Table 12. Summary of QC Requirements

- Revision 14, dated 16 March 2009
    - Method modifications section updated to identify volume of methanol extract used for analysis.
    - References section updated to include Method 5035A.
    - Nomenclature for spiking solutions has been updated.
    - Spiking volumes have been updated.
    - Calibration levels have been updated.
    - Corrected typographical errors.
    - Updated RLs in Tables 1, 2, 3, and A-1.

- Revision 13, dated 22 March 2008
    - Integration for TestAmerica and STL operations.
    - This revision is a complete rewrite and an expansion of scope.
    - This SOP is the combination of SOPs 0312.12, 0327.5, and 0381.6.

Table 1

TestAmerica Primary Analyte List for 8260B and 8260C

Current reporting limits for all methods may be found in TALS through the following pathway: Global Method Data > Methods > Select Method on left-hand column > Limits View tab > Select Sample Matrix > Select Limit Type "RL"

Compound	CAS Number
Dichlorodifluoromethane	75-71-8
Chloromethane	74-87-3
Bromomethane	74-83-9
Vinyl chloride	75-01-4
Chloroethane	75-00-3
Trichlorofluoromethane	75-69-4
Acetone	67-64-1
Carbon disulfide	75-15-0
Methylene chloride	75-09-2
1,1-Dichloroethene	75-35-4
1,1-Dichloroethane	75-34-3
trans-1,2-Dichloroethene	156-60-5
Methyl tert-butyl ether (MTBE)	1634-04-4
cis-1,2-Dichloroethene	156-59-2
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
Dibromomethane	74-95-3
2-Butanone (MEK)	78-93-3
1,1,1-Trichloroethane	71-55-6
Carbon tetrachloride	56-23-5
Bromodichloromethane	75-27-4
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
Trichloroethene	79-01-6
Dibromochloromethane	124-48-1
1,2-Dibromoethane (EDB)	106-93-4
1,2,3-Trichloropropane	96-18-4
1,1,2-Trichloroethane	79-00-5
Benzene	71-43-2
trans-1,3-Dichloropropene	10061-02-6
Bromoform	75-25-2
4-Methyl-2-pentanone (MIBK)	108-10-1
2-Hexanone	591-78-6

Table 1

TestAmerica Primary Analyte List for 8260B and 8260C

Current reporting limits for all methods may be found in TALS through the following pathway: Global Method Data > Methods > Select Method on left-hand column > Limits View tab > Select Sample Matrix > Select Limit Type "RL"

Compound	CAS Number
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,2,2-Tetrachloroethane	79-34-5
Chlorobenzene	108-90-7
Ethylbenzene	100-41-4
Styrene	100-42-5
m- and p-Xylenes	136777-61-2
o-xylene	95-47-6
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
1,2-Dichlorobenzene	95-50-1
2,2-Dichloropropane	590-20-7
Bromochloromethane	74-97-5
1,1-Dichloropropene	563-58-6
1,3-Dichloropropane	142-28-9
Bromobenzene	108-86-1
n-Propylbenzene	103-65-1
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
1,3,5-Trimethylbenzene	108-67-8
tert-Butylbenzene	98-06-6
1,2,4-Trimethylbenzene	95-63-6
sec-butylbenzene	135-98-8
4-Isopropyltoluene	99-87-6
n-Butylbenzene	104-51-8
1,2,4-Trichlorobenzene	120-82-1
Naphthalene	91-20-3
Hexachlorobutadiene	87-68-3
1,2,3-Trichlorobenzene	87-61-6
1,1,1,2-Tetrachloroethane	630-20-6
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8
Isopropylbenzene	98-82-8

Table A-1

Method 624 Analytes *5*-mL Purge

Analytes	*CAS #*
Acrolein	*107-02-8*
Acrylonitrile	*107-13-1*
Benzene	*71-43-2*
Bromodichloromethane	*75-27-4*
Bromoform	*75-25-2*
Bromomethane	*74-83-9*
Carbon tetrachloride	*56-23-5*
Chlorobenzene	*108-90-7*
Chloroethane	*75-00-3*
2-Chloroethyl vinyl ether	*110-75-8*
Chloroform	*67-66-3*
Chloromethane	*74-87-3*
Dibromochloromethane	*124-48-1*
1,2-Dichlorobenzene	*95-50-1*
1,3-Dichlorobenzene	*541-73-1*
1,4-Dichlorobenzene	*106-46-7*
1,1-Dichloroethane	*75-34-3*
1,2-Dichloroethane	*107-6-2*
1,1-Dichloroethene	*75-35-4*
trans-1,2-Dichloroethene	*156-60-5*
1,2-Dichloropropane	*78-87-5*
cis-1,3-Dichloropropene	*10061-01-5*
trans-1,3-Dichloropropene	*10061-02-6*
Ethylbenzene	*100-41-4*
Methylene chloride	*75-09-2*
1,1,2,2-Tetrachloroethane	*79-34-5*
Tetrachloroethene	*127-18-4*
Toluene	*108-88-*
1,1,1-Trichloroethane	*630-20-6*
1,1,2-Trichloroethane	*79-00-5*
Trichloroethene	*79-01-6*
Trichlorofluoromethane	*75-69-4*
Vinyl chloride	*75-01-4*

Table 2

8260B and 8260C Additional Analyte List

Compound	CAS Number
Acrolein	107-02-8
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Iodomethane	74-88-4
2-Chloroethyl vinyl ether[1]	110-75-8
Vinyl acetate	108-05-4
Methyl acetate	79-20-9
2-Methyl-2-propanol	75-65-0
tert-Butyl Ethyl Ether	637-92-3
trans-1,4-Dichloro-2-butene	110-57-6
Total Xylenes	1330-20-7
Acrylonitrile	107-13-1
Hexane	110-54-3
Tetrahydrofuran	109-99-9
Cyclohexane	110-82-7
tert-Amyl Methyl Ether	994-05-8
Methylcyclohexane	108-87-2
cis-1,4-Dichloro-2-butene	1476-11-5
Hexachloroethane	67-72-1
2-Ethyl-1-hexanol	104-76-7
1,3,5-Trichlorobenzene	108-70-3

1 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

Table 3

Appendix IX Analyte List

Compound	CAS Number
Acetonitrile	75-05-8
Isopropyl ether	108-20-3
n-Butanol	71-36-3
Methacrylonitrile	126-98-7
Isobutanol	78-83-1
Ethyl ether	60-29-7
Ethyl Acetate	141-78-6

Table 4

Typical Calibration Levels

Standard level water, Low-level Soil and Methanol preserved soil purge	**Calibration Levels, µg/L**										
	0.2	**0.4**	**1.0**	**5.0**	**10**	**20**	**50**	**100**	**150**		
Low level water purge	**Calibration Levels, µg/L**										
	0.02	**0.05**	**0.10**	**0.20**	**0.40**	**1.0**	***5.0***	***10.0***	***25.0***	***40.0***	***50.0***

Table 5

Internal Standards

Internal Standard	Standard Concentration (mg/L)	Quantitation Ion
1,4-Dichlorobenzene-d4	250	152
Chlorobenzene-d5	250	117
Fluorobenzene	250	96
1,4-Dioxane-d8	5000	96
Tert-butanol-d9	5000	65

Table 6

Surrogate Standards

Surrogate Compounds	Standard Concentration (mg/L)
1,2-Dichloroethane-d4	150
4-Bromofluorobenzene	150
Dibromofluoromethane	150
Toluene-d8	150
Trifluorotoluene	150

NOTES:

1) Recovery and precision limits for the surrogates are generated from historical data and are maintained by the QA department.

Table 7

Full List LCS and Matrix Spike Compounds

Compound	Standard Concentration (mg/L)
Acrolein	250
Vinyl acetate	250
2-Chloroethyl vinyl ether	250
1,4-Dioxane	1250
2-Butanone (MEK)	250
2-Ethyl-1-hexanol	1250
2-Hexanone	250
2-Methyl-2-propanol	250
4-Methyl-2-pentanone (MIBK)	250
Acetone	250
Acetonitrile	500
Acrylonitrile	250
Bromomethane	250
Chloroethane	50
Chloromethane	50
Cis-1,4-Dichloro-2-butene	50
Dichlorodifluoromethane	50
Ethyl acetate	250
Ethyl ether	250
Iodomethane	250
Isopropyl ether	50
Methacrylonitrile	250
Methyl acetate	250
Methyl tert-butyl ether	50
Tert-amyl methyl ether	50
Tert-butyl ethyl ether	50
Tetrahydrofuran	250
Trans-1,4-Dichloro-2-butene	250
Trichlorfluoromethane	50
Vinyl chloride	50

Compound	Standard Concentration (mg/L)
1,1,1,2-Tetrachloroethane	50
1,1,1-Trichloroethane	50
1,1,2,2-Tetrachloroethane	50
1,1,2-Trichloro-1,2,2-trifluoroethane	50
1,1,2-Trichloroethane	50
1,1-Dichloroethane	50
1,1-Dichloroethene	50
1,1-Dichloropropene	50
1,2,3-Trichloropropane	50
1,2,4-Trichlorobenzene	50
1,2,4-Trimethylbenzene	50
1,2-Dibromo-3-chloropropane	50
1,2-Dichlorobenzene	50
1,2-Dichloroethane	50
1,2-Dichloropropane	50
1,3,5-Trichlorobenzene	50
1,3,5-Trimethylbenzene	50
1,3-Dichlorobenzene	50
1,3-Dichloropropane	50
1,4-Dichlorobenzene	50
2,2-Dichloropropane	50
2-Chlorotoluene	50
4-Chlorotoluene	50
4-Isopropyltoluene	50
Benzene	50
Bromobenzene	50
Bromoform	50
Carbon disulfide	50
Carbon tetrachloride	50
Chlorobenzene	50
Chlorobromomethane	50
Chlorodibromomethane	50

Compound	Standard Concentration (mg/L)
Chloroform	50
Cis-1,2-Dichloroethene	50
Cis-1,3-Dichloropropene	50
Cyclohexane	50
Dibromomethane	50
Dichlorobromomethane	50
Ethylbenzene	50
Ethylene Dibromide	50
Hexachlorobutadiene	50
Hexachloroethane	50
Hexane	50
Isobutyl alcohol	5000
Isopropylbenzene	50
Methylcyclohexane	50
Methylene chloride	50
m- & p-Xylene	100
Naphthalene	50
n-Butanol	5000
n-Butylbenzene	50
n-Propylbenzene	50
o-Xylene	50
sec-Butylbenzene	50
Styrene	50
tert-Butylbenzene	50
Tetrachloroethene	50
Toluene	50
trans-1,2-Dichloroethene	50
trans-1,3-Dichloropropene	50
Trichloroethene	50

NOTES:

1) Recovery and precision limits for the LCS, MS, and MSD are generated from historical data and are maintained by the QA department.

Table 8

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40 % of Mass 95
75	30 to 60 % of Mass 95
95	Base Peak, 100 % Relative Abundance
96	5 to 9 % of Mass 95
173	Less than 2 % of Mass 174
174	50 to 120 % of Mass 95
175	5 to 9 % of Mass 174
176	Greater than 95 %, but less than 101 % of Mass 174
177	5 to 9 % of Mass 176

Table 9

8260B SPCC Compounds and Minimum Response Factors

Compound	8260B Min. RF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
1,1,2,2-Tetrachloroethane	0.30
Chlorobenzene	0.30

Table 10
8260B CCC Compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	≤ 30	≤ 20
1,1-Dichloroethene	≤ 30	≤ 20
Chloroform	≤ 30	≤ 20
1,2-Dichloropropane	≤ 30	≤ 20
Toluene	≤ 30	≤ 20
Ethylbenzene	≤ 30	≤ 20

Table 11

Poorly Performing Compounds

Acetone	Isopropyl alcohol
Acetonitrile	Dichlorofluoromethane
Acrolein	**1,2-Dibromo-3-chloropropane (DBCP)**
Acrylonitrile	1,4-Dioxane
n-Butanol	Ethyl acetate
2-Butanone (MEK)	**2-Hexanone**
Bromomethane	Methacrylonitrile
Bromoform	Methyl acetate
Carbon disulfide	Methyl methacrylate
2-Chloroethyl vinyl ether	**4-Methyl-2-pentanone (MIBK)**
Chloroethane	**Naphthalene**
Chloromethane	2-Nitropropane
Dichlorodifluoromethane	Proprionitrile
cis-1,4-Dichloro-2-butene	Tetrahydrofuran
trans-1,4-Dichloro-2-butene	1,1,2-Trichloro-1,2,2-trifluoroethane
Ethanol	**1,2,3-Trichlorobenzene**
Ethyl methacrylate	**Trichlorofluoromethane**
Iodomethane	Vinyl acetate
Isobutyl alcohol	Tert butyl alcohol

The laboratory's GC/MS group identified this list of compounds based on current and historical performance. The recovery performance was reviewed against full spike recovery data and method performance data, where available, to validate each compound as a "poor performer." This is not a comprehensive list and is subject to change. Each DoD projects' target analyte list should be evaluated for poor performers.

Analytes that are in bold are also represented in Table 1 Standard Analytes.

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Table 12

8260B CCV % Drift Criteria for Non-DOD Projects

Analyte	Cas No	CCV %D
1,1,1,2-Tetrachloroethane	630-20-6	30
1,1,1-Trichloroethane	71-55-6	30
1,1,2,2-Tetrachloroethane	79-34-5	30
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	50
1,1,2-Trichloroethane	79-00-5	30
1,1-Dichloroethane	75-34-3	30
1,1-Dichloroethene	75-35-4	20
1,1-Dichloropropene	563-58-6	30
1,2,3-Trichlorobenzene	87-61-6	40
1,2,3-Trichloropropane	96-18-4	30
1,2,4-Trichlorobenzene	120-82-1	40
1,2,4-Trimethylbenzene	95-63-6	30
1,2-Dibromo-3-Chloropropane	96-12-8	50
1,2-Dichlorobenzene	95-50-1	30
1,2-Dichloroethane	107-06-2	30
1,2-Dichloropropane	78-87-5	20
1,3,5-Trichlorobenzene	108-70-3	30
1,3,5-Trimethylbenzene	108-67-8	30
1,3-Dichlorobenzene	541-73-1	30
1,3-Dichloropropane	142-28-9	30
1,4-Dichlorobenzene	106-46-7	30
2,2-Dichloropropane	594-20-7	40
2-Butanone (MEK)	78-93-3	50
2-Chloroethyl vinyl ether	110-75-8	50
2-Chlorotoluene	95-49-8	30
2-Ethyl-1-Hexanol	104-76-7	50
2-Hexanone	591-78-6	50
2-Methyl-2-propanol	75-65-0	50
4-Chlorotoluene	106-43-4	30
4-Isopropyltoluene	99-87-6	30
4-Methyl-2-pentanone (MIBK)	108-10-1	50
Acetone	67-64-1	50
Acetonitrile	75-05-8	50
Acrolein	107-02-8	50
Acrylonitrile	107-13-1	50
Benzene	71-43-2	30
Bromobenzene	108-86-1	30
Bromoform	75-25-2	40
Bromomethane	74-83-9	50
Carbon disulfide	75-15-0	50
Carbon tetrachloride	56-23-5	30
Chlorobenzene	108-90-7	30
Chlorobromomethane	74-97-5	40
Chlorodibromomethane	124-48-1	40

Analyte	Cas No	CCV %D
Chloroethane	75-00-3	50
Chloroform	67-66-3	20
Chloromethane	74-87-3	50
cis-1,2-Dichloroethene	156-59-2	30
cis-1,3-Dichloropropene	10061-01-5	30
cis-1,4-Dichloro-2-butene	1476-11-5	50
Cyclohexane	110-82-7	30
Dibromomethane	74-95-3	30
Dichlorobromomethane	75-27-4	30
Dichlorodifluoromethane	75-71-8	50
Ethyl acetate	141-78-6	50
Ethyl ether	60-29-7	40
Ethylbenzene	100-41-4	20
Ethylene Dibromide	106-93-4	30
Hexachlorobutadiene	87-68-3	40
Hexachloroethane	67-72-1	40
Hexane	110-54-3	40
Iodomethane	74-88-4	50
Isobutyl alcohol	78-83-1	50
Isopropyl ether	108-20-3	30
Isopropylbenzene	98-82-8	30
Methacrylonitrile	126-98-7	50
Methyl acetate	79-20-9	50
Methyl tert-butyl ether	1634-04-4	30
Methylcyclohexane	108-87-2	30
Methylene Chloride	75-09-2	40
m-Xylene & p-Xylene	179601-23-1	30
Naphthalene	91-20-3	40
n-Butanol	71-36-3	50
n-Butylbenzene	104-51-8	30
N-Propylbenzene	103-65-1	30
o-Xylene	95-47-6	30
sec-Butylbenzene	135-98-8	30
Styrene	100-42-5	30
Tert-amyl methyl ether	994-05-8	40
Tert-butyl ethyl ether	637-92-3	30
tert-Butylbenzene	98-06-6	30
Tetrachloroethene	127-18-4	40
Tetrahydrofuran	109-99-9	50
Toluene	108-88-3	20
trans-1,2-Dichloroethene	156-60-5	30
trans-1,3-Dichloropropene	10061-02-6	30
trans-1,4-Dichloro-2-butene	110-57-6	50
Trichloroethene	79-01-6	30
Trichlorofluoromethane	75-69-4	50
Vinyl acetate	108-05-4	50
Vinyl chloride	75-01-4	20

Table 13

Summary of QC Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
BFB Tune	Prior to ICAL and at the beginning of each 12-hour period.	See Section 11.3	Retune instrument and verify. Rerun affected samples.
Minimum 5-point Initial Calibration, 6-point for quadratic curves (minimum 3-point Initial Calibration for Method 624)	Initial calibration prior to sample analysis	For Method 624: RSD for RFs: ≤ 35% for all analytes. For Method 8260B: 1. Average Response Factor for SPCCs: ≥ 0.30 for chlorobenzene, and 1,1,2,2-tetrachloroethane; ≥ 0.10 for chloromethane, bromoform, and 1,1-dichloroethane 2. RSD for RFs for CCCs: ≤ 30% For Method 8260C: 1. Average Response Factor for specified compounds: See table 14 2. RSD for all compounds: ≤ 20% **For DOD requirements above and one option below:** Option 1: RSD for each analyte ≤ 15% Option 2: Linear regression least squares regression $r^2 \geq 0.990$ Option 3: Non linear least squares regression $r^2 \geq 0.990$ and 6 points must be used.	Terminate analysis; correct the problem; recalibrate. Problem must be corrected. No samples may be run until ICAL has passed.
ICV or QCS	Following initial calibration.	Method control limits of all analytes under method 624	Terminate analysis; correct the problem; recalibrate.

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
		8260B: ±40% for non-DoD projects and ±55% for poor performers 8260C: ±30% for non-DoD projects and ±55% for poor performers **For DoD:** ±20% recovery and ±30% for poor performers with prior written approval	
Relative Retention Times (RRT)	With each sample	RRT of each target analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL. Laboratory may update RTs based on the CCV to account for minor performance fluctuations or after routine system maintenance (e.g. column clipping).
CCV	Daily before sample analysis and every 12 hours of analysis time.	8260B: 1. Avg RF for SPCCs: ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethene; ≥ 0.10 for chloromethane, bromoform, and 1,1-dichloroethane; 2. %D/Drift for CCCs ≤ 20%D. 3. %D/Drift for nonCCCs < limits in Table 12. 8260C: 1. Avg RF for specified compounds: See table 14 2. %D/Drift for 80% of compounds ≤ 20%D.	Correct problem, then rerun CCV. If that fails, then repeat ICAL. Reanalyze all sample since the last successful CCV.

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
		For DoD: 1. Avg RF: see method 2. Opening CCV: %D/Drift for all target compounds and surrogates ≤ 20%D. 3. Closing CCV: %D/Drift for all target compounds and surrogates ≤ 50%D.	
Internal Standards (IS) verification	Every field sample, standard, and QC sample	Retention time ± 30 seconds from RT of the midpoint standard in ICAL; EICP area within -50% to +100% of ICAL midpoint standard. **For DoD:** Retention time ± 10 seconds from RT of the midpoint standard in ICAL; EICP area within -50% to +100% of ICAL midpoint standard.	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples while system was malfunctioning is mandatory.
Method Blank	One per batch of 20 field samples or fewer.	The result must be < RL or < 5% the amount measured in any sample or 1/10 the regulatory limit. **For DoD:** No analytes detected > ½ RL and > 10% the amount measured in any sample or 1/10 the regulatory limit. For common laboratory contaminants no analytes detected > RL.	Re-extract and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.
LCS	One per batch of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must contain all analytes to be reported. QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits.	See Section 9.5 for additional requirements.

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Surrogate	All field and QC samples.	Must be within laboratory control limits, unless it fails high and the sample is ND, or matrix interference is confirmed by a reanalysis or MS/MSD performed on the sample, or client specific requirements exist. **For DoD:** QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits.	See Section 9.4 for additional requirements.
Matrix Spike/Laboratory Fortified Matrix	One per lot of 20 field samples or fewer.	Must be within laboratory control limits. **For DoD:** Must contain all analytes to be reported and must use LCS control limits. MD/MSD RPD ≤20%	See Section 9.5 for additional requirements.

Table 14

8260C Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification

Volatile Compounds	Minimum Response Factor (RF)a	Typical Response Factor (RF)b
Dichlorodifluoromethane	0.100	0.327
Chloromethane	0.100	0.537
Vinyl chloride	0.100	0.451
Bromomethane	0.100	0.255
Chloroethane	0.060	0.254
Trichlorofluoromethane	0.100	0.426
1,1-Dichloroethene	0.100	0.313
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100	0.302
Acetone	0.020	0.151
Carbon disulfide	0.100	1.163
Methyl Acetate	0.100	0.302
Methylene chloride	0.100	0.380
trans-1,2-Dichloroethene	0.100	0.351
cis-1,2-Dichloroethene	0.100	0.376
Methyl tert-Butyl Ether	0.100	0.847
1,1-Dichloroethane	0.200	0.655
2-Butanone	0.020	0.216
Chloroform	0.200	0.557
1,1,1-Trichloroethane	0.100	0.442
Cyclohexane	0.100	0.579
Carbon tetrachloride	0.100	0.353
Benzene	0.500	1.368
1,2-Dichloroethane	0.100	0.443
Trichloroethene	0.200	0.338
Methylcyclohexane	0.100	0.501
1,2-Dichloropropane	0.100	0.382
Bromodichloromethane	0.200	0.424
cis-1,3-Dichloropropene	0.200	0.537
trans-1,3-Dichloropropene	0.100	0.515
4-Methyl-2-pentanone	0.060	0.363
Toluene	0.400	1.577
1,1,2-Trichloroethane	0.100	0.518
Tetrachloroethene	0.200	0.606
2-Hexanone	0.060	0.536
Dibromochloromethane	0.100	0.652
1,2-Dibromoethane	0.100	0.634
Chlorobenzene	0.500	1.733
Ethylbenzene	0.100	2.827
meta-/para-Xylene	0.100	1.080
ortho-Xylene	0.300	1.073
Styrene	0.300	1.916
Bromoform	0.100	0.413
Isopropylbenzene	0.100	2.271
1,1,2,2-Tetrachloroethane	0.300	0.782
1,3-Dichlorobenzene	0.600	1.408
1,4-Dichlorobenzene	0.500	1.427
1,2-Dichlorobenzene	0.400	1.332
1,2-Dibromo-3-chloropropane	0.050	0.129
1,2,4-Trichlorobenzene	0.200	0.806

a The project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed. In addition, lower than the recommended minimum response factors may be acceptable for those compounds that are not considered critical target analytes and the associated data may be used for screening purposes.

b Data provided by EPA Region III laboratory.

Appendix A - Modifications for Method 624

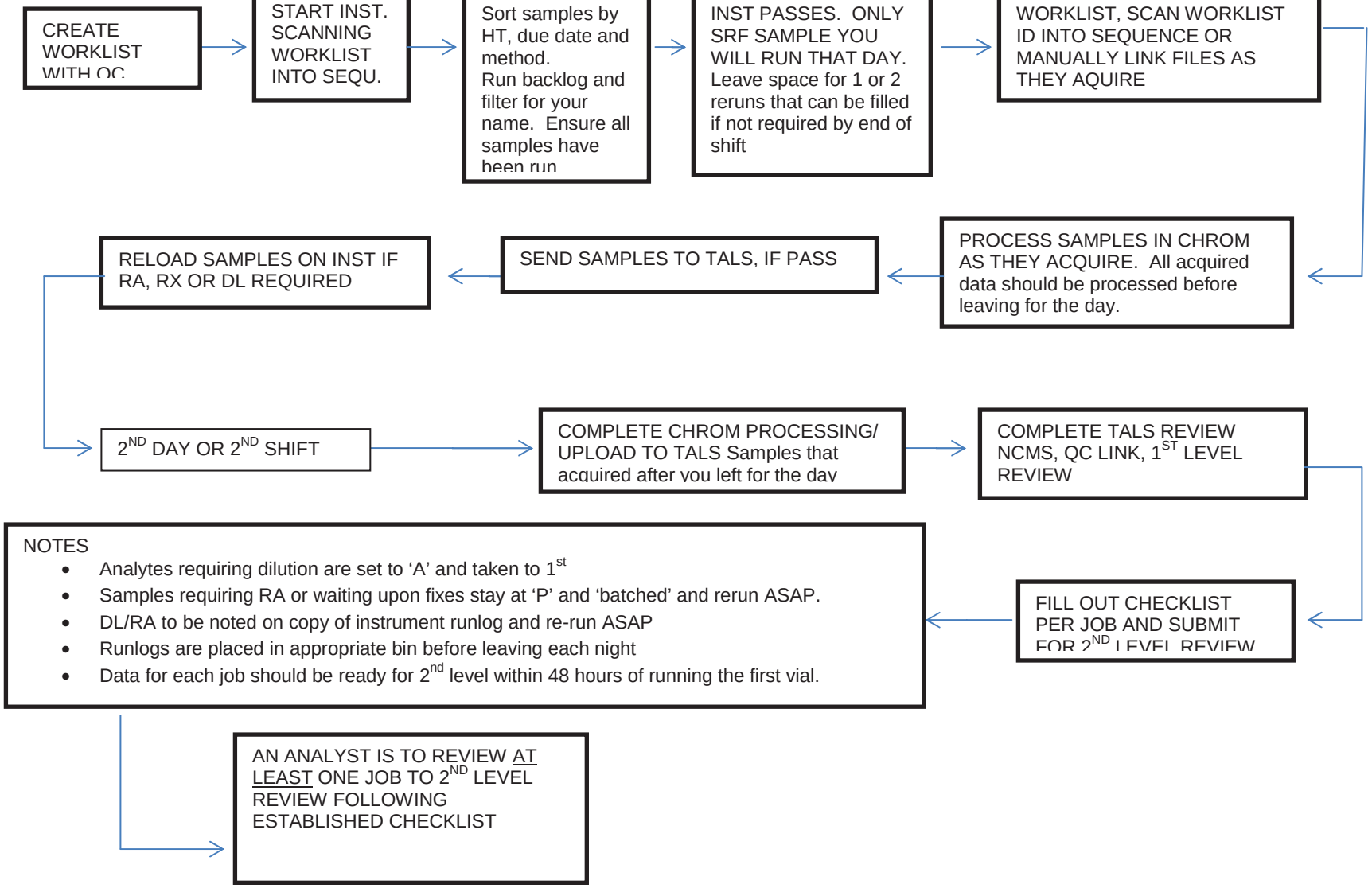
Requirements for EPA 624

1. Method 624 is required for demonstration of compliance with CWA permits, e.g., NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table A-1. If compounds are added to the analysis, all of the method criteria must be satisfied for the additional compounds.
2. The tune period for this method is defined as 24 hours, which is the maximum elapsed time before the tune check is performed. Calibration verifications are done at the same 24 hour frequency.
3. The initial calibration curve for this method requires at least three points.
4. Sample concentrations are calculated using the average RRF from the initial calibration curve.
5. CCC evaluation is consistent with the published 624 CCC recovery criteria. Refer to method 624 for ranges.
6. Each target analyte is assigned to the closest eluting internal standard.
7. Initial demonstration of Proficiency
   - The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L.
8. Initial calibration curve requirements:
   - Target compounds must have RSD ≤ 35%.
   - If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.
9. Continuing calibration verification requirements:
   - The laboratory control standard is from a different source than the initial calibration standard. The daily CCAL concentration is 50 ug/L. The LCS concentration is 20 ug/L.
10. Matrix Spike and LCS Requirements
    - The matrix spike and LCS/LCSD are spiked at 20 µg/L, prepared from the same source containing all analytes of interest. A matrix spike duplicate is not necessary for this method.
11. Consistent with the other volatile methods, corrections for recovery are not allowed.
12. Qualitative Identification - The relative intensities of ions should agree to within ±20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.)
13. Method clarifications, modifications and additions
    - Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. TestAmerica routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.
    - Section 5.3.2 of the source method describes a packed analytical column. TestAmerica routinely employs capillary columns when performing this method.
    - The source method provides a suggested list of compounds for internal and surrogate standards. Others are permitted by the method. TestAmerica uses three internal standards, including 1,4-dichlorobenzene-d4, which are not listed in Table 3 of the source method. Toluene-d8 is used as a surrogate compound, which is also not listed in the source method.
    - The lab is preparing internal standards at 10 ug/L and applying the same criteria designed for 30 ug/L in the Method. The lower the concentration is consistent with the greater sensitivity provided by capillary columns as compared to the older packed columns described in the

method. It could only be more challenging for the lab to meet the acceptance criteria at 10 ug/L; it provides a higher level of data quality.

- Method 624 describes a mass scan range of 25 to 260 amu. Table 13 lists all of the ions used for analysis. None of the ions are below 35 amu. Therefore, we scan from 35 to 300 and include all ions needed for analysis.
- Method 624 describes dilutions “if response of any m/z” exceeds the response for the highest m/z in the ICAL. As the m/z ratio is always directly proportional to the concentration, evaluation based on dilution (per 11.13) is equivalent.
- Method 624 has criteria for unresolved isomers. The problems of isomeric resolution for the routine analytes listed in this SOP were worked through when the laboratory developed its implementation of the method. For example, we know through experience that meta and para xylenes will not be resolved and it was not necessary to include an evaluation for the xylenes in each analysis. Any development work to add compounds would take this into account.
- Method 624 has requirements for purge time and desorb conditions. Purge time for samples is 11 minutes ± 0.1 minutes at ambient temperature. After the 11-minute purge time, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode, and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180℃ while b ackflushing the trap with an inert gas for four minutes.
- The purge gas flow rate (40 mL/min ± 5 mL/min) should be measured at the vent and recorded in the maintenance logbook.
- Method 624 requires the trap to be baked for 10 minutes prior to analysis.

Appendix B; PROCESS FLOW FOR SEATTLE VOA



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Gasoline Range Organics Analysis [Methods 8015B, AK101, NWTPH-Gx]

Approvals

Signatures on File	
Isaac Hooper Date	Manjit Nijjar Date
Volatiles Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

This SOP delineates the specific requirements for analyzing TPH as gasoline. This method is applicable to soil analysis via 5035 and water analysis via 5030. Providing simultaneous confirmation above the RL-secondary column confirmation is not required. Gasoline may be reported without the associated individual analytes, per client request. Table 1 provides a list of target analytes and associated RLs.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

This method describes the analysis of Gasoline Range Organics in soil and water matrices. Soil samples are extracted in methanol. An aliquot of this extract is diluted in water and the sample is analyzed by purge and trap GC with FID. Water samples are analyzed with no dilution, or diluted with reagent water; the sample is analyzed using purge and trap GC with FID.

3.0 Definitions

3.1 Gasoline Range Organics (GRO): All chromatographic peaks eluting between the following ranges are attributed to GRO:

AK101: The area including n-Hexane to the start of n-Decane*. (C6-C10)*

8015B: *The area including* Toluene through *the end of* n-Dodecane, inclusive

Hawaii: *The area including* Hexane through *the end of* n-Dodecane, inclusive *(C6-C12)*

California 8015B: *The area including* 2-methylpentane through *the end of* 1,2,4-trimethylbenzene*, inclusive (GRO)*

NWTPH-GX: at a minimum *the area including* Toluene through *the end of* 1-Methylnaphthalene inclusive is integrated and plotted against the known concentration of gasoline standard added. *(Gasoline)*

Quantitation is based on a direct comparison of the area within this range to the total area of the calibration standard within this range.

4.0 Interferences

4.1 High levels of heavier petroleum products such as diesel fuel may contain some volatile components that produce a response within the retention time range for gasoline. Other organic compounds, including chlorinated solvents, ketones, and ethers are measurable.

4.2 Samples contaminated with a single compound that is detectable using this method may result in a biased value for the compound. This is caused by the different response factors for gasoline and other various solvents.

4.3 Samples can become contaminated by diffusion of volatile organics during shipment and storage. A trip blank prepared from reagent water or methanol and carried through sampling, storage, and handling is recommended.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. For volatile samples containing high concentrations of water-soluble

materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the *autosampler* syringe or *sonicate the p*urging *vessel with MeOH, followed by a* rinse with *purged DI* water between analytical batches. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1 (per the Corporate Safety Manual), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex, nitrile, or vinyl gloves must be worn while handling samples, standards, solvents, and reagents. Cut resistant gloves must be worn when using sharp tools or when washing glassware. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.1.2 Purge vessels on purge-and-trap instruments can be pressurized by the time analysis is completed. Vent the pressure prior to removal of these vessels to prevent the contents from spraying out.

5.1.3 GC VOA instruments *with PID* use an ultraviolet (UV) light source, which must be shielded from view. There should also be a warning label/sticker on each instrument that identifies it as a UV light source.

5.1.4 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.5 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.6 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol (MeOH)	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80G hard drive or equivalent or as recommended by instrument manufacturer.
- LIMS system: TALS version 1.0 or higher.
- Data acquisition system: Agilent (Hewlett Packard) ChemStation for Windows 95 (version G1701AA) or equivalent. Agilent's ChemStation, is used for data acquisition and storage on machine-readable media. Since no processing is done by ChemStation and since there are no audit trail functions associated with data acquisition, the audit trail feature for ChemStation may be either enabled or disabled. The other component, Chrom, is used for data processing such as the measurement of peak area or peak height. By design, the audit trail feature for Chrom is always enabled.
- Data processing: Chrom version 1.2 or higher. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. In addition, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.2 Instrumentation

- Varian Archon Autosampler or Tekmar Aquatek 70 Autosampler or equivalent
- Purge/Trap Liquid Concentrator, Tekmar 3000*, 3100* or equivalent
- Gas chromatograph and detector: Hewlett Packard 5890 Series II Gas Chromatograph or equivalent with OI model 4430 Photoionization Detector (PID) or equivalent and OI Flame Ionization Detector (FID) or equivalent
- Columns: Restek RTX-VRX (75 m x 0.45 mm*ID* x 2.5*5* µm) or equivalent
  Note: Other columns may be used. This was the column in place at the time the SOP was prepared. The serial number of the column used is documented in the instrument maintenance logbook.
- Analytical balance, 0.01 g accuracy
- *Muffle furnace*

6.3 Supplies

- Scintillation vials
- Volumetric flasks: 10-mL, 50-mL, 100-mL, and 200-mL
- Glass standard vials with screw caps and Teflon-coated septum

- *Class A glass, gas-tight syringes ranging from 10uL to 2.5mL*

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Methanol, Baker Purge and Trap Grade or equivalent.

7.3 Neat standards used for surrogate/standard solution preparation should be purchased from *Restek* or other certified supplier. Analyte list below:

7.3.1 1-Bromo-4-fluoro-benzene *(10,000 ug/mL)*

7.3.2 α,α,α-Trifluorotoluene *(1190 mg/L)*

7.4 Surrogate: A 250 mg/L and 500 mg/L standard is prepared by diluting 2500-uL and 5000uL: 1-Bromo-4-fluorobenzene to 100.0-mL of methanol and added to the Internal Standard reservoir for Aquatek auto samplers and Archon autosamplers respectively.

7.5 TFT Stock Solution: A 10,000 mg/L solution is prepared by diluting 420.0-uL α,α,α-Trifluorotoluene to 50.00-mL in methanol.

7.6 Soil TFT Preservation/Surrogate Solution: A 4.00 mg/L TFT solution is prepared by diluting 400 uL TFT Stock Solution to 1.00 L in methanol.

7.7 Water TFT S*pike Surrogate* Solution: A 400 mg/L TFT solution is prepared by diluting 4 mL *of TFT Stock in reagent grade methanol with a final volume of* 100-mL.

7.8 Retention Time Standard: A custom mix Ultra Scientific Standard with the components necessary for defining retention time windows is used *as supplied from the manufacturer. RTC vials are prepped* by *adding* 22uL of *custom source* standard *and 2.5mL Soil TFT Preservation/Surrogate Solution to* DI H_2O *for a final volume of 100mL*.

RT Standard Analyte	Concentration
1,2,4-trimethylbenzene	100 mg/L
1-methylnaphthalene	200 mg/L
2-methylpentane	100 mg/L
benzene	100 mg/L
n-decane	100 mg/L
n-dodecane	100 mg/L
n-hexane	100 mg/L
naphthalene	100 mg/L
toluene	100 mg/L
n-tetradecane	100 mg/L

7.9 Unleaded Gasoline Composite Standard: 50,000-ug/mL purchased from *Accustandard* or other certified supplier.

7.10 GRO *Primary S*olution *ICAL/CCAL/LCS:* A *2*,000 ug/mL solution is prepared by diluting *2*-mL Unleaded Gasoline Composite Standard to *5*0-mL in methanol.

7.11 GRO *Secondary* Solution (ICV): A *1*000-ug/mL solution *is prepared from a second source Unleaded Gasoline Composite Standard (5500ug/mL). It* is purchased from a separate manufacturer than the ICAL/CCAL/*LCS* standard. *The working reagent is prepared by adding 1 mL of second source standard to 4.5mL reagent grade methanol for a final volume of 5.5mL.*

7.12 GRO Initial Calibration: An initial calibration is prepared using 9 calibration points as follows:

***Standard* Level**	**GRO *Primary Solution* (uL)**	***TFT Spike Surrogate Solution* (uL)**	**Methanol (uL)**	**Final Volume (mL)**	**Final Concentration (ug/L)**
1	*2.5*	5.0	2500	100.0	50.0
2	*5*.0	10.0	2500	100.0	100.0
3	*12.5*	15.0	2500	100.0	250.0
4	*25*.0	20.0	2450	100.0	500.0
5*	*50*.0	25.0	24*50*	100.0	1000.0
6	*250*.0	37.5	22*50*	100.0	5000.0
7	*500*.0	50.0	*2000*	100.0	10,000
8	*750*.0	--	17*50*	100.0	15,000
9	*1250*.0	--	*1250*	100.0	25,000
* This level is used as the Continuing Calibration Verification (CCV) standard.					

7.13 A GRO initial calibration verification standard is prepared at the 1,000-ug/L concentration by diluting the GRO *Secondary* Solution in ASTM Type II water *(DI)* in a 100-mL volumetric flask as follows:

***Standard* Level**	***GRO Secondary Solution* (uL)**	***TFT Spike Surrogate Solution (uL)***	**Methanol (uL)**	**Final Volume (mL)**	**Final Concentration (ug/L)**
ICV	*100*.0	25.0	-	*100*.0	1000.0

7.14 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards/reagents and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 All samples are to be stored at 0-6°C in 43-mL VOA vials or jars with Teflon-lined caps. Water samples should be preserved to a pH <2.0 with HCl. Unpreserved soil samples should be preserved in methanol within 48 hours of collection.

8.2 The holding time for preserved waters and soil (from date of collection to date of analysis is 14 days. Unpreserved waters should be analyzed within 7 days of collection. AK101 GRO 5035 field preserved samples have a 28-day holding time limit.

8.3 VOA vials are inverted to check for air bubbles. If at all possible, samples should not be opened prior to analysis.

8.4 Field preserved soil sampling procedure. Soil samples must be collected in appropriately

sized containers and submerged in methanol or methanol containing surrogate at a 1:1 ratio *(g:mL).* The tare weight of the sample container, the weight of the methanol, and the weight of the sample must be known in order to accurately quantitate gasoline range organics. Soil samples must be stored below 25°C. Methanol preserved soil samples must be analyzed within 28 days of collection.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in the TestAmerica Seattle QAM.

9.1.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS and may also come in the form of email or written notifications distributed at "project kick off" meetings.

9.1.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the *analyst* and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument and in each analytical batch.

9.3 Method Blanks

For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards and before any samples. For aqueous samples, the method blank consists of *DI water with a 10.75uL spike of TFT Spike Solution.* For solid samples, the method blank consists of 10 mL of Reagent ID: V-4TFT_EX_xxxxx and *10* grams of muffled Ottawa sand (reagent ID VOA-Sand_xxxxx). *BFB* surrogate *is* added automatically by the autosampler at the time of analysis. The method blank is carried through the entire analytical procedure.

Acceptance Criteria: The method blank must not contain any analyte of interest at or above one-half the reporting limit or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher.

The method blank must have acceptable surrogate recoveries.

Corrective Actions: Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the associated samples.

If there is no target analyte greater than the RL (less than one half the RL for LaMP and DoD clients) in the samples associated with an unacceptable method blank, the data may be reported with qualifiers and an NCM.

If surrogate recoveries in the blank are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all affected analytes in the associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.4 Laboratory Control Samples (LCS*/LCSD)*

An LCS is analyzed for each batch. An LCS Duplicate (LCSD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS is prepared from *the same* source *as* the calibration standards. The LCS contains all the required analytes of interest (See Table 5), and must contain the same analytes as the matrix spike *(MS/MSD). The RPD between the LCS and LCSD is compared to the established acceptance limit.*

Acceptance Criteria: The LCS recovery for the control analytes must be within established control limits. Unless otherwise specified in a reference method or project requirements, the control limits are set at ± 3 standard deviations around the mean of the historical data. An LCS that is determined to be within acceptance criteria effectively demonstrates that the analytical system is in control and validates system performance for the samples in the associated batch. Recovery limits are updated at a set frequency by QA and are stored in the LIMS

Corrective Actions: If any analyte or surrogate is outside established control limits as described above, the system is out of control and corrective action must occur. Corrective action will normally be re-preparation and reanalysis of the batch.

If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records (via NCMs and the case narrative) and in the final report. Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS. This type of justification should

be reviewed and documented with the client before reporting. (LaMP: Bias high recoveries– NCM and flag ND samples)

If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

For each QC batch, analyze a matrix spike and matrix spike duplicate if sufficient sample volume is received. If an MS/MSD is not possible due to limited sample, then an LCS duplicate should be analyzed. Spiking compounds and levels are given in Table *3*. The matrix spike/duplicate must be analyzed at the same base dilution as the unspiked sample, even if the matrix spike compounds will be diluted out, dilutions (beyond the base dilution if necessary) of MS/MSD analyses are not required unless there are specific client instructions to do so. If necessary, this requirement will be passed to the laboratory through the PM by means of the mechanisms described in section 9.1.3 of this SOP.

LaMP: MS required if >10 samples. The client consultant is to identify the sample to be used.

Acceptance Criteria: The MS/MSD recovery for the control analytes must be within established control limits. Unless otherwise specified in a reference method or project requirements, the control limits are set at ± 3 standard deviations around the mean of the historical data. The relative percent difference (RPD) between the MS and the MSD must be less than the established RPD limit, which is based on statistical analysis of historical data. MS/MSD recovery and RPD limits are updated at a regular frequency by QA and are stored in the LIMS.

Corrective Actions: If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

If the recovery for any component is outside QC limits for both the matrix spike/matrix spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch, except in cases where a high bias is indicated and no target is detected above the reporting limit in any associated sample.

9.6 Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table *2*.

Acceptance Criteria: Acceptance limits for surrogate recoveries are set at ± 3 standard deviations around the historical mean. Surrogate recovery limits are updated at a fixed frequency by QA and stored in the LIMS.

Corrective Actions: If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- *Verify proper integration in peak review*
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Re-prepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is necessary to re-prepare/reanalyze a sample only once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and re-preparation/reanalysis is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

NOTE: For LaMP samples, if the surrogate percent recovery fails, the recovery must be confirmed by re-extraction and reanalysis with the following exceptions:

- The lab has unequivocally demonstrated a sample matrix effect and informed the LaMP representative.
- The recovery exceeds control limits and all target analytes in the sample are non-detect.

9.7 If batch QC samples or trip blanks are re-analyzed to confirm a recovery or result, and an improvement in results would cause the re-analysis to be reported, then the associated client samples must also be re-analyzed. The only exception to this protocol would be if an obvious problem occurred during the initial analysis (i.e. no internal standard added, bent autosampler needle, *carryover from a contaminated sample* etc).

9.8 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of management to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. *DoD projects require a variance request and approval prior to second level data review.* The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP # TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

10.1 Sample Preparation

10.1.1 Check the Balance logbook to determine if the daily calibration check has been completed. If it has not, the analyst must perform this check according to SOP TA-QA-0014.

10.1.2 Soil Extraction

10.1.2.1 Method 5035 Laboratory preserved:

10.1.2.2 Weigh 10 g of the sample into a tared 20 mL scintillation vial. Record scintillation vial lot number, the sample weight, the methanol lot number, the preparation date and the analyst who prepared it in the 5035 preparation batch in TALS. Sample weights are calculated in the laboratory by taring the scintillation vial*, adding ~10g of sample to the vial, and entering the weight* into the "*initial amount*" column of the preparation batch sheet for the corresponding sample container ID. This can be done by either a direct read from the balance in the volatiles prep area (preferred method), or by manually entering the weight. If the samples were preserved in MeOH at another TALS lab the calculated initial sample weight can be manually entered into the "Initial Amount" column of the preparation batch sheet for the corresponding sample container ID.

10.1.2.3 *Waste extractions are prepared by adding 1g of sample to 10mL of reagent grade methanol.*

10.1.2.3.1 To prepare the blank spike (LCS)/blank spike duplicate (LCSD), add 200-uL of GRO_LCS and 10-mL of the TFT Preservation*/Surrogate* Solution to 10g muffled Ottawa sand. (NOTE: The same metal spatulas to weigh soil samples must be used for measuring out the Ottawa sand).

10.1.2.3.2 To prepare the matrix spike (MS)/matrix spike duplicate (MSD), add 200-uL of GRO_LCS and 10-mL of the TFT Preservation Solution to 10g pre-weighed soil samples. To prepare the method blank (MB); add 10-mL of the TFT Preservation Solution to 10 g Ottawa sand.

10.1.2.3.3 All spiking solutions must be added to the sample immediately before the addition of the TFT Preservation Solution.

10.1.2.4 Vortex the samples for the extraction batch for approximately 10 to 30 seconds to break up any large clumps in the extraction vials. If after 30 seconds a pellet still remains, vortex for an additional 30 seconds. If pellet still remains, further vortex mixing is not recommended, proceed to next step. It should be noted that the MB and LCS must be vortex mixed the same amount of time as the longest associated sample.

10.1.2.5 After all samples have been vortex mixed, place all samples for the extraction batch into shaker box and set timer for *ten* minutes. It is recommended that the caps of all vials are checked and tightened before placing in shaker box to prevent leaking. If samples are present which still contain pelletized sample after vortex mixing in step 10.1.2.3, set the timer for 10 to 15 minutes. It is not recommended to

shake samples for more than 15 minutes. If a sample still contains pelletized sample after shaking for 15 minutes, vortex the sample for an additional 15 seconds and shake entire batch for additional 5 minutes. Any pelletized sample remaining after second shaking is noted in batch record and an "other anomaly" NCM is generated to accompany the extraction batch.

10.1.2.6 After samples are shaken, place samples four at a time into centrifuge with inserts for scintillation vials. Spin samples for a sufficient time to create a transparent but not necessarily uncolored layer of methanol extract above the extracted material. The time will vary depending on the nature and particle size of the extracted material. Three to five minutes at 50% speed is usually sufficient. Again it should be noted that the MB and LCS must be centrifuged at the same rate and for the same time as the longest centrifuged associated sample.

10.1.2.7 *Extracts are stored in the scintillation vial used for extraction and are stored at 0-6°C. The extracts are removed from cold storage and are allowed to return to ambient temperature prior to analysis.*

10.1.2.8 Method 5035 Field preserved:

10.1.2.9 All soil samples for AK101 analysis must be field preserved and any analysis performed with less than 48 hours allowed for the sample to equilibrate in the methanol (from time of sampling to analysis) noted in an NCM in the analytical batch.

10.1.2.10 *The* tare weight *of each container* is recorded in the TALS preparation batch. Most containers will contain a bar code with the tare weight information that can be scanned for automatic entry into the tare weight entry field in the preparation batch. Sample weights are calculated in the laboratory by adding the received weight of the sample jar to the "Vial & Sample" column of the preparation batch sheet for the corresponding sample container ID. This can be done by either a direct read from the balance in the volatiles prep area (preferred method), or by manually entering the weight. If the samples received are in 4 oz jars with 25 mls of *2.4 TFT* methanol (AK*101* samples) the calculated initial weight of the sample must be adjusted to correct for the weight of the methanol which is not included in the container tare weight. TALS will perform this calculation; however the analyst must enter a "1" into the "*Cor for density*" column *and "25" into the "MeOHVol" column* of the preparation batch sheet for the corresponding sample container ID. *The nominal amount of initial soil should be 10g for VOA vials with 10mL of methanol, or 25g with 25mL of methanol. When the calculated initial weight of the soil deviates by more than 20% of the expected value, high or low, an NCM should be written detailing that the 1:1 ratio of soil:methanol is significantly exceeded. Acceptable weights are 8g-12g for a 10g:10mL sample, and 20g-30g for 25g:25mL sample.*

10.1.2.10.1 To prepare the ***lab control sample*** (LCS)/ ***lab control sample*** duplicate (LCSD), add *200*-uL of GRO *Primary* Working Solution and 10-mL of the TFT Preservation Solution to 10g muffled Ottawa sand. All spiking solutions must be added to the sample *immediately prior to* the addition of the TFT Preservation Solution.

10.1.2.10.2 To prepare the **matrix spike** (MS)/**matrix spike duplicate** (MSD), *fill an appropriately labeled 43 mL VOA vial with approximately 40mL ASTM Type II water.* Add a 1075-uL aliquot of sample methanol extract and 25-uL of GRO *Primary* Working Solution*. Top off with water and cap vial so no headspace remains.*

10.1.2.10.3 To prepare the **method blank** (MB), *fill an appropriately labeled 43 mL VOA vial with approximately 40mL ASTM Type II water. Add a 1075-uL aliquot of TFT Preservation Solution (section 7.8). Top off with water and cap vial so no headspace remains.*

10.1.2.11 *Follow vortexing instruction from section 10.1.2.3 for MB/LCS/LCSD.*

10.1.2.12 *Follow shaking instruction from section 10.1.2.4 for MB/LCS/LCSD.*

10.1.2.13 *Samples and MB/LCS/LCSD* are stored at 0-6°C. The *samples* are removed from cold storage and are allowed to return to ambient temperature prior to analysis.

10.1.3 Extract preparation for analysis

10.1.3.1 A 1075-uL aliquot of each methanol extract is added to *approximately* 42mL of ASTM Type II water contained in appropriately labeled 43 mL VOA vials.

10.1.3.2 If the water solution becomes milky, cloudy *or oily* in appearance, this is an indication of potential high concentrations of target and/or non-target compounds and a higher dilution may be prepared at this time. *If results come back as non-detect, sample should be re-run at a lower dilution when possible. "Amount added" is to be changed in worklist rather than dilution factor.*

10.1.4 Dry Weight.

10.1.4.1 Percent solids (dry weight) is determined by weighing approximately 10 grams of sample, completely drying the sample and then re-weighing and recording the difference in weight. SOP TA-WC-0160 describes this procedure in further detail.

10.1.5 Water Prep

10.1.5.1 All aqueous samples will be spiked with 10.75-uL of Water Surrogate Solution (section 7.7) and analyzed as received *unless dilution is required due to matrix or dilution history*.

10.1.5.2 Samples may be screened for gasoline by analyzing a spare VOA, if available.

10.1.5.3 To prepare the Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS/LCSD), add *5mL* of *V-4TFT* Surrogate Solution and *100*uL

of GRO *Primary* Working Solution to a *2*00-mL volumetric flask partially filled and brought to final volume with ASTM Type II water. The volumetric is then gently inverted *three* times to ensure homogenization and transferred to two appropriately labeled VOA vials.

10.1.5.4 To prepare the matrix spike/matrix spike duplicate (MS/MSD), add *21.5*-uL of GRO *Primary* Working Solution to each of two additional samples provided before adding *10.75uL Water* Surrogate *Solution*. To prepare the method blank (MB), *spike* 1*0.75*uL of the Water Surrogate Solution *through the septa of* a *43*-mL *VOA vial* filled *and capped* with ASTM Type II water..

10.1.5.5 All aqueous sample VOA vials should be inverted to check for headspace/air bubbles prior to analysis. If multiple VOA vials are submitted for analysis, the one with the least amount of headspace should be used first. Any headspace is measured and documented in an NCM in the analytical batch.

10.1.5.6 For AK101 analysis, amber glass vials should be used for aqueous samples. If clear glass vials are submitted for analysis, the samples should be protected from light.

10.2 Calibration

10.3 Recommended Instrument Conditions

10.3.1 Gas Chromatograph Suggested Temperature Program

The following temperature programs vary with the column type used.

In-use column dimensions and serial numbers are recorded in each instrument's maintenance logbook.

Sample Analysis

Injector Temperature:	2*10*˚C
Detector Temperature:	*180*˚C
Initial Temperature:	45˚C
Initial Hold Time:	3.5 minutes
Temperature Program:	45°C to *60*°C at 15°C/min hold for 0.50 minutes *60*°C to 130°C at 20°C/min hold for 0.50 minutes 130°C to 230°C at 25°C/min hold for *3.00* minutes Total run time is 1*6*.00 minutes.
Final Temperature:	230 ˚C
Final Hold Time:	*3.00* minutes

Note: These conditions can vary by instrument. This is only a guideline. Actual instrument conditions are posted in each maintenance logbook.

10.4 Initial Calibration

10.4.1 A series of five or more initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Nominal calibration levels for GRO are listed in sections 7.13 and 7.14. Other calibration levels may be used depending on the capabilities of the specific instrument or program requirements. Calibration levels below the reporting limit may be removed provided that there is a

minimum of five calibration points, and the lowest standard is at or below the TestAmerica Seattle reporting limit.

10.4.1.1 For GRO the following carbon ranges are determined:

AK101: The area including n-Hexane to the start of n-Decane

8015B: Toluene through n-Dodecane, inclusive

Hawaii: Hexane through n-Dodecane, inclusive

California 8015B: 2-methylpentane through 1,2,4-trimethylbenzene

NWTPH-Gx: at a minimum Toluene through 1-Methylnaphthalene inclusive is integrated and plotted against the known concentration of gasoline standard added.

10.4.2 The same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

10.4.3 It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for some tests.

10.4.4 Calibration is valid when the following conditions have been met: a correlation coefficient (r) value ≥0.995 for each target analyte, *or* a higher order polynomial that is continuous and monotonic with a coefficient of determination (r^2) ≥ 0.990, *and* the mean RSD of each target analyte is less than 15%. NOTE: When using a higher order polynomial, there must be an additional calibration standard for each degree beyond linearity (i.e. 5 for linear, 6 for quadratic, etc.). Recalibration must occur when either the continuing calibration standard value falls outside +/-20% of the true value twice consecutively or, the linear coefficient (r) falls below 0.995, or other conditions such as a major instrument changes warrant recalibration.

10.4.5 Initial surrogate calibration is performed by average RF of all standards used unless matrix effects are observed. Calculation is performed using average of response factors when less than or equal to 15 %, linear regression with coefficient value (r) >0.995 for each target analyte, or higher order polynomial that is continuous and monotonic with a coefficient value (r) > 0.995. Recalibration occurs when surrogate recoveries consistently fail to meet established control limits.

10.4.6 See Corporate SOP CA-Q-S-005 for information on acceptable initial calibration models and associated algorithms.

10.4.7 Initial Calibration Verification (ICV)

Once the initial calibration has been evaluated and determined to be valid, the calibration must be verified with initial calibration verification (ICV) using a standard prepared from a source other than the calibration solutions. Multiple levels of ICV may be needed to validate all compounds in the initial calibration curve. Acceptance limits are as follows:

For 8015, the ICV must be <15% Drift.

For NWTPH-Gx, the ICV must be <20% Drift.

For AK101, the ICV must be <25% Drift.

If the %Drift falls outside acceptance criteria, assess the system for possible problems (eg. Standard degradation, etc.), re-prepare the ICV and re-analyze. *If it is outside the 24 hour window, also run a new RTC.* If the second ICV also fails,

corrective action is required (e.g., System maintenance, re-preparing intermediate standards, etc.) and the calibration must be re-prepared and re-analyzed. An acceptable ICV must be achieved before analysis.

10.4.8 A secondary source QC check standard (*ICV*) is performed using a Certified Gasoline with certified individual analytes standard from a source separate from that used for the calibration. Quantitation is performed identically as samples and standards and the result compared to the true value. Acceptance criteria for each parameter is determined by performance based empirical data.

10.4.8.1 For all DoD projects a second source calibration verification will be performed immediately following the initial calibration. The value for all analytes must be within +/- 20% of the expected value. This criterion must be met before any samples are analyzed.

10.4.9 A retention time standard (7.12) is analyzed each analytical day and every 12 hours for 8015B. The standard concentration is approximately *1*00 ug/*mL* and contains at a minimum n-Hexane, Toluene, n-Decane, n-Dodecane, and 1-Methylnaphthalene. Adjustments in the retention time windows for the respective hydrocarbon groups are made, if necessary, prior to any standard or sample quantitation. See Attachment 2 for an example retention time standard chromatogram.

The default retention time ranges are established as follows:

Gasoline Range Organics NWTPH-Gx:	Toluene to 1-Methylnapthalene
Gasoline Range Organics AK101:	Hexane to the start of Decane
Gasoline Range Organics CA 8015:	2-methylpentane to 1,2,4-Trimethylbenzene
Gasoline Range Organics HI 8015:	Hexane to Dodecane

10.4.9.1 For all DoD projects the retention time window position will be established for each analyte and surrogate once per ICAL and at the beginning of the analytical shift. The position must be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.

10.5 Continuing Calibration

10.5.1 The initial calibration must be verified every twelve hours.

10.5.2 A continuing calibration check standard is analyzed at the beginning of each analytical sequence and at the end of each analytical sequence or every 10 samples, whichever is more frequent. The percent recovery must be within +/-15%, 20% or 25% of the true value for 8015 California-G/Hawaii-G, NWTPH-Gx, and AK101, respectively. If the CCV recoveries exceed the method specified upper %Recovery limits and there are no associated sample detections above the RL, the data may be qualified and reported as the system has shown a potentially high bias (*a variance must be requested from t*he client *if DoD)*. If the CCV recoveries exceed method specified %D, the CCV may be re-prepared and re-analyzed. If two sequential CCVs fail the system must be re-calibrated and all samples analyzed since the last acceptable CCV must be re-analyzed.

10.5.2.1 For BP LaMP projects CCV is run at beginning and end of sequence and every 10 samples. Recoveries should be *+/-15%.*

10.5.2.2 Instrument response should be monitored daily by recording the absolute response of an individual peak. The internal standard is the peak chosen

for these instruments. The absolute response for this peak, in the CCVRT, needs to be documented *in Chrom* on a daily basis.

10.5.3 Once the above criteria have been met, sample analysis may begin.

10.6 Sample Analysis

10.6.1 Analysis - All samples are injected into the GC using the auto sampler and the purge and trap system to increase reproducibility. Data is acquired from the GC detector on the Chrom data acquisition system. The resultant area amounts are compared to the calibration curve, and the concentration of each analyte is calculated.

10.6.2 The presence of Gasoline is indicated if compounds are detected in the appropriate hydrocarbon range.

10.6.3 Refer to section 11.15 of SOP MV-0312 for dilution procedures.

10.6.4 An example analysis sequence log is provided as Attachment 1.

10.6.5 pH for aqueous samples

Immediately after analysis or immediately after opening the sealed VOA vial and obtaining the necessary aliquots for dilutions, the analyst must check the pH of aqueous samples with narrow range pH paper (0-*6.0*) to ensure the pH is <2. Record the pH of aqueous samples on the analytical batch sheets. In those cases where the pH is >2, initiate a non-conformance report and qualify the data, noting if the sample(s) was analyzed outside of the shortened seven-day hold time.

10.7 Data Reduction and Review

10.7.1 Upon completion of the analytical sequence:

10.7.1.1 Review chromatograms online and determine whether manual data manipulations are necessary.

10.7.1.2 Manual Integrations

All manual integrations must be justified and documented. See Corporate SOP CA-Q-S-002 for requirements for manual integration.

10.7.1.3 Manual integrations are processed using Chrom, which stores the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature.

10.7.1.4 Confirm that run logs *include* the instrument ID, the analyst **and the method** used.

10.7.1.5 Update the sequence log.

10.7.2 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 field samples.

10.7.2.1 Perform a level 1 data review and document the review on the data review checklist (GC and GCMS Data Review Checklist).

10.7.2.2 Submit the data package and review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP TA-QA-0635.

10.8 Instrument Maintenance

10.8.1 All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each

major component (e.g., GC, autosampler, column) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a tune, CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, tune, etc as may be the case).

If columns were replaced during maintenance procedures the specific make, model and serial numbers of the columns installed need to be entered in the instruments maintenance logbook.

See section 11.15 of SOP MV-0312 for additional details about instrument maintenance.

10.9 Troubleshooting

10.9.1 To ensure optimum performance of the FID, you must keep it clean and free of dust and deposits. Symptoms such as reduced sensitivity and increased noise indicate that detector needs cleaning.

10.9.2 Baseline noise:

10.9.2.1 Contaminated injector and or column. Clean the injector and solvent rinse the column.

10.9.2.2 The column is inserted into the flame of the FID. Reinstall the column.

10.9.2.3 Incorrect combustion gases or flow rates. Check and reset the gases at their proper values.

10.9.2.4 Physical defect in the detector. Clean or replace parts as necessary.

10.9.2.5 Defective detector board. Consult the instruction manual or contact the GC manufacturer.

10.9.3 Baseline spiking:

10.9.3.1 Particulate matter passing through the detector. Clean the detector per section 9.7.4.

10.9.3.2 Loose connections on cables or circuit boards (usually random spiking). Clean and repair the electrical connections as needed.

10.9.4 Baseline Drift (Upward):

10.9.4.1 GC or column contamination. Clean the injector. Solvent rinse the column.

10.9.4.2 Damaged stationary phase. Replace the column. Determine the cause of the damage to prevent future problems.

10.9.5 Baseline Drift (Downward):

10.9.5.1 Incomplete conditioning of the column. Condition the column until a stable baseline is obtained.

10.9.5.2 Unequilibrated detector. Allow the detector enough time to equilibrate.

10.9.6 Irregular Peak Shapes or Sizes

10.9.6.1 No peaks.

10.9.6.1.1 Plugged syringe. Clean or replace the syringe.

10.9.6.1.2 Broken column. Replace or reinstall the column.

10.9.6.1.3 Detector gases improperly set or not on. Check and reset the detector gases.

10.9.6.1.4 Very low or no carrier gas flow. Immediately lower the column temperature to 35-45C. Measure and verify the carrier gas flow rate. Check for leaks.

10.9.6.2 Tailing Peaks.

10.9.6.2.1 Active injector liner or column. Clean or replace liner. Replace the column if it is damaged.

10.9.6.2.2 Contaminated injector liner or column. Clean or replace the injector liner. Solvent rinse the column.

10.9.6.2.3 Poorly installed column, liner or union. Check and verify the installation of each fitting. Reinstall the column if needed.

10.9.6.2.4 Poorly cut column end. Re-cut and reinstall the column.

10.9.6.3 Rounded or Flat Topped Peaks.

10.9.6.3.1 Exceeding the range of the integrator. Dilute the sample.

10.9.7 Retention Time Shifts

10.9.7.1 Leak in the injector, especially the septum. Find and repair the leak. Change the septum.

10.9.7.2 Contaminated column. Solvent rinse the column.

11.0 Calculations

11.1 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Response Factor (RF)

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard, ng.
C_x = Concentration of the compound being measured, ng.

11.4 Standard Deviation (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2}{n-1}}$$

Where:

X_i = Value of X at i through n.
n = Number of points.
$\overline{X}$ = Average value of Xi.

11.5 Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD}{\overline{RF}} \times 100\%$$

Where $\overline{RF}$ is the mean of RF values for the calibration.

11.6 Percent Drift between the initial calibration and the continuing calibration:

$$\%Drift = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100\%$$

Where:

$C_{expected}$ = Known concentration in standard.
C_{found} = Measured concentration using selected quantitation method.

11.7 Concentration = mg/kg or L $= \frac{C \times V \times D}{W}$

Where:
C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor

W = Weight/Volume of sample aliquot extracted (grams or mLs)

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

11.8 Calculation of Results for Methanol Extracts

Sample Conc (ug/Kg) = [On Column (ug/L)] x Extraction Final Volume (mL) x VOA Vial Volume (mL) x 1L (CF) x 1000g (CF)
Amount of Soil Sample (g) Amt of MeOH Extract (mL) 1000mL 1Kg

VOA vial volume is 43 ml and when the extract doesn't require a dilution, 1.075 mL of the methanol extract is used. So, the equation becomes:

$$\text{Sample Conc (ug/Kg)} = [\text{On Column (ug/L)}] \times \frac{\text{Extraction Final Volume (mL)}^{1}}{\text{Amount of Soil Sample (g)}^{2}} \times \frac{43\ (\text{mL})}{1.075\ (\text{mL})} \times \frac{1\text{L (CF)}}{1000\text{mL}} \times \frac{1000\text{g (CF)}}{1\text{Kg}}$$

[1]Extract Final Volume, miscible solvent corrected (mL) = ((g of samples * % moisture/100) + ml of MeOH) * 40 (used when % Moisture of the soil sample is greater than 10%).

[2]Amount of Soil, dry-weight corrected (g) = sample mass (g) * (100 - % moisture/100)

When the Extraction Final Volume is 10mL, the Soil Extract Volume expressed on Form 1 will be 400mL. [10 * (43/1.075)]
When the Extraction Final Volume is 25mL, the Soil Extract Volume expressed on Form 1 will be 1000mL. [25 * (43/1.075)]

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Methanol with trace levels of volatile analytes described by this method is temporarily stored in appropriately constructed (i.e. plastic) satellite waste containers labeled "Hazardous Waste." When filled, the container is bulked into the mixed solvent waste

drum in the waste disposal warehouse. This waste stream is sent out for fuel blending.

14.1.2 VOA vials are collected in large plastic satellite waste bins marked "Hazardous Waste." At or before the waste reaches 55 gallons, the contents are transferred to the sample disposal area where the vials are bulked into a 55 gallon waste barrel and sent out for incineration.

14.1.3 Expired Standards. Expired standards are collected in satellite containers marked "Hazardous Waste." At or before the containers reach 55 gallons the containers are taken to the waste warehouse where they are bulked into an expired standards lab pack and sent out for incineration.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Methods 5035A, 5030B, and 8015B.

15.2 Method AK101 for the Determination of Gasoline range organics Version 4-8-02.

15.3 NWTPH-Gx Volatile Petroleum Products Method for Soil and Water. Washington DOE Publication No. ECY 97-602, June 1997.

15.4 Department of Defense Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Quality Workgroup, Final Version 4.2, October 2010.

16.0 Method Modifications:

Item	Method	Modification
1	NWTPH-Gx	The method states one duplicate and one method blank per 10 samples. TestAmerica Seattle batches 2 duplicate sets (if sufficient sample exists), one LCS/LCSD set, and one method blank per 20 samples
2	NWTPH-Gx	The method states 5 g of soil is to be added to 10-mL Methanol followed by a 100-uL aliquot added to 5-mL water. TestAmerica Seattle extracts 10 g of soil with 10-mL Methanol followed by an 1075-uL aliquot added to 43-mL water

17.0 Attachments

Attachment 1: Example Instrument Sequence

Attachment 2: Example Chromatogram for RT Standard

Table 1: Reporting Limits

Table 2: Surrogate Standards

Table 3: LCS and Matrix Spike Compounds

18.0 Revision History

- Revision 14 dated 27 June 2017
  - Updated Approval Managers on title page
  - Removed outdated column information and added muffle furnace in section 6.2.
  - Added class A glass syringes to section 6.3
  - Updated concentrations and volumes of solutions in section 7.1

- Added concentrations of standards to section 7.3
- Updated reruns for over-diluted non-detects in section 10.1.3.2
- Updated spike volumes to section 10.1.5
- Updated instrument conditions in section 10.3

- Revision 13 dated 18 April 2016
  - Updated Approvals
  - Updated MSDS to SDS in section 5.2.
  - Removed section 4.5 and 7.8 not applicable to GRO analysis
  - Updated standard and reagent concentrations to current throughout SOP
  - Changed instrumentation section to requirement of 0.01g balance accuracy
  - Added table to section 7.8 listing compounds and concentration in retention time standard

- Revision 12, dated 30 April 2014.
  - Removed all references to BTEX by GCMS.
  - More clearly defined GRO ranges for the different methods in section 3.1.
  - Added computer hardware and software to section 6.1.
  - Added clear instructions on the preparation procedures for MeOH 5035 Soil samples, section 10.1.2.
  - Added troubleshooting, section 10.9

- Revision 11, dated 13 March 2013.
  - Added section 10.1.2.3.1 to better describe the preparation procedures and documentation.
  - Added section 14.1 Waste Streams Produced by the Method.

- Revision 10, dated 12 October 2012.
  - Added an elaborated calculation for methanolic extracts 11.8

- Revision 9, dated 20 June 2011
  - Specified software in section 6.1
  - Updated standard information in section 7
  - Incorporated ROMDs 00019 and 00026 in sections 6.1 and 10.4
  - Added hold time information for aromatics in unpreserved water samples, section 8
  - Incorporated ROMD 00025 in Section 9.4 and 9.5
  - Incorporated ROMD 00020 in section 10.4
  - Incorporated ROMD 00022 in section 10.6.8
  - Updated surrogated Methanol reagent name section 9.3
  - Changed 5% to 10% per QSM 4.2 section 9.3
  - Added spiking criteria per LaMP sections 10.1.2.1.4 and 10.1.2.2.3
  - Adjusted reagent water volume from 43 to 42.1 mL in sections 10.1.2.1.6, 10.1.2.2.2 and 10.1.2.2.5 for final volume of 43 mL.
  - Added section 10.1.2.2.6 specifying field preservation for AK101.
  - Added sections 10.1.3.5 and 10.1.3.6 to address headspace and glass for Aq.
  - Added reference to corporate tuning policy section 10.5
  - Added two consecutive CCV failures section 10.6.5
  - Added explicit ICV section 10.6.9
  - Added more detail/condensed CCV analysis in sections 10.7.2 and 10.7.2.1
  - Incorporated ROMD 00024 in section 10.7.2
  - Incorporated ROMD 00033 in section 10.7.2.2

- Added dilution procedures (by reference) in section 10.8.4.
- Added pH section 10.8.6
- Added data reduction/data review (10.9) and maintenance (10.10) sections
- Corrected section/table references and grammar where necessary.

- Revision 8, dated 16 April 2010
  - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
  - Added removal of expired standards Section 7.24.
  - Added LaMP matrix spike requirements Section 9.5
  - Added BP LaMP surrogate requirements, Section 9.6.
  - Added criteria for additional QC, Section 9.7.
  - Added daily balance check to Section 10.1.1.
  - Added BP LaMP CCV criteria Section 10.7.2.2
  - Updated DoD Table (Attachment)
  - Integration for TestAmerica Bothell and TestAmerica Tacoma operations.

- Revision 7, dated 17 December 2008
  - Integration for TestAmerica and STL operations.
  - This revision is a complete rewrite and an expansion of scope.

Attachment 1. Example Instrument Sequence

Page 1

Sequence Log

Directory : i:\1\DATA\01092009

#	Filename	Sample Name	Date/Time
1	ms176640.d	Fife Rinse	01/09/09 11:43
2	ms176641.d	Rinse/Tune	01/09/09 12:04
3	ms176642.d	RT standard	01/09/09 12:26
4	ms176643.d	1000 ug/L GRO ccal	01/09/09 12:47
5	ms176644.d	25 ug/L 8260 ccal	01/09/09 13:08
6	ms176645.d	MB 580-39682/1-A	01/09/09 13:30
7	ms176646.d	LCS 580-39682/2-A	01/09/09 13:51
8	ms176647.d	580-12421-E-1-A	01/09/09 14:12
9	ms176648.d	580-12421-E-3-A	01/09/09 14:34
10	ms176649.d	580-12421-E-3-B MS	01/09/09 14:55
11	ms176650.d	580-12421-E-3-C MSD	01/09/09 15:17
12	ms176651.d	580-12421-B-5-A	01/09/09 15:38
13	ms176652.d	Rinse/Tune	01/09/09 16:00
14	ms176653.d	1000 ug/L GRO ccal	01/09/09 16:21

Attachment 2. Example Chromatogram for RT Standard

```
File        : I:\2\DATA\04282006\CS165056.D
Operator    : jc
Acquired    : 4-28-2006 09:33:19 AM using AcqMethod GBTEX.M
Instrument :   Instrumen
Sample Name: rt std
Misc Info   : 1369-18-1
Vial Number: 3
```

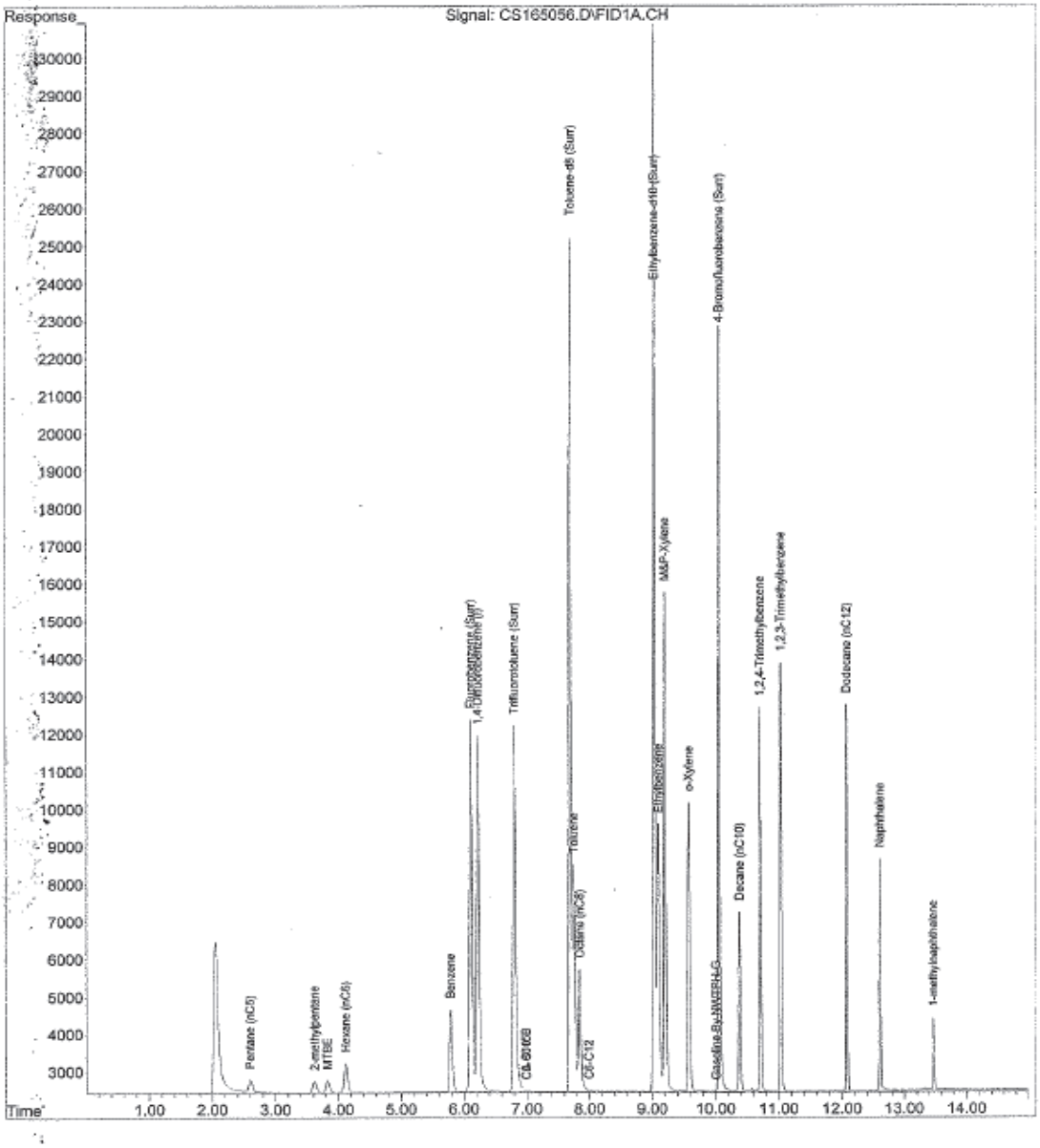


Table 1. Reporting Limits

Compound	CAS Number	Reporting Limits[1]	
		Water (µg/L)	Soil (mg/kg)
Gasoline Range Organics, NWTPH-Gx	STL00228	50	4.0
Gasoline Range Organics, AK101	8006-61-9	50	4.0
Gasoline Range Organics, Hawaii-Gx	STL00061	50	4.0
Gasoline Range Organics, CA 8015B	STL00215	50	4.0

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

Table 2. Surrogate Standards

Surrogate Compounds	Standard Concentration (mg/L)
Trifluorotoluene	400, *4.0 and 2.4*
4-Bromofluorobenzene	*0.2*50 & *0.500* auto sampler dependent

NOTES:

1) Recovery and precision limits for the surrogates are generated from historical data and are maintained by the QA department.

Table 3. *ICV* Compounds

Compound	Standard Concentration (ug/mL)
Gasoline Range Organics	*1000*

NOTES:

1) Recovery and precision limits for the LCS, MS, and MSD are generated from historical data and are maintained by the QA department.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Record of Management Decision

SOPs: TA-WC-0121 Rev. 18

Title: N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) in Aqueous Samples by Extraction and Gravimetry (EPA 1664A) (Oil & Grease and Total Petroleum Hydrocarbons)

ROMD ID: 00069

Effective Date: 11/7/2017 Expiration Date: When indicated SOP is revised

Laboratory Approvals:

Signatures on File

Stan Palmquist Date
Inorganic Department Manager

Manjit Nijjar Date
Health & Safety Coordinator

Terri Torres Date
Quality Assurance Manager

Dennis Bean Date
Laboratory Director

1. **Description Of and Reason For Decision:**

   Added instructions on removing methanol from the extraction disk after activation.

2. **Method Modifications:**

   The following change will be made to section 10.1.8;

10.1.8 Add 15 mls methanol to the reservoir, *Apply a light vacuum and pull approximately 1 ml through the disk. Allow the disk to soak for* 2 minutes. ***It is critical that the disc is not allowed to go dry during this stage of conditioning.*** *Add 30 ml of reagent grade water to the reservoir. Apply a light vacuum and pull the reagent grade water through the disk until the surface is covered with a 1-2 mm of water. Allow the disk to soak for 2 minutes.*

NOTE**: The extraction disk should be brought to near dryness during this step, but it is important that the disk is not allowed to dry before introducing the sample. The sample must not come into contact with residual methanol. Drying of the disk could lead to decreased yields

Title: N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) in Aqueous Samples by Extraction and Gravimetry (EPA 1664A) (Oil & Grease and Total Petroleum Hydrocarbons)

Approvals

Signatures on File	
Stan Palmquist Date	Manjit Nijjar Date
Inorganic Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

This method is intended for determining n-hexane extractable material (HEM) and n-hexane extractable material that is not absorbed by silica gel (SGT-HEM) in surface and saline waters and industrial and domestic aqueous wastes. *The method reporting limits for 1 liter of water for HEM and SGT-HEM are 5 mg/L.*

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Method Summary

A 1L sample is acidified to pH<2 and extracted with n-Hexane through an apparatus that employs a vacuum system and solid phase extraction disk. The extract is dried through sodium sulfate. After collecting the extract in a pre-weighed container, the solvent is evaporated and HEM is determined.

If HEM is to be used for determination of SGT-HEM, the HEM is redissolved in n-Hexane. For SGT-HEM determination, an amount of silica gel proportionate to the amount of HEM is added to the solution containing the redissolved HEM to remove absorbable materials. The solution is then filtered to remove the silica gel, the solvent evaporated and the SGT-HEM determined.

3.0 Definitions

3.1 Batch - A group of 20 or fewer *client* samples prepared and/or processed together within the same shift using the same reagents. Each batch must contain a minimum QC of one method blank, one laboratory control sample, one laboratory control sample duplicate and one matrix spike (when sufficient volume is provided by the client).

3.2 Bench Sheet – Work list created from the laboratory's LIMS which includes all of the pertinent information for the batch including sample IDs, quantity of sample, prep date/time, LCS standard IDs, QC sample, etc.

3.3 n-Hexane Extractable Material (HEM) – Material that is extracted from a sample and determined by this method (oil and grease). This material includes relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

3.4 Silica gel treated n-hexane extractable material (SGT-HEM) – Components of n-Hexane extractable material (HEM) that are not adsorbed by silica gel; i.e. non-polar material.

4.0 Interferences and Comments

4.1 In order to eliminate contaminates from glassware, all glassware must be cleaned in accordance with SOP TA-QA-0010 prior to being utilized.

4.2 All reagents used to prepare samples must be documented on the analytical bench sheet and demonstrated to be interference free.

4.3 All standards added to any samples within a batch must be documented on the analytical bench sheet.

4.4 Sodium sulfate and silica gel fines have the potential to inflate results for HEM and SGT-HEM by passing through the filter paper. If the filter paper specified in this method is inadequate for removal of these fines, use of a 0.45-micron filter is recommended.

4.5 Changes in temperature between weighings can greatly affect results. Higher temperatures will result in lower weights.

4.6 The laboratory analyst will perform the method in accordance with this SOP. The analyst will resolve non-conformances in methods and data, either individually or with the assistance of the department supervisor or operations manager. Deviations from this SOP must be documented. Bench sheets and raw data must capture information related to a deviation. The laboratory analyst or supervisor will report deviations or non-conforming events to the operations, project and/or QA manager via a non-conformance report.

4.7 The Supervisor, Operations Manager, and/or QA Manager will assist the laboratory analyst in resolving non-conformances.

4.8 The Department Supervisor or qualified analysts shall review and approve data, methodology, final reports, bench sheets and notebooks for all analyses performed in his/her department.

4.9 The QA manager shall verify adherence to this SOP through annual audits, non-conformance reports, and performance evaluation studies.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure involves hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific safety concerns or requirements as they relate to this procedure include:

5.1.1 Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP and should not be used.

5.1.2 Unknown samples may contain high concentrations of toxic volatile compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

5.1.3 Glassware should be inspected for chips or cracks before use. Chipped/broken glassware that poses a safety hazard must be removed from service and repaired or discarded.

5.1.4 Remember NEVER to use hotplates or other similar devices to heat or evaporate any flammable solvent such as hexane due to a high risk of fire

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS. Electronic copies of SDS can be located on the EH&S webpage of Oasis.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Silica Gel	Irritant		Silica gel is harmful if inhaled. It may cause irritation to the lungs and respiratory system. Silica gel should be weighed in a hood.
Hydrochloric Acid	Corrosive Poison	5 ppm – Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reactions			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Balance; Top loading -- Mettler Bas Bal BB2400, BB300, BB202 or equivalent with a 2000g capacity and capable of weighing to 0.01g

6.2 Balance; Analytical -- Denver Instrument S-234 or equivalent, capable of weighing to 0.0001g

6.3 Class A 10 mL Repeating pipettor, accurate to ±3%

6.4 pH indicator strips

6.5 Amber Sample Bottle -- 1000 ml

6.6 Stainless steel spatulas

6.7 Filter paper -- Fisher Brand P8

6.8 StepSaver SPE filtration set-up

6.9 CPI Pre filter fast flo 47 mm glass, P/N 4350-010089

6.10 Dried receiving flasks with 24/40 ground glass joints

6.11 Sodium sulfate

6.12 Silica Gel

6.13 Collection flasks – 250 ml

6.14 Disposable Polypropylene cups-250ml. Fisher P/N 14955106

6.15 Kim wipes

6.16 Disposable pipette tips

6.17 Speed vap

6.18 Aluminum pans

6.19 SPE 1000 mL filter funnel reservoir for 47 mm step saver

6.20 3M EPORE 47 mm solid phase extraction disk

6.21 Environmental Express spiking solution 10 mL EPA Method 1664 LCS solution P/N G3025

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 n-Hexane (C_6H_{14}), reagent grade or better

7.3 Sodium sulfate (Na_2SO_4), granular anhydrous.

7.3.1 Bulk material must be dried at 200-250^{o}C for 24 hour minimum and store in a tightly sealed container until use. Alternatively use commercial Anhydrous Sodium Sulfate cartridges, Environmental Express PN G1065. Cool beakers on a cooling rack and cover with aluminum foil. Place in 1 liter containers, label and seal. Document the preparation of the sodium sulfate in the reagent prep module of TALS.

7.4 Methanol (CH_3OH)

7.5 Hydrochloric Acid (HCl) or Sulfuric acid (H_2SO_4) – Diluted 1:1 with DI water

7.6 Silica gel, Fisher 100-200 mesh. P/N s679-500

7.7 Spiking solution, Purchased from Environmental Express, CAT# G3025 or prepared as outline below.

7.7.1 1:1 Hexadecane/Stearic acid [$(CH_3(CH_2)_{14}CH_3)$/ $(CH_3(CH_2)_{16}COOH)$].

7.7.2 Weigh 0.2 $\pm$ 0.002 g of stearic acid and 0.2 $\pm$ 0.002 g hexadecane into a 100 mL volumetric flask and fill to the mark with acetone. The total concentration of this stock is 4000 mg/L HEM. Mark the solution level on the vial. Store in a glass container with a fluoropolymer-lined cap in a cupboard at room temperature. Commercial purchased standard must be stored at < 6°C.

7.7.3 The spiking solution requires warming for complete dissolution of stearic acid before use.

7.7.4 Immediately prior to use, verify the level on the vial and bring to volume with acetone, if required. Warm to redissolve all visible precipitate.

7.7.5 If there is doubt of the concentration, remove 10.0 $\pm$ 0.1 mL with a volumetric pipet, place in a tared weighing pan, and evaporate to dryness in a fume hood. The weight must be 40 $\pm$ 1 mg. If not, prepare a fresh solution.

7.7.6 The spiking solution must be checked frequently for signs of degradation or evaporation. The solution must be replaced after six months, or sooner if degradation has occurred. If purchased spike is used, it must be used or discarded by the vendor's expiration date.

7.8 Reagent Water

7.9 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards/reagents and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Aqueous samples should be collected in one liter amber bottles with Teflon lined lids.

8.2 The samples should be preserved to pH<2 with HCl. Check the pH of samples using the procedures described in section 10.1.13 of this SOP.

8.3 Samples must be stored at 0-6°C, away from light prior to analysis.

8.4 Water samples must be analyzed within 28 days of the date and time of collection.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.2 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in SOP TA-QA-0620, Quality Control Program.

9.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.5 Sample QC - The following quality control samples are prepared with each batch of samples.

9.5.1 Preparation Batch

A preparation batch is a group of up to *20 client and QC* samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a laboratory control sample (LCS), laboratory control sample duplicate (LCSD), a matrix spike (MS), and a matrix spike duplicate (MSD). If no additional sample volume is available for an MS and MSD then a LCSD must be done. If enough sample volume is available for an MS and MSD then the LCSD is optional. As discussed in the following sections, special program, project, or method requirements can include additional requirements or increased frequency of QC sample analysis. Always refer to special project instructions for details before proceeding with the analysis.

9.5.2 Method Blank: An interference-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analysis. The method blank is used to gauge contamination resulting from the analytical process.

9.5.2.1 The method blank must be less than one-half the reporting limit. If the method blank is greater than one-half the reporting limit, the source of the contamination must be investigated and appropriate corrective measures must be taken and documented. Corrective action may include reanalysis, re-extraction and reanalysis or inspection of the sample data to determine if all samples associate with the method blank are non-detect or ten times the contamination level found in the blank. For the latter, data may be reported with appropriate qualification. If re-extraction is required, initiate a nonconformance report, re-extract and reanalyze the entire batch (method blank, LCS, LCSD and all samples including MS/MSD). A nonconformance report is used to document the out of control situation and its resolution.

9.5.3 Laboratory Control Sample and Duplicate (LCS/LCSD): A known matrix spiked with the target analytes that is used to assess laboratory performance or accuracy. A LCSD must be processed when adequate sample volume for a MSD is not provided.

9.5.3.1 **The on-going precision and recovery limits are specified in Table 1 of the source method as follows:**

HEM Recovery Limits = 79 - 114%

SGT-HEM Recovery Limits = 66-114%

9.5.3.2 Compare the percent recovery of the LCS to the control limits. If the recovery fails low, initiate a nonconformance report and re-extract and reanalyze the entire batch (method blank, blank spike, blank spike duplicate and all samples including MS). A nonconformance report is used to document the out of control situation and its resolution. If there is no sample remaining, contact the project manager immediately. The client may elect to resample.

If the recovery fails high and there are positive results for the target analyte, initiate a nonconformance report and re-extract and reanalyze the entire batch (method blank, blank spike and all samples including MS). If the %R of the LCS fails high and there are no positive results for the target analyte(s) in the associated samples, qualify the analyte and report the results.

9.5.4 Matrix Spike and Duplicate (MS/MSD): **This method requires a MS if client supplies sufficient volume; an MSD is optional.** However, if a MSD is not processed an LCSD must be included in the batch. An aliquot of sample is spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. A matrix spike is used to assess the bias of a method in a given sample matrix.

9.5.4.1 **The acceptable MS/MSD recovery and relative percent difference (RPD) limits are specified in the source method as follows:**

HEM Recovery = 79 – 114 %

HEM RPD = 18 %

SGT-HEM Recovery = 66 - 114 %

SGT-HEM RPD = 24 %

9.5.4.2 If the MS/MSD %R or RPD fails, flag the data.

9.6 Anomalous situations occurring during sample preparation must be documented on the bench sheet, and non-conformance reports must be issued if necessary. Possible anomalous situations resulting in non-conformance reports include loss of a sample or batch QC through spillage or breakage or blank contamination.

10.0 Procedure

One time procedural variations are allowed only if deemed necessary in the professional judgment of the analyst or supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo (NCM) that is approved by a Technical Director and/or the QA Manager. If contractually required, the client shall be notified. The NCM shall be filed in the project file. See TA-QA-0610 for details.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

This method is entirely empirical. Precise and accurate results can be obtained only by strict adherence to all details.

10.1 Procedures Applicable to StepSaver SPE Filtration Device.

10.1.1 Before beginning a batch, ensure that a daily calibration check using 2 mg and 1000 mg weights was performed on the analytical balance and that their measurements fell within the specified tolerances.

10.1.2 Allow spike solution and samples to warm to room temperature.

10.1.3 Inspect all glassware used in this procedure for chips and cracks.

10.1.4 Set aside an aluminum pan for each client sample and QC sample that is to be processed. Label and then weigh each aluminum pan when it attains constant mass. Record the mass to four decimal places (0.0001) in TALS.

10.1.5 Assemble the StepSaver unit in a hood with a waste flask attached.

10.1.6 For extremely dirty samples, add a prefilter such as glass wool or *CPI Pre filter, fast flo 47 mm glass.*

10.1.7 Position the valve on the manifold to the OFF/VENT position. Wash the disk and walls of the reservoir with 10-15ml of n-hexane (enough to cover the top of the disk). Quickly turn the manifold to the WASTE position and then quickly back to OFF/VENT position to draw a small amount of hexane through the disk. Apply vacuum and pull remaining hexane through the disk into the waste collection vessel. Repeat *two* more times, and then allow the disk to vacuum dry for a minimum of two minutes. It is very important that all the hexane is eliminated from the disk at this time as any residual hexane could cause analytes from the QC/samples to pass through the disk as waste.

10.1.8 Add 15 mls methanol to the reservoir, draw a small amount through and soak for *2 minute*. Make sure the disk is moist and DO NOT LET THE DISK GO DRY AT THIS POINT.

10.1.9 **Determine if a client specified any samples for site-specific QC (MS). Otherwise, choose a sample. One additional 1L amber of sample is needed for the MS**.

10.1.10 Weigh each sample bottle before any processing and enter the weight into TALS.

10.1.11 For the blank and LCS, measure 1000 mL of DI water in a graduated cylinder and transfer to a labeled SPE funnel reservoir. *Alternatively, use clear one liter jars, fill with DI water, acidify to pH <2. Add spike solution to LCS/LCSD. Weigh the bottles before and after just like client samples.*

10.1.12 Verify the pH of samples and adjust the pH of QC samples (blank, LCS, LCSD) to <2 with an acid from 7.5.

10.1.12.1 Dip a *disposable pipette tip* into the sample as it sits in the SPE funnel reservoir. Place a drop of sample on the pH paper.

10.1.12.2 If the pH is greater than 2, adjust it to <2 using 4-6ml of an acid from 7.4.

10.1.12.3 Rinse the glass stir rod into a separate labeled collection vessel with hexane. Set collection vessel aside to add to the sample during the hexane extraction.

10.1.12.4 Record the pH in TALS

10.1.13 Pour samples into respective SPE funnel reservoirs.

10.1.14 If you are using lab prepared standard: Using the class A 10 mL repeating pipettor, add 10 ml of spike solution to LCS/LCSD and MS/MSD in the SPE funnel reservoir. Record the spike ID on the bench sheet.

10.1.14.1 If the spiking solution, Purchased from Environmental Express, CAT# G3025 is used simply cut one end off and transfer the entire contents from the Teflon tube into sample with the SPE funnel reservoir. Rinse the empty tube with DI water placing each rinse in the SPE funnel reservoir.

10.1.15 Position stopcock to the WASTE position. Extract the sample with the stopcock in the WASTE position. The extraction should take no less than 15 minutes for a one liter sample.

10.1.16 After sample extraction is complete, maintain full vacuum for 2 minutes to strip most of the water from the extraction disk. Drying for an extended period of time can cause a cooling effect and the stearic acid could become crystallized again in the SPE disk. Soaking with hexane may not be enough to get the stearic acid back into the hexane during the elution step. Turn manifold valve to the OFF/VENT position.

10.1.17 Position stopcock to the COLLECTION position.

10.1.18 Remove waste flask and properly dispose of collected solvents. Attach a Sodium Sulfate cartridge and clean collection flask.

10.1.19 Add 10-15 mls of hexane to the amber bottle, cap and shake to ensure the hexane has come in contact with all surfaces of the bottle. Use this rinse as the first aliquot of elution solvent by pouring it into the reservoir. Add the hexane used to rinse the glass stir rod. Use a small amount of hexane to rinse the sides of the reservoir to get any analytes adhering to the glass surfaces. Draw a small amount through the disk and allow the hexane to soak the filter for *2* minutes.

10.1.20 Carefully and slowly apply vacuum (turn the manifold to the COLLECTION position) to gradually pull the remaining hexane through the disk and into the clean collection flask. Turn manifold valve to the OFF/VENT position.

10.1.21 For the second elution step add 10-15mls fresh hexane to the reservoir. Draw a small amount through the disk and allow the hexane to soak the filter for *2* minutes. Carefully and slowly apply vacuum (turn the manifold to the COLLECTION position) to gradually pull the hexane rinse through the disk and into the collection flask.

10.1.22 Turn the manifold valve to OFF/VENT position.

10.1.23 Determine the volume of each sample gravimetrically by weighing the now empty bottle and entering the amount in mL into the respective Initial Amount field of the TALS prep batch sheet.

10.1.23.1 The Final Amount field of the prep batch sheet will be automatically populated with the nominal amount entered on the batch information screen (i.e., 1000). The initial and final amounts in the analysis batch should be equal to the final amount from the prep batch (1000), as long as all of the extract generated in the prep was used in the analysis.

10.1.24 If water or dissolved sodium sulfate has passed through the sodium sulfate cartridge, pour the hexane from the collection flask through filter paper containing sodium sulfate and into a clean polypropylene cup. Rinsing is a key step since analytes tend to adhere to the filter, sodium sulfate, and glass funnel. Thorough rinsing is vital!

10.1.25 Place each labeled and weighed aluminum pan, section 10.1.4, in the Speed Vap III and transfer the hexane extract in to the pan. Thoroughly rinse the collection flask, added each rinse to the pan.

10.1.26 Repeat steps 10.1.18 - 10.1.23 for each sample and QC. Once all the pans are loaded on the Speed VAP turn the vacuum adjust all the way the right (-). Turn on the unit on and adjust the vacuum to the left (+) until the hexane shows it is under vacuum. Do not adjust so high liquid hexane splashes from the pans.

10.1.27 Using the Speed Vap, evaporate the n-hexane until dry.

WARNING: A rapidly drying vessel may form condensation on the inside of the vessel. Decant through sodium sulfate into a new vessel to remove any excess water.

10.1.28 Allow vessel to attain constant mass after removing from the speed vap by allowing them to cool to room temperature for about *1-2 minutes (See Attachment 1, for speed vap manufacturing drying procedure)*. On the same balance used in step 10.1.4, weigh the pan and record the first weight (to four decimal places - 0.0001) in TALS. Take the second reading and record. The difference must be less than 0.0005g. If not, take a third reading. If the third reading fails, see your supervisor. Also, document balance ID number in the TALS.

10.1.29 TALS will determine the weight (mg) of extractable material (W_h) by subtracting the tare weight from the total weight of the vessel. HEM is determined by the formula provided in section 11.1. If silica gel treatment is required, proceed to section 10.1.30.

10.1.29.1 After all the sample weighings are completed, perform a final balance calibration check using the 2 mg weight and record the measurements in the balance log. All measurements must fall within the specified tolerances.

10.1.30 If sample results for HEM are below the reporting limit (RL) the results for the silica gel treated – hexane extractable material (SGT-HEM) can be reported as non-detect. If the client is only requesting SGT-HEM

analysis the QC (MB, LCS/D, MS/D) must go through the silica gel treatment below.

10.1.31 Because the capacity of silica gel is not known for all substances, it is presumed that 3g will adsorb 100 mg of all absorbable materials. The amount of silica gel that can be used for adsorption in the SGT-HEM procedure below has been limited to 30g.

10.1.32 If the extract contains more than 1000 mg of HEM continue to step 10.1.33. If the extract is less than 1000 mg of HEM continue with step 10.1.34.

10.1.33 If the extract contains more than 1000 mg of HEM, split the extract per the following procedure:

10.1.33.1 Add 70 ml of n-hexane to the vessel to re-dissolve the HEM. If necessary, heat the solution on an explosion-proof hot plate or in a water bath to completely re-dissolve the HEM.

10.1.33.2 Transfer the extract to a 100-ml volumetric flask. Rinse the vessel sequentially with three, 10 ml portions of n-hexane and add to the volumetric flask. Dilute to the 100 ml mark with n-hexane.

10.1.33.3 Calculate the extract volume that contains 1000 mg of extractable material according to the following equation:

$$V_a = \frac{1000\ V_t}{W_h}$$

where:

V_a= Volume of aliquot to be withdrawn (mL)
V_t= Total volume of solvent used in section 10.32.
W_h= Weight of extractable material HEM measurement (mg)

10.1.33.4 Using a calibrated pipette, remove the volume to be withdrawn V_a and dilute to approximately 100 ml with hexane into new pre-weighed vessel. Proceed to 10.1.33.

10.1.34 From step 10.1.31, rinse extract into clean polypropylene up using sufficient hexane to remove residue thoroughly.

10.1.35 Add 3.0 ± 0.3g of anhydrous silica gel to the cup for every 100 mg of HEM, or fraction thereof, to a maximum of 30 g of silica gel.

NOTE: For example, if the weight of the HEM is 335 mg, add 3 x 4 = 12 g of silica gel.

10.1.36 Agitate the cup by swirling the hexane and silica gel slurry to ensure it is well mixed. Let sit at least 10 minutes.

10.1.37 Filter the solution through n-hexane rinsed filter paper into a clean polypropylene cup. Make sure to rinse out vessel 3 times with small portions of hexane.

10.1.38 Rinse the silica gel and filter paper 3 times with small amounts of hexane to complete the transfer.

10.1.39 Label and weigh an addition aluminum pan and record the mass in TALS under the SGT Tare Weight column.

10.1.40 Place each labeled and weighed aluminum pan the Speed Vap III and transfer the hexane extract in to the pan. Thoroughly rinse the collection flask, adding each rinse to the pan. Allow the solvent to evaporate until dry.

WARNING: A rapidly drying vessel may form condensation on the inside of the vessel. Decant through sodium sulfate into a new vessel to remove any excess water.

10.1.41 Allow vessel to attain constant mass. On the same balance used in steps 10.1.4 and 10.1.28, weigh each vessel and record the mass to four decimal places (0.0001) in the Oil & Grease- 1664 TALS.

10.1.42 Repeat 10.1.41 until masses agree within 0.0005 g.

10.1.43 TALS will determine the weight (mg) of silica gel treated extractable material (W_s) by subtracting the tare weight from the total weight of the vessel. SGT-HEM is determined by the formula provided in either section 11.2 or 11.3. Report results to three significant figures.

10.1.44 After all the sample weighings are completed, perform a final balance calibration check using the 2 mg and 1000 mg weights and record the measurements in the balance log. All measurements must fall within the specified tolerances.

11.0 Calculations / Data Reduction

11.1 HEM

$$\text{HEM (mg/L)} = \frac{W_h \text{ (mg)}}{V_s \text{ (L)}}$$

where:

W_h = Weight (mg) of extractable material in section 10.1.28
V_s = Original sample volume (L)

SGT-HEM

$$\text{SGT-HEM (mg/L)} = \frac{W_s \text{ (mg)}}{V_s \text{ (L)}}$$

where:

W_s = Weight (mg) of extractable material in section 10.1.42
V_s = Original sample volume (L)

11.2 If the extract was split to decrease the total amount of material to 1000mg, determine the corrected total weight of SGT-HEM in the un-split extract (W_c) using the following equation:

$$W_c \text{ (mg)} = \frac{V_t}{V_a} W_d \text{ (mg)}$$

where:

W_d = Weight (mg) in the portion of the extract split for adsorption (the SGT-HEM calculation figured from the split portion in mg's) from section 10.1.42.
V_a = Volume (mL) of aliquot to be withdrawn
V_t = Total volume (mL) of solvent used in section 10.1.32.

11.3 % Recovery (%R)

$$\%R = \frac{C_s * 100}{C_a}$$

where: C_s = Calculated sample concentration
C_a = Theoretical sample concentration

11.4 Relative Percent Difference (RPD)

$$RPD = \frac{|X_1 - X_2| * 100}{(X_1 + X_2)/2}$$

where: X_1 = Concentration of sample analyte
X_2 = Concentration of duplicate analyte

12.0 Method Performance

12.1 A Method Detection Limit (MDL) study must be performed annually according to the current SOP for MDL completion (TA-QA-0602).

12.2 Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., processing one set of MDLs on all applicable instruments, examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Where reasonably feasible,

technological changes have been implemented to minimize the potential for pollution of the environment.

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method.

The following waste streams are produced when this method is carried out:

14.1.1 Solvent waste. Any waste solvents are collected in beakers and then poured into a waste container labeled “Hazardous Waste” located in the hood. After the extraction has been completed the solvent is emptied into the $MeCl_2$ satellite waste barrel located next to the neutralization tank in lab hood #17. The funnel lid on the drum must be closed after each use At or before the satellite waste reaches 55 gallons the barrel is transferred to the waste disposal room from where it is sent out for recycling or fuel blending.

14.1.2 Acidic waste generated by the analysis. Any remaining acidified sample is dumped into the neutralization tank in organic extractions.

14.1.3 Contaminated filter paper and weighing tins generated in the laboratory. Contaminated filter paper and weigh tins are disposed of in the garbage

14.1.4 Any used pipettes or disposable glassware is to be discarded in the broken glassware boxes located next to each vialing station. The box needs to be changed before it becomes too full and cannot be closed with out risk of cuts or pokes.

15.0 References

15.1 TA Seattle Quality Assurance Manual (QAM), current version.

15.2 TestAmerica Environmental Health and Safety Manual, current version.

15.3 NELAC Quality Systems, 2009 Standards; Effective July 1, 2011

15.4 Method 1664, Revision A, “n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry”, EPA-821-R-98-002, February 1999.

15.5 TA-QA-0010, Glassware

15.6 TA-QA-0602, Method Detection Limit Studies

15.7 TA-QA-0620, Quality Control Program

15.8 TA-QA-0610, Laboratory Corrective Actions

15.9 TA-QA-0608, Training of Technical Staff

15.10 TA-QA-0617, Analyst Demonstration of Capability

16.0 Attachments

16.1 Attachment 1: Horizon Technology Speed-Vap EPA Method 1664A.

17.0 Revision History

SOP Rev No. and Date:	Revised Section No.:	Revised Text	Comments
Revision 18, Dated 4/12/17	16.0	Added Horizon Technology recommended methodology for EPA 1664A.	
Revision 18, Dated 4/12/17	10.1.11	Added alternative method to prepare LCS.	
Revision 18, Dated 4/12/17	10.1.7 10.1.8 10.1.16	Changed minimum time solvent is on the disk.	
Revision 18, Dated 4/12/17	10.1.6	Updated prefilter supplies.	
Revision 18, Dated 4/12/17	9.5.3.1 9.5.4.1	Updated precision and recovery limits for LCS/LCSD and MS/MSD.	
Revision 18, Dated 4/12/17	7.5	Removed nitric acid from reagents and standards section	
Revision 18, Dated 4/12/17	6.9 6.16 6.19 6.20	Updated and added equipment and supplies list.	
Revision 18, Dated 4/12/17	5.2	Removed Acetone from primary materials used.	No longer being used
Revision 17, Dated 6/28/16	10.1.7, 10.1.8, 10.1.20 and 10.1.21	Changed minimum time solvent is on the disk (per Empore Extraction Disk instructions.	
Revision 16, Dated 5/18/15	3.1	Added; when sufficient volume is provided by the client	Clarification
Revision 16, Dated 5/18/15	4.1	Removed; by the extraction room.	
Revision 16, Dated 5/18/15	6.13 and 6.17	Removed; Beakers – 250-ml and Aluminum foil.	No longer used.
Revision 16, Dated 5/18/15	7.8	Removed; Acetone, to rinse glassware.	No longer used.
Revision 16, Dated 5/18/15	10.1.3	Removed; and then rinsed with methanol (1X) followed by hexane (3X). Allow to dry.	No longer performed.
Revision 16, Dated 5/18/15	10.1.28	Changed minimum time in	

		desiccator from 1 hour to 30 minutes.	
Revision 16, Dated 5/18/15	10.1.34	Changed to “rinse extract into clean polypropylene cup using sufficient hexane to remove residue thoroughly.”	Clarification
Revision 16, Dated 5/18/15	10.1.34	Changed to “ Place in desiccator 30 minutes and repeat 10.1.41. Masses must agree within 0.0005 g.”	Clarification
Revision 15, Dated 5/28/14	10.1.30	Added the allowance to report SGT-HEM as ND if HEM is <RL..	
Revision 14, Dated 5/29/13	9.5.3.1 and 9.5.4.1	Updated the control limits for LCS/LCSD and MS/MSD.	
Revision 14, Dated 5/29/13	10.1.13.3 and 10.1.19	Updated the procedures for the rinsing of the glass stir rod used to take pH.	
Revision 13, Dated 4/2/12	6.0 and 7.0	Changed the analytical balance to reflect new lab equipment. Added new filter to lab equipment. Updated Silica gel manufacturer and grade used.	
Revision 13, Dated 4/2/12	14.1	Updated waste streams	
Revision 12, Dated 5/16/11	9.5.1	Incorporated ROMD 00025	
Revision 12, Dated 5/16/11	10.1.26	Incorporated ROMD 00029	
Revision 11, Dated 11/1/10	9.5.3 and 9.5.4	Added requirement to include a LCSD in batches lacking a MSD so that precision can be assessed.	For compliance with QSM 4.X
Revision 11, Dated 11/1/10	9.5.2	Changed method blank criteria to ½ RL	For compliance with QSM 4.X
Revision 11, Dated 11/1/10	10.1.8	Changed SPE disk conditioning steps	For compliance with method
Revision 11, Dated 11/1/10	10.1.10 and 10.1.25	Changed volume determination to a gravimetric process	
Revision 11, Dated 11/1/10	10.1.28	Provided additional details on steps needed to attain constant mass.	
Revision 10, Dated 4/16/10	10	All	Major rewrite due to equipment change
Revision 9, Dated 12/21/07	All	General formatting changes	For the integration of TestAmerica and STL operations

18.0 Discrepancies to the Method

18.1 Extraction is per SPE, not separatory funnel.

Attachment 1: Horizon Technology Speed-Vap EPA Method 1664A

Horizon technology

Complying with Both EPA Method 1664A or 1664B Utilizing the SPE-DEX® 1000XL/3000XL Controller v1.08

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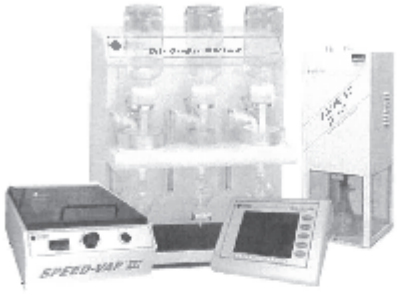
Introduction

The purpose of this application note is to ensure that your environmental laboratory is in compliance with EPA Method 1664A Modifications or EPA Method 1664B utilizing the Horizon Technology SPE-DEX® 1000XL/3000XL Controller with application firmware version 1.08. A modification to the firmware programming will enable quick and seamless compliance with the new EPA Method 1664A modifications or B Revision.

On January 16, 2009, the US EPA released information regarding modifications to EPA Method 1664A. Access the EPA memorandum by visiting the EPA web site http://www.epa.gov/waterscience/methods/method.html and clicking on the "Modifications to Method 1664A" link. One of the modifications to EPA Method 1664A regarded the use of co-solvents and/or alternate solvents. These modifications were later promulgated into Revision B. This modification affects the Controller v1.08 methods because the function of eluting methanol is no longer allowed. To elute with any solvent (with the exception of n-Hexane) into the collection vessel is now unacceptable. Labs are allowed to rinse with methanol, with the stipulation that the methanol be discarded into solvent waste and not eluted into the collection vessel.

Using the current Controller v1.08 it is no longer permissible to rinse the bottle with methanol. This is because the equipment is currently programmed to elute the rinse into the collection vessel, and not to solvent waste, as is now required. Horizon Technology has developed new methodology for the Controller v1.08 that is compliant with the EPA Method 1664A modification or B revision, and still achieves maximum extraction efficiency via automation.

The SPE-DEX® 1000XL and 3000XL Automated Extraction Systems were specifically designed to automatically extract oil and grease from a wide range of clean and dirty aqueous samples using EPA method 1664A/B. The Speed-Vap™ III Solvent Evaporation System uses precise and controlled heating and vacuum to assure consistent and gentle heating and air flow over the sample which prevents the loss of volatile analytes. The Solvent Trap™ Recovery System is designed to recover up to 70% of the n-hexane solvent vapors for reuse or disposal.



Horizon Technology Pacific™ Premium SPE Disks

Horizon Technology Speed-Vap™ III Evaporation System, SPE-DEX® 3000XL Automated Extraction System, Controller v1.08, and Solvent Trap™ Solvent Recovery System

Instrumentation

- Horizon Technology
  - SPE-DEX® 1000XL Automated Extraction System
  - SPE-DEX® 3000XL Automated Extraction System
  - Speed-Vap™ III Evaporation System
  - Solvent Trap™ Solvent Recovery System
  - Pacific™ Premium SPE Disks (47 mm and 100 mm)
  - Oil & Grease QC Standard containing 4 mg/mL Hexadecane and 1 mg/mL Stearic acid
- Ahlstrom #6 grade paper 105 mm
- Mettler AE 200 (Balance)

Method Summary

1) A 1 liter sample of water is used.
2) Samples should be acidified with hydrochloric acid.
3) Agitate the bottles by hand to mix the acid throughout the sample bottle.
4) Verify the pH is 2.0 (+/- 0.1).
5) Spike 40 mg/L of oil and grease standard into the Laboratory Control Spike.
6) Nitrogen pressure should be set between 60-80 psi.
7) The vacuum pump should be set at -25 in. Hg.
8) Load samples onto the SPE-DEX 1000XL/3000XL.
9) Start extraction method 1 (refer to Table 1 for 47 mm disk and Table 3 for 100mm disk).
10) After Method 1 is finished, leave the sample bottle and collection vessels on the instrument and change the method for the station(s) to Method 2 (refer to Table 2 for 47 mm disk and Table 4 for 100 mm disk).
11) Run Method 2.
12) It may be necessary to squirt a small amount of methanol into the Dispenser when the station is in the Sample Process step. This will "prime" the dispenser into thinking a sample is present and allow the station to continue.
13) Once Method 2 is completed the sample is ready to be evaporated.

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14) The methanol rinse typically acts as the drying agent to ensure that there is no water in the hexane layer. Since this step is removed, the sample may need to be dried with sodium sulfate prior to evaporation.
15) Also, adding about 5 mL of clean methanol to the final extract, swirling it for 15 seconds, and letting it sit for one minute will remove the residual water from the hexane layer.
16) Pre-weigh 105 mm aluminum pan(s).
17) Discard any residual water.
18) Pour the hexane into the aluminum pan.
19) Rinse the collection vessel three times with hexane pouring each rinse into the aluminum pan. Try not to get any residual water into the pan that may be stuck to the sides of the collection vessel.
20) Place the pans in the Speed-Vap III start the evaporation process (See Table 5 for Speed-Vap III conditions).
21) Concentrate the extract to dryness.
22) Weigh the pan with the dried sample. Calculate the percent n-hexane extractable material (HEM). Results can be seen in Table 6 and 7.

Table 1: Method 1, 47 mm Pacific Premium Disk

Prewet			
Hexane		Methanol	
Dispense	6 sec	Dispense	6 sec
Saturate	1 sec	Saturate	[illegible] sec
Soak	30 sec	Soak	30 sec
Drain	1 min	Drain	3 sec
Air Dry			3 min
Rinse	Dispense	Soak	Elute
Hexane	4 sec	45 sec	0 sec
Hexane	[illegible] sec	45 sec	45 sec
Hexane	4 sec	45 sec	0 sec
Hexane	4 sec	45 sec	45 sec

Table 2: Method 2, 47 mm Pacific Premium Disk

Prewet			
Hexane		Methanol	
Dispense	0 sec	Dispense	[illegible] sec
Saturate	0 sec	Saturate	1 sec
Soak	0 sec	Soak	20 sec
Drain	0 sec	Drain	1 min
Air Dry			0 sec
Rinse	Dispense	Soak	Elute
Hexane	4 sec	45 sec	0 sec
Hexane	4 sec	45 sec	30 sec
Hexane	4 sec	15 sec	1 min

Table 3: Method 1, 100 mm Pacific Premium Disk

Prewet			
Hexane		Methanol	
Dispense	10 sec	Dispense	10 sec
Saturate	1 sec	Saturate	1 sec
Soak	1 min	Soak	1 min
Drain	1 min	Drain	3 sec
Air Dry			3 min
Rinse	Dispense	Soak	Elute
Hexane	7 sec	45 sec	0 sec
Hexane	7 sec	45 sec	45 sec
Hexane	7 sec	45 sec	0 sec
Hexane	4 sec	45 sec	45 sec

Table 4: Method 2, 100 mm Pacific Premium Disk

Prewet			
Hexane		Methanol	
Dispense	0 sec	Dispense	4 sec
Saturate	0 sec	Saturate	1 sec
Soak	0 sec	Soak	20 sec
Drain	0 min	Drain	[illegible] sec
Air Dry			0 min
Rinse	Dispense	Soak	Elute
Hexane	4 sec	45 sec	0 sec
Hexane	4 sec	45 sec	30 sec
Hexane	4 sec	45 sec	1 min

Table 5: Speed-Vap III Evaporation System Conditions

PARAMETER	SETTING
Temperature	40° C
Vacuum	Adjust the knob so that there is a gentle agitation of the extract.

Results

Table 6: Results from spikes run at 40 mg/L on 47 mm Pacific Premium SPE disks with method 1 and 2. Average recovery is 101% with a standard deviation of 4.14.

Initial Weight (g)	Final Weight (g)	Recovery
6.2934	6.3254	99%
6.3024	6.3478	104%
6.2721	6.3129	102%
6.2785	6.319	101%
6.1939	6.2316	95%

Table 7: Results from spikes run at 40 mg/L on 100 mm Pacific Premium SPE disks with method 1 and 2. Average recovery is 95.8% with a standard deviation of 2.58.

Initial Weight (g)	Final Weight (g)	Recovery
6.2464	6.2812	97%
6.2194	6.258	97%
6.3109	6.3504	99%
6.2687	6.3097	98%
6.3072	6.344	97%

Conclusions

This application note demonstrates that the Horizon Technology SPE-DEX 1630XL/3000XL Controller with application firmware version 1.08 is able to handle the modifications to EPA Method 1664A and 1664B once programmed with the new two-step methods and utilizing the Pacific Premium SPE disks. Your laboratory will receive the highest recoveries and the fastest sample process times while ensuring your laboratory is in compliance with both EPA Method 1664A and 1664B. Pacific Premium disk extraction times were typically 25 minutes and evaporation times were approximately 20 minutes.

The Horizon Technology SPE-DEX 1660XL/3000XL Automated Extraction Systems coupled with the Speed-Vap III Evaporation System and the Solvent Trap Solvent Recovery System are proven to reduce analyst labor, solvent usage, turnaround time and greatly improve the accuracy and precision of results.

Horizon Technology, Inc., 41 Stanley Kerr Dr. Salem, NH, 03079 USA
Tel: (603) 893-3663 Fax: (603) 894-4994

Title: Seta Flash Ignitability
[Method SW 1020A, ASTM D3278-78]

Approvals

Signatures on File	
Stan Palmquist Date	Manjit Nijjar Date
Inorganic Department Manager	Health & Safety Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This SOP is applicable to the operation of the Seta Flash Closed-Cup tester to determine the flash point of liquids. Soil, semi-solid or solid samples may be run if the lab agrees to do so and with the client understanding that this is a method modification. Method 1030 is better suited for solids, granular material and the like.

1.1.2 The practical working range of this method is <70℉ to <212℉.

1.1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 By means of a syringe, 2.5 mL of sample is introduced through a leak-proof entry port into the tightly closed Setaflash Tester or into the cup which has been brought to within 5℉ (3℃) below the expected flash point.

2.2 As a flash/no-flash test, the expected flash-point temperature may be a specification (e.g., 212℉). For specification testing, the temperature of the apparatus is raised to the precise temperature of the specification flash point by adjustment of the temperature switch. After 1 minute, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a repeat test is necessary, a fresh sample is used.

2.3 For a finite flash measurement, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5℉ (3℃) intervals until the flame approximately doubles in size then applied at 1℉ (0.5°C) intervals until a flash is observed.

3.0 Definitions

3.1 Flash point - the lowest temperature at which a liquid or waste can form an ignitable mixture in air near the surface of the liquid or waste.

4.0 Interferences

4.1 Liquids that tend to form surface films under the test conditions or those that contain non-filterable suspended solids should be tested for ignitibility using Method 1010.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 In the event a sample ignites in the test apparatus, do not attempt to remove the sample. Turn off the apparatus and flame. The flame should go out when the cup is closed. If this does not happen the flame may be extinguished by covering the sample with a non-flammable material. After the apparatus has cooled the sample may be removed.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Toluene	Flammable Poison Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
p-xylene	Flammable Irritant	100 ppm-TWA	Inhalation of vapors may be irritating to the nose and throat. Inhalation of high concentrations may result in nausea, vomiting, headache, ringing in the ears, and severe breathing difficulties, which may be delayed in onset. High vapor concentrations are anesthetic and central nervous system depressants. Skin contact results in loss of natural oils and often results in a characteristic dermatitis. May be absorbed through the skin. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Seta Flash Closed-Cup Tester

6.2 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- LIMS system: TALS version 1.0 or higher

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 p-xylene

7.3 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Liquids	Glass	15 mLs	Minimum headspace; Cool 0-6℃	N/A	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section.

9.2 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in SOP TA-QA-0620, Quality Control Program.

9.4 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.5 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.6 Batch Definition

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a laboratory control sample (LCS), and duplicate (DUP). As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.7 Method Blank (MB)

Method blanks (MB) are not applicable to this technique.

9.8 Laboratory Control Sample (LCS)

A p-xylene standard is flashed in duplicate to ensure proper working of the system.

Acceptance Criteria: p-xylene mean should be at 81 ± 1.5°F (27.2 ± 1°C).

Corrective Action: If p-xylene does not flash within the specified temperature range, the analysis is stopped, the cup is cleaned and the LCS is re-started. No samples are analyzed until an acceptable result is achieved with the p-xylene.

9.9 Duplicate Sample Analysis

A duplicate pair is required with each analytical batch and must be within 20% RPD. If there isn't sufficient sample for a duplicate sample analysis, then a LCSD (9.8) must also be processed and reported. The process of establishing control limits is described in more detail in the QC SOP TA-QA-0620.

Corrective Action: If the RPD is greater than 20 the sample should be reanalyzed.

9.10 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of management to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP # TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

10.1 Sample Preparation

None

10.2 Calibration

10.2.1 The thermometer is calibrated annually per SOP TA-QA-0024.

10.3 Sample Analysis

10.3.1 Record barometric pressure for the batch at the time the first sample is started.

10.3.2 Shake or stir the sample and note any odor (to determine the presence of gasoline or similarly combustible material).

10.3.3 Place 2.5 mL of a liquid sample through the sample tube into the flash chamber.

10.3.4 Liquids should be analyzed by 1020, and solids/soils by 1030 whenever possible. If the client asks for 1020 on a soil/solid sample, the appropriate NCM must be attached to the data to indicate that 1020 is designated for liquids and a modification to the method has been done for the soil/solid sample(s) in question.

10.3.5 For samples like alcohol-saturated wipes, paint filters, cotton gauze and the like, for 1020 modified analysis, the sample should be cut into 1cm pieces or smaller, filling the instrument sample cup to the fill-line normally used for liquid samples, and then analyzed to assure enough vapors, if present, can be captured for analysis. Cutting the sample for analysis should be done as quickly as possible to minimize loss of vapor to the atmosphere during the cutting process.

10.3.6 Push the time-start button and light the flame.

10.1.1 When the timer sounds, slowly lower the flame into the flash chamber.

10.1.2 If the sample flashes at room temperature or does not flash by 212°, report the sample as <70° or >212°. If the sample flashes bet ween 70° and 212°, repeat the analysis and report the average.

10.1.3 Clean the cup out with toluene if necessary. Check clean cup for flash to be sure all toluene is consumed.

10.1.4 Record the uncorrected temperature and then apply the thermometer's temperature correction factor to the temperature reading and record the corrected temperature.

10.2 Maintenance

10.2.1 No regular maintenance is required – see troubleshooting section for resolutions to any problems during operation.

10.3 Troubleshooting

10.3.1 If the analyst is unable to get the LCS to pass, check that there is sufficient heat transfer paste surrounding the thermometer to provide good heat transfer from the cup to the thermometer.

10.3.2 If the flash results are too high –

- Check thermometer for breaks in mercury column. Replace thermometer if damaged.
- Inspect lid/shutter for excessive wear on slides. Check sealing ring. If worn, replace.
- Ensure gas-tight seal between lid and seal by lightly smearing the seal with oil. Close lid/shutter. On opening, check for continuous print line of oil on underside of lid. If print line is broken check for flatness of lid, strained hinge, smoothness of seal.

10.3.3 If the flash results are too low –

- Check for contamination. Thoroughly clean sample well and lid/shutter if applicable.
- Inspect silicone rubber gas tubing. Replace if necessary.

10.3.4 Issues with gas flow –

- Adjust the gas regulator gear
- Inspect jets and gas tubing for leaks or plugs. Replace gas tank assembly if necessary.

10.1 Calculations / Data Reduction

The results are reported in ℉. If a ℃ thermometer is used, the following temperature conversion must be used. F=C*9/5+32

For the barometric pressure correction calculations use the following formula:
Calculated Flash = F+0.06*(760-P)
Calculated Flash = C+0.03*(760-P)
Where F is Fahrenheit and C is Centigrade and P is the observed barometric pressure in mm Hg

Note: If the barometric pressure is between 760 ± 8 mm Hg no correction is needed.

11.0 Method Performance

11.1 Method Detection Limit Study (MDL)

A method detection limit (MDL) study is not performed for this analysis.

11.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

11.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

12.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036.

13.1 The following waste streams are produced when this method is carried out:

Excess flammable samples/solvents. Any waste samples or solvents from the procedure are collected in a flammable satellite container labeled "Hazardous Waste" located in the cabinet under the hood. When the satellite container is full it is emptied into the waste solvent barrel located next to the neutralization tank in lab hood #17. The funnel lid on the drum must be closed after each use. At or before the satellite waste reaches 55 gallons, the barrel is transferred to the waste disposal room from where it is sent out for recycling or fuel blending.

14.0 References / Cross-References

14.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 1020A.

15.0 Method Modifications:

None

16.0 Attachments

None

17.0 Revision History

- Revision 18.1, dated 26 September 2017
  - Updated approvers.

- Revision 18, dated 15 August 2016
  - Added modification requirements and verbiage for soil/solid samples, sections 1.1.1, 10.3.4 and 10.3.5

- Revision 17, dated 15 January 2016
  - Added computer hardware and software, Section 6.2
  - Added instrument maintenance, section 10.4
  - Added troubleshooting, section 10.5

- Revision 16, dated 20 November 2013
  - Added instructions to record barometric pressure, Section 10.3.1
  - Added Celsius to Fahrenheit conversion and calculation for barometric pressure correction, section 10.4

- Revision 15, dated 8 October 2012
  - Procedural and reporting instructions were added, Section 10.3.5
  - Updated waste streams, section 13.1

- Revision 14, dated 16 May 2011
  - Removed soil testing procedures (ROMD 00014)
  - Incorporated ROMD 00021 in section 10.3.6
  - Incorporated ROMD 00025 in section 9.9

- Revision 13, dated 16 April 2010
  - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
  - Added removal of expired standards Section 7.4.
  - Added criteria for additional QC, Section 9.10.

- Revision 12, dated 2 December 2008
  - Integration for TestAmerica and STL operations.

Title: Determination of Total Organic Carbon in Liquid Matrices [Methods 415.1, 9060, SM 5310B *and SM 5310C*]

Approvals

Signatures on File	
Stan Palmquist Date	Mike Ridenhower Date
Inorganic Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

This SOP describes the procedure for analysis of organic carbon in liquid matrices. Liquid matrices include groundwater, surface and saline waters, and domestic and industrial wastes. The standard reporting limit is 1.0 mg/L.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

Liquid samples are introduced into the carbonaceous analyzer. After the inorganic carbon component has been purged, the remaining organic carbon is converted to carbon dioxide by catalytic combustion or *UV-persulfate oxidation* (total carbon). An infrared detector then directly measures the carbon dioxide formed. The concentration of carbon dioxide is directly proportional to the total organic carbon in the sample.

3.0 Definitions

The quality control terms used in this procedure are consistent with SW-846 terminology. Definitions are provided in the glossary of the TestAmerica Seattle Quality Assurance Manual (QAM)

4.0 Interferences

4.1 For liquids, this procedure is applicable only to homogeneous samples with only slight amounts of sediment. Samples containing high levels of particulate matter can have reproducibility problems. Samples may have to be diluted for reproducible analysis.

4.2 Samples that contain or that are preserved with HCl will form HCl gas in TOC instruments. Since the analyzer is equipped with a gold lined sample cell use an NDIR to detect CO2 gas, the corrosive nature of HCl can damage the NDIR. The Apollo 9000 and *Phoenix 800* copper scrubbers manage to scrub out some HCl, but HCl breakthrough is common and causes NDIR detector corrosion.

4.3 Nitric Acid in combustion instruments will form N2O4, which is a corrosive gas. The copper and tin scrubber will remove some of the gas, but not all and there is the potential for corrosion in the detector.

4.4 Analysis of samples containing high concentration of salt offers a big challenge for high temperature combustion analyzers. Metal cations, such as sodium, have the effect of devitrifying the quartz combustion tube causing it to crystallize and break. Salts can also deposit on the catalyst resulting in a loss of efficiency.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Phosphoric Acid	Corrosive	1 Mg/M3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Sodium Persulfate	*Oxidizer Corrosive*	*0.1 Mg/M3-TWA as Persulfates*	*Causes irritation to the respiratory tract. Symptoms may include sore throat, shortness of breath, inflammation of nasal passages, coughing, and wheezing. Causes severe irritation or burns to the skin and eyes. Symptoms include redness, itching, pain and burns. May cause allergic skin reactions. Can cause eye damage.*
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Tekmar Apollo 9000 TOC Analyzer
- Tekmar Phoenix 8000 UV-Persulfate TOC Analyzer

6.2 Software

- TestAmerica LIMS (TALS), current version
- TOCTalk Ver *3.6.429 or 4.22.109*.

6.3 Supplies

- 40-mL VOA vials with septa

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 ASTM Type II water

7.3 21% Phosphoric Acid

7.4 *10% Sodium Persulfate in 5% Phosphoric Acid*

7.5 1000-mg/L TOC Standard, Accu Standard P/N WC-TOC-10X-1 or equivalent.

7.6 1000-mg/L TOC Second Source Standard, Ultra Scientific P/N IQC-106 or equivalent

7.7 *0.5-mg/L TOC Standard prepared by diluting 20 microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 to 40 mL with DI water.*

7.8 1.0-mg/L TOC Standard prepared by diluting 40 microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 to 40 mL with DI water.

7.9 2.0-mg/L TOC Standard prepared by diluting 80 microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 standard to 40 mL with DI water.

7.10 5.0-mg/L TOC Standard prepared by diluting 200 microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 standard to 40 mL with DI water.

7.11 10-mg/L TOC Standard prepared by diluting 400 microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 standard to 40 mL with DI water.

7.12 20-mg/L TOC Standard prepared by diluting 800 microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 standard to 40 mL with DI water.

7.13 *40-mg/L TOC Standard prepared by diluting 1000 microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 standard to 40 mL with DI water.*

7.14 *10-mg/L* TOC Continuing Calibration Standard (CCV) and LCS Standard prepared by diluting *400* microliters of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 standard to 40 mL with DI water.

7.15 10-mg/L TOC Calibration Verification Standard (ICV) prepared by diluting 400-uL of the 1000-mg/L Ultra Scientific P/N IQC-106 standard to 40-mL with DI water.

7.16 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples should be stored at 0-6°C and protected from sunlight.

8.2 Samples can be collected in either glass or plastic containers.

8.3 Samples not analyzed within two hours of the time of sampling, must be acidified to pH less than 2 with H_2SO_4 or H_3PO_4. Sample preservation should be checked prior to analysis.

8.4 No holding specified for a preserved sample.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Amber Glass *or HDPE*	50 mLs	H_2SO_4 or H_3PO_4, pH < 2; Cool 0-6°C	28 Days	40 CFR Part 136.3

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in SOP TA-QA-0620, Quality Control Program.

9.1.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

A batch is a group of no greater than 10 samples excluding QC samples (Method Blank, LCS, and MS), which are processed similarly, with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3 Method Blank (MB)

One method blank (MB) must be processed with each batch. The method blank consists of DI water. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

Acceptance Criteria: The method blank should not contain any analyte of interest above one-half the reporting limit.

Corrective Action: If the analyte level in the method blank exceeds one-half the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data must be taken in consultation with the client and must be addressed in the project narrative.

If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

If all samples associated with a blank greater than one-half the RL are greater than 10 times the blank value, the samples may be reported with an NCM to qualify the high blank value.

9.4 Laboratory Control Sample (LCS)

One LCS must be processed with each batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

The LCS is prepared by adding 400-uL of the second source 1000-ug/mL TOC standard (section 7.5) to 40 mL DI water (10 mg/L).

Acceptance Criteria: The LCS recovery must fall within ±15% of the true value. The control limits are maintained in the LIMS.

Corrective Action: If any analyte is outside established control limits, the system is out of control, and corrective action must occur. Corrective action will be re-preparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.5 Matrix Spike (MS) Samples

One MS must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to an MS. The MS results are used to determine the effect of a matrix on the accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked.

The MS is prepared by adding 400-uL of the second source 1000-ug/mL TOC standard (Section 7.5) to 40 mL sample volume.

Acceptance Criteria: The recovery of the analyte in the MS must fall within ±15% of the true value.

Corrective Action: If the analyte recovery falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch.

If an MS, MSD or sample duplicate is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) must be analyzed.

9.6 Duplicate Sample Analysis

A duplicate pair is required with each analytical batch and must be within 20% RPD. Note that the control limits only apply to samples with results greater than 5 times the RL. The process of establishing control limits is described in more detail in the QC SOP TA-QA-0620.

Corrective Action: If the RPD is greater than 20%, the sample should be reanalyzed if within holding time and sufficient sample is remaining.

9.7 **Instrument QC**

9.8 Calibration Acceptance Summary

The instrument calibration is verified each day prior to sample and method blank analysis; a single combustion of the appropriate standard must yield results within 15% of the true value in order to proceed.

9.9 Initial Calibration Verification (ICV)

The ICV standard is analyzed immediately following the ICAL. The ICV is a second-source TOC standard with a true value of 10 mg/L TOC (prepared by adding 400-uL of the second source 1000-ug/mL TOC standard (section 7.5) to 40 mL DI water). The analyte recovery must fall within the 85-115% range. If it is outside the acceptance limits, check the equipment and standards, correct any problems, and then recalibrate.

9.10 Continuing Calibration Verification (CCV)

The calibration is checked at the beginning of an analytical sequence (ICV), after every ten samples (CCV), and at the end of the sequence (CCV) by measuring a CCV standard.

The CCV is a TOC standard with a true value of 10 mg/L TOC (prepared by adding 400-uL of the 1000-mg/L Accu Standard P/N WC-TOC-10X-1 standard (section 7.4) to 40 mL DI water). The CCV recovery must be within the 85-115% range. If it is outside the acceptance limits, check the equipment and standards, correct any problems, recalibrate, and rerun all samples analyzed since the last successful CCV.

9.11 Initial and Continuing Calibration Blank (ICB and CCB)

System cleanliness is checked at the beginning of an analytical sequence, after every ten samples (CCB), and at the end of the sequence (CCB) by analyzing a blank.

The CCB for the automated method is DI water.

Results must be less than one-half the reporting limit. If the blank result is greater than one-half the reporting limit, check for carry-over from high level samples, clean the system, recalibrate, and rerun all samples analyzed since the last successful CCB.

Note: ICV/CCVs need to be followed by a ICB/CCB. ICV/CCVs cannot be preceded by a ICV/CCB unless a blank is analyzed before each sample in the bracket.

9.12 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

10.1 Sample Preparation

None

10.2 Instrument Operating Conditions

10.2.1 Instrument operating parameters are defined in the instrument's maintenance logbook. The absolute response of the daily ICV is evaluated and tracked in the logbook.

10.3 Calibration

10.3.1 A five-point calibration is performed using the standards specified in sections 7.6 through 7.10. Standard concentrations and volumes injected are programmed into the instrument before calibration. Standards are injected in duplicate by the autosampler; the instrument reports the average result.

10.3.2 The initial calibration is analyzed following the manufacturer's instructions for calibration.

10.3.3 The calibration points used must meet the criteria specified in corporate SOP CA-T-P-002.

10.3.4 The calibration standards listed in section 7.0 and a blank standard are analyzed.

10.3.5 The results are plotted in a calibration curve area vs. concentration (see corporate SOP CA-Q-S-005, Calibration Curves). The calibration curve is valid if the r-squared value is 0.995 or greater.

10.4 Sample Analysis

10.4.1 If a sample contains gross solids or insoluble matter, homogenize until satisfactory replication is obtained. Analyze a homogenizing blank consisting of reagent water carried through the homogenizing treatments. (SM5310B)

10.4.2 Ensure the compressed Zero grade air tank has sufficient pressure for the run. Also check that the DI water rinse container and 21% *reagent* containers are full and the waste container is empty.

10.4.3 On the main screen, click on the 'Setup' drop down menu, select 'Instrument' and click on the 'Ready' button on the new screen.

10.4.4 Allow the analyzer to warm up for thirty minutes or until baseline is stable (flow rate should be 200 ± 20 mL/min, furnace temperature should be 900°C).

10.4.5 Click on the 'Sample Setup' button. Update the rack ID by saving to a new file using a mmddyyyy format.

10.4.6 Enter all samples and QC in the sample table. The Sample Type should be 'Sample' for all samples and 'Cal Verification' for all ICVs, CCBs and CCVs. The Method should be set to 'TOC 0-20 ppmC'. When analyzing samples for either EPA 415.1 or SM 5310B the Reps should be set to '2'. When analyzing samples for Method 9060 the Reps should be set to '4'. The Status should be set at 'Ready'. Once the *sequence* is set up, click on 'Save and Use'. All replicates must integrate properly or the sample must be re-analyzed. If one or more of the replicates fails again, see your supervisor.

10.4.7 Label and fill the 40-ml VOA vials with standards and samples as they have been entered in the sample table.

10.4.8 On the main screen, click on 'Start'.

10.5 Standards and samples are analyzed in the following sequence:

Rinse
ICV
CCB
MB
LCS
QC sample
MS
MSD
5 samples
CCV
CCB
5 samples
New batch QC plus samples if over 10 samples are analyzed (Section 9.2)
CCV
CCB

10.6 Instrument Maintenance

All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., GC, autosampler) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, etc as may be the case).

11.0 Calculations / Data Reduction

11.1 Calibration Curves

See corporate SOP CA-Q-S-005, Calibration Curves

11.2 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.3 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.4 Concentration = mg/L = C x D

Where:
C = sample concentration (ppm)
D = Dilution Factor

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Waste Disposal SOP TA-EHS-0036.

14.1 Waste Streams Produced by the Method

14.1.1 Expired/off spec phosphoric acid may be disposed of into the neutralization tank.

15.0 References / Cross-References

15.1 *Phoenix 8000 UV-Persulfate TOC Analyzer Operating Manual.*

15.2 Apollo 9000 High Temperature TOC Analyzer Operating Manual.

15.3 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 415.1.

15.4 Standard Methods for Analysis of Water and Wastewater, 19th Edition, 1995, Method 5310B.

15.5 SOP CA-Q-S-005, Calibration Curves

16.0 Method Modifications:

Item	Method	Modification
1	9060	Section 6.4 of Method 9060 specifies preserving samples with HCl or H_2SO_4. TestAmerica Seattle follows Tekmar Dohrman's recommendation of preserving samples with H_3PO_4.
2	9060	Section 7.1 of Method 9060 specifies homogenizing samples in a blender. If a sample contains gross solids or insoluble matter, homogenize until satisfactory replication is obtained. Analyze a homogenizing blank consisting of reagent water carried through the homogenizing treatments. (SM5310B).
3	9060	Section 7.3 of Method 9060 specifies purging the sample for 10 minutes with nitrogen. TestAmerica Seattle uses Tekmar Dohrman's method recommendation of purging for 4 minutes with zero air.
4	9060	Section 7.6 of Method 9060 specifies reporting both the average result and the range. TestAmerica Seattle only reports the average result

17.0 Attachments

None

18.0 Revision History

- Revision 10 dated 22 December 2015
  - Updated title to include SM 5310C
  - Updated to include the new UV-Persulfate instrument, sections 2.0, 4.2, 5.2, 61, 6.2, 7.0, 10.4.2 and 15.1.
  - Updated to include HDPE containers, section 8.4.

- Revision 9 dated 27 May 2015
  - Updated LCS preparation instructions and concentration, section 9.4.
  - Updated CCV preparation instructions and concentration, section 9.10.
  - Updated the replicates entered for analytical run based on the method being analyzed, section 10.4.6.
  - Removed section 10.4.9 as this is now covered in section 10.4.6 (see above).

- Revision 8 dated 31 May 2013
  - Updated Safety section 5.0.

- Changed ICV concentration from 5 to 10 mg/L to verify mid-point of curve, section 9.9.
- Added instructions on the preparation of the CCV/LCS, section 7.11 and 9.10.

- Revision 7 dated 2 April 2012
  - Revised method summary to reflect procedure used, section 2.0.
  - Changed ICV concentration from 15 to 5 mg/L to verify low end of curve, section 9.9 (LCS @ 15 mg/L verifies the middle of the curve).
  - Incorporated ROM 00033 in section 10.2.1.
  - Changed ICAL standard injections from quads to dups, section 10.3.1
  - Added method 415.1/5310 sample injection procedures (dups), Section 10.4.9
  - Updated sequence in section 10.5
  - Updated waste streams, section 14.1

- Revision 6 dated 6 December 2010
  - Replaced references for TestAmerica Tacoma with TestAmerica Seattle throughout document.
  - Updated standard sources, section 7.5 through 7.12
  - Revised method blank criteria for DOD QSM compliance Section 9.3
  - Incorporated ROMDs 00020 (section 10.1) 00022 (sections 10.3.5 and 11.1), 00024 (sections 9.9 and 9.10) 00025 (section 9.5)
  - Added sections 10.4.1, 10.4.2 and 10.4.7
  - Updated example sequence in Section 10.5
  - Added section on instrument maintenance, section 10.6
  - Updated item 2 (homogenization procedure) in Section (table) 16.0

- Revision 5 dated 12 November 2009
  - Added documentation of standards/reagents and standard/reagent preparation Section 7.1
  - Added removal of expired standards Section 7.12.
  - Added criteria for additional QC, Section 9.12.

- Revision 4 dated 5 November 2008
  - Removed pH check in sample preparation section.
- Revision 3, dated 26 December 2007
  - Integration for TestAmerica and STL operations.
  - Removed higher-level calibration standards that are no longer in use.
  - Added acceptance limits for airflow.
  - Updated the combustion chamber temperature from 680°C to 900°C.
  - Updated the instrument method name from TCO1-400 to TOC1-20mg/L.
  - Updated sample analysis from triplicate to quadruplicate.
  - Added sample duplicate frequency.
  - Removed the modification that samples are analyzed in triplicate.

Title: Anions by Ion Chromatography [Methods 300.0, 9056A]

Approvals

Signatures on File	
Stan Palmquist — Date	Manjit Nijjar — Date
Inorganic Department Manager	Health & Safety Coordinator
Terri Torres — Date	Dennis Bean — Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure describes the determination of the anions fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate, and sulfate in water samples by ion chromatography, based on EPA Method 300.0 and SW-846 Method 9056A.

This procedure can also be applied to leachates from soil samples. The soil leaching procedure is described in Section 10.5.3.

The anions included in this procedure and their routine working ranges for interference-free samples are as follows:

Analyte	CAS Number	Working Range* (mg/L)	Working Range* (mg/kg)
Fluoride	16984-48-8	0.2 – 10	1.0 – 100
Chloride	16887-00-6	0.5 – 100	5.0 – 1000
Nitrite as N	14797-65-0	0.4 – 10	2.5 – 100
Bromide	24959-67-9	0.5 – 10	4.0 – 100
Nitrate as N	14797-55-8	0.2 – 10	1.5 – 100
Sulfate	14808-79-8	1.2 – 100	10 – 1000

*The working range can be extended by dilution of the sample.

The reporting limits for the following analytes are based on a 25 µL injection volume:

Analyte	Water RL (mg/L)	Soil RL (mg/kg)
Fluoride	0.2	1.0
Chloride	*0.9*	5.0
Nitrite	0.4	2.5
Bromide	0.5	4.0
Nitrate	0.2	1.5
Sulfate	1.2	10

NOTE 1: Report nitrite (NO_2^-) as N, nitrate (NO_3^-) as N.

NOTE 2: Depending client or project requirements, reporting limits may be higher than those shown above.

NOTE 3: Reporting limits for soils are based on the DI Leach procedure using a soil to water ratio of 1:10. Client-specific soil to water ratios may differ.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual.

2.0 Summary of Method

2.1 Aqueous samples are all filtered with a 0.45 µm filter (Pall Acrodisc Nylon Membrane #4438T or equivalent). High concentration samples must be diluted for analysis. Soil samples are leached using deionized water in accordance with Section 10.5.3, and the water leach is analyzed.

2.2 A small volume of sample is introduced into the ion chromatograph with the AS40 autosampler to flush and fill a constant volume loop.

2.3 The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids.

2.4 The separated anions in their acid forms are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3.0 Definitions

This procedure includes the drinking water QC terminology from Method 300.0 and the solid waste terminology from SW-846 Method 9056A. Where there are two terms for the same concept, the cross reference is explained below. The frequency and evaluation of these QC samples are discussed in Sections 9 and 10.

3.1 Calibration Blank (CB) - A volume of reagent water fortified with the same matrix as the calibration standards, but without the addition of any of the analytes of interest.

3.2 Laboratory Reagent Blank (LRB, also referred to as a Method Blank) - For water samples, which do not require any preparation steps, the calibration blank and the method blank are the same thing. When soils are being analyzed, the method blank consists of the same reagents and preparation steps as applied to samples.

3.3 Laboratory Fortified Blank (LFB, also referred to as a Laboratory Control Sample, LCS) - An aliquot of reagent water or other blank matrix to which known quantities of method analytes are added in the laboratory. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of measurements the meet data quality objectives for accuracy and precision.

3.4 Laboratory Fortified Sample Matrix (LFM, also referred to as a Matrix Spike, MS) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix affects the accuracy of the analytical result. The background concentrations of the analyte in the sample matrix must be determined if method analytes or other interference is present in the laboratory environment, the reagent, or the apparatus.

3.5 Instrument Performance Check Solution (IPC, also referred to as Initial and Continuing Calibration Verification Standards, ICV and CCV) - The ICV and CCV serve to monitor instrument drift from the beginning to the end of a given analytical sequence.

3.6 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.

3.7 Quality Control Sample (QCS) - The QCS provides an independent verification of the accuracy of calibration standards and instrument performance. For the purposes of this SOP, the second-source ICV provides this verification (see Section 9.12).

4.0 Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion or cause the retention times of the other anions to shift. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

4.3 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other low molecular weight organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.4 The acetate anion elutes early during the chromatographic run. The retention times of the anions may also differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.5 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Nitrate	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
Sodium Fluoride	Poison	2.5 Mg/M3-TWA as F	**Highly Toxic.** Causes severe irritation to the respiratory tract, symptoms may include coughing, sore throat, and labored breathing. Causes irritation, with redness and pain. Solutions are corrosive. Eye irritant! May cause irritation and serious eye damage. Effects may not appear immediately.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation and Software

- Dionex Ion chromatographic system, including: automated sampler; gradient pump; degas module; inline filter; guard column (4 x 50 mm; Ion pac AG14A, AG18 or equivalent); analytical column (4 x 250 mm; Ion pac AS14A, AS18 or equivalent); anion self-regenerating suppressor column; conductivity detector; computer interface; and, computer data handling system.

  Note: Other columns may be used. These were the columns in place at the time the SOP was prepared.
- Analytical balance, capable of accurately weighing to the nearest 0.0001 g

6.2 Computer hardware and software

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- Data acquisition/processing system: *Chromeleon Version 7.2 or higher*
- LIMS system: TALS version 1.0 or higher

6.3 Supplies

- Dedicated Volumetric Flasks (Class A): 2-L (eluent prep) and 100 mL (standards prep)
- Dedicated glass syringes, 10 uL to 1000 uL
- Dedicated glass pipettes, 5 mL to 10 mL
- Adjustable pipettes that are verified quarterly.
- 5 mL Sample vials with filter caps, 2 um filter.
- 0.45 µm filter (Pall Acrodisc Nylon Membrane #4438T or equivalent)

7.0 Reagents and Standards

7.1 Document reagent/standards and reagent/standard preparation in TALS using the reagent module as described in SOP TA-QA-0619.

7.2 Reagent water: Type II, free of anions of interest.

7.3 Eluent solution:

7.3.1 AS14 Eluent concentrate purchased from Dionex, P/N 053560. A 100x dilution is required before use.(20ml concentrate to 2000ml DI water). After dilution the solution is 3.5mM Sodium Carbonte and 1.0 mM Sodium Bicarbonte. Or eluent generator EGCII KOH purchased from Dionex, P/N 058900. This is a cartridge that is installed on the IC and the working eluent is generated as need by the instrument.

7.3.2 *Dionex Integrion: AS22 Eluent concentrate, P/N 063965.A 100x dilution is required before use. After 100X dilution the solution is 4.5 mM Sodium Carbonate and 1.4 mM Sodium Bicarbonate.*

7.4 Calibration and Continuing Calibration Check Standard solutions, purchased from Accustandard (Multi-Compound Anion Standard) or another vendor that offers certified standards. The following concentrations are suggestions and differ as required by the instrument*:

Anion	Concentration, ug/mL
Fluoride	100
Chloride	1000
Bromide	100
Nitrate	100
Sulfate	1000

Anion	Concentration, ug/mL
Nitrite	100

*alternate equivalent source at similar concentrations may be purchased.

7.5 Working ICAL standards. The Accustandard stock or other certified standard is diluted as described below to give the final concentrations listed below:

Standard Level	Aliquot (mls)	Final Volume (mls)	Concentration (mg/l) Fluoride, Nitrite, Bromide, Nitrate	Concentration (mg/l) Chloride, Sulfate
Level #1	0.0	100	0	0
Level #2**	0.1	100	0.1	1.0
Level #3	0.2	100	0.2	2.0
Level #4	0.5	100	0.5	5.0
Level #5	1.0	100	1.0	10.0
Level #6	2.0	100	2.0	20.0
Level #7*	5.0	100	5.0	50.0
Level #8	10.0	100	10.0	100.0

*This level is used as the CCV standard.
**This level is used as the CCVL standard (if required).

7.6 Initial Calibration Verification (ICV). Purchased from a different source than the ICAL Standards. (Currently Environmental Express standards)

Standard	Aliquot (mls)	Final Volume (mls)	Concentration (mg/l) Fluoride, Nitrite, Bromide, Nitrate	Concentration (mg/l) Chloride, Sulfate
ICV	5.0	100	5	50

7.7 Laboratory Control Spike (LCS). This solution can be made from the standard stock solution or the outside check solution. (Currently Environmental express standards.)

Standard Level	Aliquot (mls)	Final Volume (mls)	Concentration (mg/l) Fluoride, Nitrite, Bromide, Nitrate	Concentration (mg/l) Chloride, Sulfate
LCS	5.0	100	5	50

7.8 Matrix Spike (MS). The matrix spikes are prepared and spiked at the following levels:

Matrix Spike	Aliquot (mls)	Final Volume (mls)	Concentration (mg/l) Fluoride, Nitrite, Bromide, Nitrate	Concentration (mg/l) Chloride, Sulfate
MS	0.25	5	5	50

7.9 Managers/supervisors or a designee are expected to check their areas on a monthly basis for expired standards and dispose of them according to SOP TA-EHS-0036.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples are stored at 0-6℃ in the container receiv ed. Samples should be collected in scrupulously clean glass or polyethylene bottles.

8.2 The holding time for samples submitted for bromide, fluoride, chloride, sulfate, and/or nitrate/nitrite (sample preserved to pH less than 2.0) analysis is 28 days.

8.3 Holding time for samples submitted for nitrate-N, and/or nitrite-N is 48 hours.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters NO_2, NO_3,	HDPE	50 mLs	Cool 0-6^oC	48 Hours	40 CFR Part 136.3
Waters Fl, Cl, Br, SO_4, NO_2/NO_3	HDPE	50 mLs	Cool 0-6^oC	28 Days	40 CFR Part 136.3
Soils	Glass	3 grams	Cool 0-6^oC	180 Days	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. The process of establishing control limits, and the use of control charts are described more completely in TA-QA-0620, Quality Control Program. Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.3 Attachment 1 reconciles the various QC requirements specified in the reference methods with the QC requirements specified in this SOP.

9.4 Before analyzing samples, the laboratory must establish a method detection limit (MDL) and the linear calibration range (LCR) as described in Section 12.1. In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument they will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 12.2 for more details.

9.5 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. See SOP TA-QA-0620 for further details.

9.6 Method Blank (same as Laboratory Reagent Blank, LRB)

A method blank (MB) is required with every batch of 20 or less samples. The MB is deionized water taken through the procedure as if it were a sample.

Acceptance Criteria: The MB must not contain anions of interest above one-half the reporting limit or above one-tenth of the concentration found in the associated samples (for samples with concentrations above the RL).

NOTE: Some programs (e.g., DoD) require control of method blanks to have a concentration less than or equal to one-half of the RL. Some programs (LaMP) and MMethod 300.0 and Method 9056A require no detections in the method blank more than 10% of the low limit calibration check solution. This can not be obtained in most cases. TestAmerica Seattle will only evaluate the method blank to 1/2 the RL or Project DQOs and when specific DQOs are not provided by the client the RL will be defined as the DQO.

Corrective Action: If the method blank exceeds allowable levels, laboratory contamination is suspected and corrective action must be taken before continuing. All samples associated with the failed blank must be reanalyzed.

9.7 Laboratory Control Sample (same as Laboratory Fortified Blank, LFB)

One Laboratory Control Sample (LCS) is required with each analytical batch. Depending on client or project requirements, an LCS duplicate may also be analyzed. The LCS and LCSD are prepared as described in Section 7.7. An LCS that is determined to be within acceptance criteria effectively demonstrates that the analytical system is in control and validates system performance for the samples in the associated batch.

If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed.

Acceptance Criteria: For Method 300.0, the LCS recovery for each analyte of interest must be within 90-110%. For Method 9056A, the LCS recovery for each analyte of interest must be within statistical control limits, not to exceed 85-115%. The absolute value of the relative percent difference (RPD) between the LCS and LCSD must be $\leq$ 10%. Statistical control limits are set at $\pm$ 3 standard deviations around the historical mean. The process of establishing control limits is described in more detail in SOP TA-QA-0620. Control limits are maintained in the LIMS.

Corrective Action: If the LCS recovery falls outside of the established control limits, and/or when the RPD for the LCS/LCSD exceeds the RPD limit, check instrument conditions and the standards being used for problems. Correct any problems before continuing. Reanalyze all samples associated with the failed LCS.

9.8 Matrix Spike / Matrix Spike Duplicate (MS/MSD, same as Laboratory Fortified Matrix)

For Method 9056A, one MS/MSD pair is required with each analytical batch of 20 or fewer samples. For Method 300.0, one MS is required for every 10 routine samples. The MS and MSD are prepared as described in Section 7.8.

If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed.

Acceptance Criteria: The recovery of each anion of interest must be within the established statistical control limits. Statistical control limits are set at ± 3 standard deviations around the historical mean, and must be within 80/120%. The relative percent difference (RPD) between the MS and MSD must be less than 15%, or less than the established control limit, depending on project requirements. The process of establishing control limits is described in more detail in SOP TA-QA-0620. Control limits are maintained in the LIMS.

Corrective Action: The information obtained from MS data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If the MS and/or MSD recovery falls outside of the established control limits, the bracketing CCV and batch LCS recoveries must be within control limits in order to accept results for the associated samples. The following corrective actions are required for MS/MSD recovery failures:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly;
- Consider objective evidence of matrix interference (e.g., heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses); and
- Document the failure in an NCM and note it on the final report.

For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample non-homogeneity; and document the failure in an NCM.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

9.9 Matrix Duplicate

For clients requiring a matrix duplicate, one will be processed in each analytical batch of 20 or fewer samples.

If a duplicate is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed.

Acceptance Criteria: The relative percent difference (RPD) between the sample and Duplicate must be less than 10%, or less than the established control limit, depending on project requirements. The process of establishing control limits is described in more detail in SOP TA-QA-0620. Control limits are maintained in the LIMS.

Corrective Action: See corrective actions under section 9.8.

9.10 Instrument QC

9.11 Initial Calibration (ICAL)

9.11.1 An initial calibration is performed every three months, or as needed, based on instrument performance and maintenance.

9.11.2 Calibrate the instrument at seven levels. See Section 7.5 for preparation of calibration standards. Note that it is generally NOT acceptable to remove points from a calibration for the purposes of meeting calibration criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. The only exception is that a level may be removed from the calibration if the reason is clearly documented, for example a cracked tube, and a minimum of five levels remain. Curves may not be forced through the origin.

9.11.3 Construct a calibration curve using a least squares linear regression or a quadratic curve (see corporate SOP CA-Q-S-005, Calibration Curves and Attachment 4 for the verbiage from the method update rule).

Acceptance Criteria: Six calibration points must be used when using a quadric curve. The r^2 of a 2^{nd} order quadratic curve must be 0.990 or greater. The absolute value of the correlation coefficient must be 0.995 or greater.

Corrective Action: If the correlation coefficient is less than the acceptance limit, recheck instrument conditions and calibration standards. Samples cannot be analyzed until the initial calibration is successful.

9.12 Initial Calibration Verification (ICV)

The second-source ICV is the same as the LCS and is described in Section 7.6; it is analyzed immediately following the ICAL.

Acceptance Criteria: The ICV recovery for each anion must be 90-110%. The retention time for each analyte in the ICV must be within ± 10% of the established retention time for that analyte.

Corrective Action: If the recovery and/or retention time is outside of the acceptance limits, repeat the test. If the test fails on the second attempt, then the problem must be investigated and the instrument recalibrated for the failed analyte(s). There are no exceptions (DOD QSM).

9.13 Initial Calibration Blank (ICB)

An ICB is analyzed following the ICV.

Acceptance Criteria: The result must be less than one-half the reporting limit.

Corrective Action: If the blank is above the acceptance limit, check for carryover or the need for instrument maintenance. The instrument must be recalibrated, and all samples analyzed since the last successful CCV must be reanalyzed.

9.14 Continuing Calibration Verification (CCV, same as IPC in Method 300.0)

A CCV is required at the beginning of every run, after every 10 or fewer samples and after the last sample.

Acceptance Criteria: The CCV recovery must be 90-110%. The retention time for each analyte in the CCV must be within ± 10% of the established retention time for that analyte.

Corrective Action: If the recovery and/or retention time is outside of the acceptance limits, all samples analyzed since the last successful CCV must be reanalyzed. There are no exceptions (DOD QSM).

9.15 *Low-Level Continuing Calibration Verification (CCVL)*

For any samples analyzed under the BP LaMP program a CCVL is required at the beginning of every run, after every 10 or fewer samples and after the last sample.

Acceptance Criteria: The CCVL recovery must be 90-110%. The retention time for each analyte in the CCVL must be within ± 10% of the established retention time for that analyte.

Corrective Action: If the recovery and/or retention time is outside of the acceptance limits, all samples analyzed since the last successful CCVL must be reanalyzed.

9.16 Continuing Calibration Blank (CCB)

A CCB is analyzed after each CCV.

Acceptance Criteria: The result must be less than one-half the reporting limit.

Corrective Action: If the blank is above the acceptance limit, check for carryover or the need for instrument maintenance. All samples analyzed since the last successful CCB must be reanalyzed.

Note: CCVs need to be followed by a CCB. CCV cannot be preceded by a CCB, unless a blank is analyzed before each sample in the bracket.

9.17 RT Study

Retention time window widths are calculated for each analyte after a major maintenance event (i.e., column change). Using data obtained from the analysis of at least five continuing calibration verification standards over a 24-hour period, calculate the mean retention time and standard deviation for each analyte. Assign a retention-time window of ± 3 standard deviations around the mean for each analyte. If the standard deviation is 0.00, use a default retention-time window of 0.3 minutes

9.18 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of management to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate.

The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP TA-QA-0610. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.3 Attachment 2 summarizes the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the data quality objectives can be met. If operating conditions are different than those listed in the SOP, they should also be documented in the maintenance logbook.

10.4 Check system calibration daily by analyzing a CCV and CCB (see Sections 9.124 and 9.13) and, if required, recalibrate as described in Section 10. A passing CCV must be run daily before any samples are analyzed.

10.5 Sample Preparation

10.5.1 Water samples are prepared for analysis by filtering an aliquot through a 0.45 µm membrane type filter.

10.5.2 Check the Balance Logbook to determine if the daily calibration check was completed. If the balance requires a check, verify the calibration as detailed in TA-QA-0014.

10.5.3 The following extraction should be used for solid materials. Add an amount of reagent water equal to 10 times the weight of dry solid material taken as a sample. This slurry is mixed together for 30 minutes using a shaker table. Filter the resulting slurry before injecting using a 0.45 u membrane type filter. This can be the type that attaches directly to the end of the syringe.

10.6 Calibration

10.6.1 Ion chromatographic operating parameters and start up procedure:

10.6.1.1 Flow rate/psi: 1 mLs/minute, approximately 2000 psi.

10.6.1.2 Conductivity with eluent: ≤ 25 umhos.

10.6.1.3 Typical retention times: see attached. Window: ± 15%

10.6.1.4 Program schedule:

- pull up previous schedule;
- *save new schedule under* current date;
- delete sample ID and information;
- *copy ICAL, ICV, and ICB from original sequence;*
- *click "yes";*
- *click "yes";*
- put CCV (RTC, retention time check), CCB, MB, LCS, LCSD, Samples and Sample Dup *into autosampler;*
- *place vials in AS-DV/AS-AP autosampler;*
- *click "resume";*
- click on current schedule;

- click on "ok";
- click on "run";
- click on "start"; and
- click on "ok".

10.6.2 Calibration

10.6.2.1 Initial Calibration Procedures. Analyze all six working standards and a blank. Typical retention times are listed in Table 2. Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values (see corporate SOP CA-Q-S-005, Calibration Curves). Quadratic models are not permitted. The ICV and ICB must be analyzed immediately following the initial calibration. The ICV must agree within 10% of the true value. There are no exceptions (DOD QSM).

10.6.2.2 Continuing Calibration Procedures. The CCV serves as the daily calibration and retention time check. At the beginning of each analysis batch and after every ten sample analyses, a continuing calibration verification (CCV) standard is analyzed. The CCV must agree within 10% of the true value, or all samples analyzed since the last successful CCV must be reanalyzed. There are no exceptions (DOD QSM).

10.6.2.3 LCS standard analysis: the LCS is analyzed daily prior to sample analysis, and must agree within 10% of the true value.

10.7 Sample Analysis

10.7.1 Load 5 mL of sample in the vial. *For Integrion, load 1.5 mL sample vials.* The majority of the volume is used to flush the loop; 25 uL of the sample is injected into the instrument.

10.7.2 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

10.7.3 Compute sample concentration by comparing sample peak response with the standard curve.

Report results in mg/L: NO_2^- as N
NO_3 as N

NOTE: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

10.8 Following is a typical analytical sequence:

ICAL and ICV and ICB or CCB and CCV *(CCVL if required)*
Method Blank
LCS and LCSD (if included)
7 injections (or 8 if LCSD is not included)
CCV *(CCVL if required)* and CCB
10 injections

CCV and CCB

10 injections

CCV and CCB

10.9 Retention Times and Anion Identification

10.9.1 The width of the retention time window used to make identifications is based on measurements of actual retention time variations of standards over 24 hours. (This should be done prior to analysis of samples since the retention time window must be entered into the software before starting the run and each time major maintenance is performed such as installing a new column).

10.9.2 Make an injection of all analytes of interest over a 24-hour period. Calculate the standard deviation of three retention time observations for each analyte. Three times the standard deviation of a retention time is used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.9.3 Calculate the mean and standard deviation for the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RT_i - \overline{RT}\right)^2}{n-1}}$$

Where:

RT_i = Retention time for the i^{th} injection.

n = Number of injections (typically 3).

SD = Standard deviation.

10.9.4 Set the width of the RT window for each analyte at ± 3 standard deviations of the mean RT for that analyte.

10.9.5 The center of the RT window for an analyte is the RT for that analyte from the last of the three standards measured for the 24-hour study. The width of each window remains the same until new windows are generated following the installation of a new column, or in response to an RT failure. The RT window width may be expanded if the RT drift observed in the ICAL is greater than the established window. The expanded window is noted on the ICAL checklist.

10.9.6 If the RT window as calculated above is less than ± 0.3 minute, use ± 0.3 minute as the RT window. This allows for slight variations in retention times caused by sample matrix.

10.9.7 The calibration curve is verified each working day, whenever the eluent is changed, and after every 10 injections by analyzing a CCV and CCB. If the response or retention time for any analyte varies from the expected values (± 5% for SO_4^{-2} and ± 10% for F^-, Cl^-, NO_2^-, Br^-, and NO_3^-) or all samples analyzed since the last successful CCV must be reanalyzed.

10.9.8 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an

appropriate amount of standard and reanalyze. The addition of one to two times the sample concentration normally provides the best peak height for analyte identification.

NOTE: Concentration can affect retention time and cause peak migration. Late eluting species, e.g., nitrate and sulfate, exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration may produce poor resolution or misidentification. If a peak has shifted outside of its retention time window (as confirmed by a CCV or Matrix Spike), change the window in the software and reprocess the chromatogram. Document the reason for reprocessing the chromatogram along with the date and initials.

10.9.9 Should more complete resolution be needed between peaks, the eluent can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

10.10 If the response for the peak exceeds the working range of the system, dilute the sample with reagent water and reanalyze.

10.11 Preventative and Routine Instrument Maintenance

All maintenance and repairs need to be documented in the instrument's maintenance logbook. If operating conditions are different than those listed in the SOP, they should also be documented in the maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., IC, autosampler, column) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, etc as may be the case).

10.11.1 As stated in the ICS-2000 Instrument Manual the following maintenance procedures are especially important for keeping the ICS- 2000 operating reliably:

10.11.1.1 Check weekly for leaks or spills. Locate and repair leaks and clean up spills. Rinse any dried eluents or reagents off system components with deionized water.

10.11.1.2 Check all air and liquid lines weekly for crimping. Relocate pinched lines and replace damaged lines.

10.11.1.3 Every six months:

10.11.1.3.1 Calibrate the cell. See section 5.13 of the user manual.

10.11.1.3.2 Calibrated the vacuum degas assembly. See section 5.1.5 of the user manual.

10.11.1.3.3 Replace the pump piston rinse seals and piston seals. See section 5.6 of the user manual.

10.11.2 The Dionex automated sampler should be checked weekly for spills on the input/output tray. Rinse off any dried spills that may interfere with the smooth operation of the sampler.

10.11.3 The absolute response of Nitrite in the opening CCV is evaluated and tracked in the logbook. Differences greater than 20% should be investigated.

10.11.4 Use deionized water to rinse any eluent spills off all valve surfaces. In addition, check all air and liquid lines for discoloration or crimping. Reposition pinched lines and replace damaged lines.

10.11.5 As stated in the AGP Operators Manual, several preventative maintenance procedures must be performed on the AGP routinely to keep it operating smoothly.

10.11.5.1 Rinse the piston before and after daily operation to help prevent the build-up of salt crystals or other contaminants that can damage the piston seal. Use the procedure described in Section 4.1.1 of the AGP operator's manual.

10.11.5.2 Check for leaks from the piston rinse tubing, interior of the pump, pump heads and the metal pump casting (see Sec. 4.1.2, AGP manual) every week.

10.11.5.3 The AGP requires regular lubrication (i.e. every three to six months) to keep the left piston operating smoothly (the right piston, however, requires no lubrication.). Follow the instructions in sect. 4.1.2 of the Advanced Gradient Pump operator's manual.

10.11.5.4 Normal friction and wear will gradually cause small leaks around the piston seals. If you do not replace the pistons seals regularly, these leaks can eventually contaminate the cam followers and metal casting. This will impair operation and cause irreversible damage to the pump. Replace the piston seals in both pump heads (Sec. 4.3.5) every six months. Check the piston drain tubes (Figure 2.2) weekly. A drop of solvent trapped in the end of these tubes is normal. However, solvent flowing from the tube probably indicates a leak: in this case replace both the primary and the back-up seals.

10.11.6 The conductivity Detector requires very little routine maintenance. Check the line connections to the cell (inside the Chromatography Module) for leaks and remove spills (Section 5.3.1) weekly. Once a month, use the procedures listed in 5.1 of the Conductivity Detector-3 operator's manual to clean the cell electrodes and calibrate the cell (Section 5.1.1 and 5.1.2).

10.12 Instrument Maintenance

10.12.1 Daily

- Check seals for leakage

10.12.2 As required;

- Replace seals/valves/lamps
- Replace suppressor
- Replace column
- Clean source/analyzer

10.13 Trouble Shooting

See Attachment 5 of this SOP

11.0 Calculations / Data Reduction

11.1 Calibration Curves

See corporate SOP CA-Q-S-005, Calibration Curves

11.2 Accuracy

$$\textbf{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\textbf{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.3 Precision (RPD)

$$\textbf{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.4 Concentration

11.4.1 Liquid samples, report as mg/L, direct instrument reading

11.4.2 Solid samples, report as mg/kg:

$$\text{mg/kg} = \frac{\text{(instrument reading) (final volume)}}{\text{(sample weight) (dry weight correction)}}$$

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstrations of Capability (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP TA-EHS-0036. The following waste streams are produced when this method is carried out.

14.1 Waste Streams Produced by the Method

14.1.1 IC process waste – aqueous carbonate/bicarbonate eluent waste: Non-hazardous may be disposed of through the public sewer system.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW846, 3rd Edition, Final Update IIIB (December 1996), Method 9056A, "Determination of Inorganic Anions by Ion Chromatography", Revision 0, September 1994.

15.2 Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, Revision 2.1, August 1993.

16.0 Method Modifications:

Item	Method	Modification
1	300.0	Method 300.0 specifies that target analytes must be less than the MDL in the Laboratory Reagent Blank. TestAmerica Seattle QA SOP (TA-QA-0620) defines the acceptance limit for the method blank as the laboratory reporting limit (RL) and not the MDL. If specified in client or project requirements, the method blank acceptance limit may be set at the MDL.
2	9056A	Method 9056A specifies bomb combustion for solid waste samples. Method 300.0 specifies water leaching for solid samples. This SOP specifies a deionized water leach procedure. In this respect, this SOP complies with Method 300.0, but deviates from Method 9056A.

17.0 Attachments

Attachment 1: Quality Control Summary

Attachment 2: Suggested Standard Instrument Operating Parameters
Attachment 3: Example Ion Chromatogram
Attachment 4: Verbiage on quadratic calibrations from the method update rule (MUR)
Attachment 5: Troubleshooting Scheme for Anion Chromatograph Systems

18.0 Revision History

- Revision 25, dated 27 September 2017
  - Chloride RL updated, section 1.1
  - Updated Chromeleon version to 7.2
  - Added eluent concentrate used for new instrument Dionex Integrion, section 7.4
  - Added CCVL requirement for BP LaMP program, sectons 7.6, 9.15 and 10.8
  - Updated program schedule, section 10.6.1.4
  - Added sample vial volumes for new instrument, section 10.7.1
  - Added table for Dionex Integrion instrument conditions, attachment 2
  - Updated approvers

- Revision 24, dated 15 August 2016
  - Removed requirement to preserved Nitrate/Nitrite samples with sulfuric acid and references to sulfuric acid, throughout
  - Removed section 14.1.2: The chemicals Potassium Nitrate and Sodium Fluoride are not available for use in this method. All calibration and second source standards for this method are purchased dilute in water and disposed in the neutralization waste stream.

- Revision 23, dated 5 November 2015
  - Updated reporting limits and working ranges, section 1.1
  - Updated section 7.3.1 to include both possible eluents
  - Added preparation details to standards, sections 7.5 to 7.8
  - Updated attachment 2 to include both possible columns and eluents

- Revision 22, dated 28 May 2015
  - Removed reference to out of service instrument (TAC036)
  - Updated reporting limits, section 1.1
  - Updated CCV Standard solution concentrations, section 7.4
  - Updated working standards, section 7.5
  - Updated LCS and matrix spike concentrations, sections 7.6.1 and 7.6.2

- Revision 21, dated 02 February 2014
  - Added computer hardware and software, section 6.2
  - Added blank information sections 9.6 and 16.0
  - Updated copy position and types of samples loaded, section 10.6.2.4
  - Added ICV and CCB to section 10.6.3.1
  - Added that CCV serves at the RTC and calibration check, section 10.6.3.2
  - Added instrument maintenance to section 10.12
  - Added Attachment 5 for troubleshooting and reference to the attachment in section 10.13

- Revision 20, dated 20 March 2013
  - Updated working ranges and RLs, section 1.1
  - Updated standards section 7.0

- Updated CCV criteria sections 9.14 and 10.4
- Updated ICAL section 9.11.3
- Removed reference to out of service instrument (TAC038)
- Removed Attachment 3 (duplicated in sections 7.6.1 and 7.6.2)
- Added Attachment 4 (Verbiage on quadratic calibrations from the method update rule (MUR))

- Revision 19, dated 10 September 2012
  - Updated section 5.1.1
  - Updated working range for Br, Section 1.1 (Table).
  - Updated working standards for Br, Section 7.5
  - Updated waste streams, section 14.1
  - Updated eluent concentration, Attachment 2

- Revision 18, dated 7 September 2011
  - Incorporated ROMDs 00019 rev1 and 00026 (column identification) into sections 6.1 and 10.11.
  - Incorporated ROMD 00020 (instrument operating conditions) in Sections 10.3 and 10.11.
  - Incorporated ROMD 00022 (Calibration Curves/Calculations) in Sections 9.11.3, 10.6.7 and 11.1.
  - Incorporated ROMD 00024 (CCV corrective actions) in Section 9.14 and 10.6.7
  - Incorporated ROMD 00035 (no quadratic modeling) in Sections 9.11.2 and 10.6.7.
  - Incorporated ROMD 00025 (LCSD requirements) in Sections 9.7, 9.8 and 9.9
  - Incorporated ROMD 00033, adding process for evaluating absolute response of a check standard in Section 10.11.3
  - Changed blank acceptance criteria from less than the RL to less than one-half the RL

- Revision 17, dated 13 September, 2010
  - Updated tables Section 1.1
  - Added information/procedures for TAC-038 and differentiated information/procedures for TAC-044 throughout document.
  - Added removal of expired standards Section 7.8.
  - Added CCV/Blank requirement, Section 9.14.
  - Added RT study, Section 9.15
  - Added criteria for additional QC, Section 9.16.
  - Added daily balance check to Section 10.5.2.
  - Integration for TestAmerica Bothell and TestAmerica Tacoma operations.
  - Updated to incorporate BP LaMP requirements.

- Revision 16, dated 6 April 2009
  - Updated the Working Range for Fluoride in Section 1.1.
  - Updated RLs to reflect current values.
  - Revised section 3.7 to indicate second source QCS is the LCS.
  - Updated Fluoride calibration information in section 7.5
  - Included a default retention time window in section 10.9
  - Updated the Quality Control Summary in Attachment 1.
  - Updated instrument conditions (columns) in Attachment 2.
- Revision 15, dated 28 March 2008
  - Integration for TestAmerica and STL operations.

- This revision is a complete rewrite and an expansion of scope.

Attachment 1. Quality Control Summary

QC Samples	Frequency	Acceptance Criteria	Corrective Action	Reference Method Equivalent
Retention time (RT) window width determination	At method set-up and after major maintenance (e.g. column change)	RT width is ± 3 times std dev for each analyte RT over a 24-hour period.	NA	NA
Minimum 3-point Initial Calibration	Initial calibration prior to sample analysis	One of the options below: Linear least squares regression: r ≥ 0.990 **Linear least squares regression for DoD: r ≥ 0.995** For quadratic regression: r^2 ≥ 0.990.	Terminate analysis; correct the problem; recalibrate. Problem must be corrected. No samples may be run until ICAL has passed.	NA
Initial Calibration Verification (ICV)	Immediately following the initial calibration.	90 - 110% of true value RT must be ± 10% of established RT.	Repeat once, and recalibrate and reanalyze if it fails a second time.	QC Reference Sample (9056A) IPC and QCS (300.0)
Initial Calibration Blank (ICB)	After the ICV and prior to sample analysis.	< RL. **For DoD, LaMP**: ≤ ½ RL.	Re-prepare and reanalyze	Calibration Blank (300.0)
Method Blank (MB)	1 per QC batch	≤ RL **For DoD, LaMP**: ≤ ½ RL.	See Section 9.6 or SOP TA-QA-0620.	LRB (300.0)
Laboratory Control Sample (LCS)	1 per QC batch	Within laboratory historical limits but not to exceed 90-110% recovery **For DoD**: control limits may not exceed *the limits listed in the QSM*.	Recalibrate and reanalyze all samples associated with unacceptable LCS	LFB (300.0)
Matrix Spike Sample/Matrix Spike Duplicate (MS/MSD)	1 MS/MSD pair per QC batch for 9056A. 1 MS/MSD pair per 10 samples for 300.0.	%R within laboratory historical limits but not to exceed 80-120% recovery and RPD ≤	If LCS and CCVs are in control, then document in an NCM, unless project requires reanalysis.	Matrix Spike (9056A) LFM (300.0)

QC Samples	Frequency	Acceptance Criteria	Corrective Action	Reference Method Equivalent
		laboratory historical limits not to exceed 20%. **For DoD**: *limits listed in the QSM*.		
Continuing Calibration Verification (CCV)	Between each group of 10 injections and at the end of the analytical sequence.	90 - 110% of true value	Repeat. If repeat fails, reanalyze all samples since the last acceptable CCV.	Mid-range Calibration Standard (9056A) IPC (300.0)
Continuing Calibration Blank (CCB)	Between each group of 10 injections and at the end of the analytical sequence	< RL **For DoD**: ≤ ½ RL.	Repeat. If repeat fails, reanalyze all samples since the last acceptable CCB.	Calibration Blank (300.0)
Sample Duplicate	**For DoD,** 1 per 10 samples. BP LaMP 1 per 20 - may use either MSD or SDUP	%D ≤ 10% between sample and duplicate	Correct problem and reanalyze sample and duplicate.	NA

Attachment 2. Suggested Standard Instrument Operating Parameters

Typical Retention Times

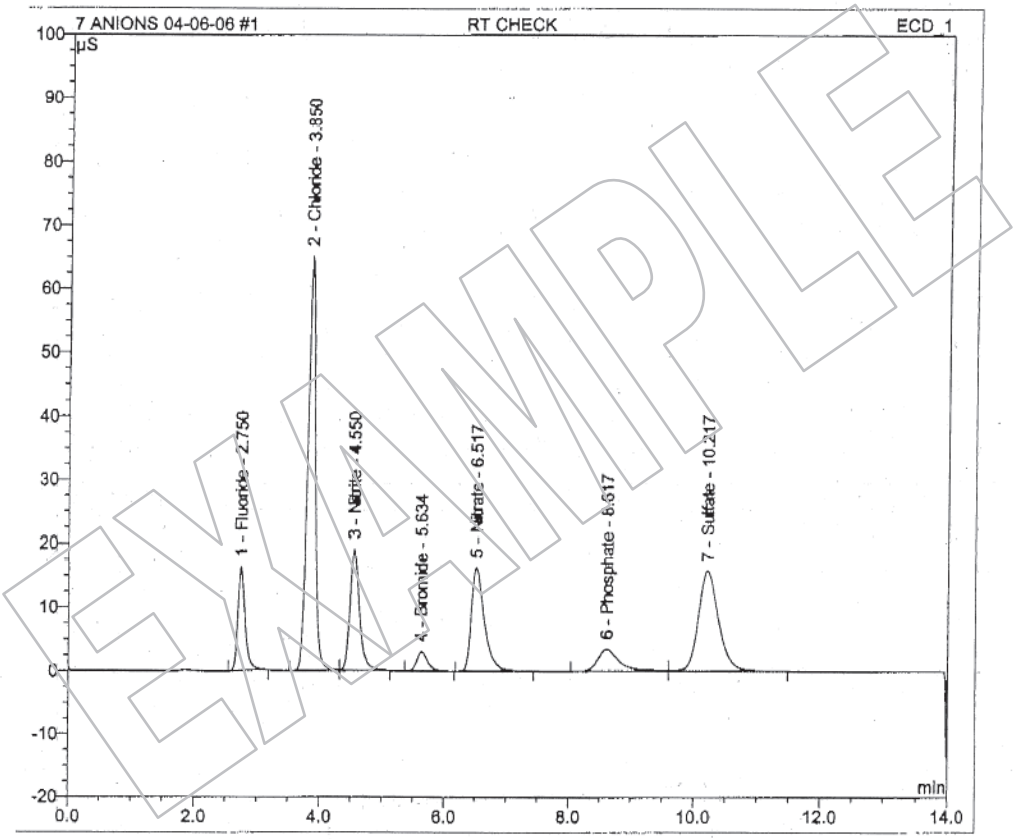
Analyte	Peak #	Retention Time (Minutes)
Fluoride	1	3.3
Chloride	2	4.7
Nitrite as N	3	5.7
Bromide	4	7.1
Nitrate as N	5	8.1
Sulfate	7	11.9

Instrument Conditions

Anion Guard Column	AG14A, AS18 or equivalent (4X50mm)
Anion Separator Column	AS14A, AS18 or equivalent (4X250mm)
Supressor Device	SRS 300 Self-Regenerating Suppressor (4mm)
Pump Rate	1.0 mL/min
Sample Loop	25 µL
Eluent	1.0 mM sodium bicarbonate, 32.0 mM sodium carbonate or Potassium hydroxide cartridge
Detector Output	Baseline conductivity should be between 24 - 28 µS prior to sample analysis.

Anion Guard Column	AG22 fast (4mm)
Anion Separator Column	AS22 fast (4x150mm)
Supressor Device	AERS Carbonate (4mm)
Pump Rate	1.0 mL/min
Sample Loop	25 µL
Eluent	4.5 mM sodium bicarbonate, 1.4 mM sodium carbonate
Detector Output	Baseline conductivity should be between 18 - 22 µS prior to sample analysis.

Attachment 3. Example Ion Chromatogram



Attachment 4. Verbiage on quadratic calibrations from the method update rule (MUR)

Changes in calibration model. (A) Linear calibration models do not adequately fit calibration data with one or two inflection points. For example, vendor-supplied data acquisition and processing software on some instruments may provide quadratic fitting functions to handle such situations. If the calibration data for a particular analytical method routinely display quadratic character, using quadratic fitting functions may be acceptable. In such cases, the minimum number of calibrators for second order fits should be six, and in no case should concentrations be extrapolated for instrument responses that exceed that of the most concentrated calibrator. Examples of methods with nonlinear calibration functions include chloride by SM4500–Cl–E–1997, hardness by EPA Method 130.1, cyanide by ASTM D6888 or OIA1677, Kjeldahl nitrogen by PAI–DK03, and anions by EPA Method 300.0.

Attachment 5. Troubleshooting Scheme for Anion Chromatograph Systems

Troubleshooting Scheme for Anion Chromatography Systems

Symptom	Possible source of error	Action
• High background conductivity, but a relatively low noise.	• The eluent has been contaminated with an anion of a strong acid.	• Check the electrolytic conductivity of the deionised water used to prepare the eluent and standards, and for dilution of the samples. • Prepare a new eluent (→ page 5). Change also the stock solution.
• High background conductivity in combination with high noise.	• The suppressor reaction does not work. • High backpressure in the detector. • The membrane of the suppressor is worn out or is inhibited by metal ions or hydrophobic cations.	• Check that the regenerant solution flows in a closed loop, as it should. • Check the detector by manually flushing water through the cell. Clean if necessary. • Wash the membrane with an alkaline magnesium EDTA solution (→ page 15). If this do not restore the full function of the suppressor, it is worn out and needs to be replaced with a new unit.
• High (often regular) noise with normal background level.	• Trapped air or malfunctioning valves in the eluent pump.	• Remove air from the pump and carefully degas the eluent (→ page 5). • Rinse with isopropanol (→ page 7). Change the pump valves if these are worn out.
• The sensitivity for anions of weak acids has decreased.	• Incomplete suppression. • The pH after the suppressor is too low.	• Check the regenerant flow – thereafter check if the cartridge lifetime is exceeded. • Check the pH of the eluate after the suppressor (→ page 14) and compare to the SOP (→ page 20).
• The sulfate or fluoride peak has decreased height and broadened, while other peaks are as usual.	• The suppressor or the separator column is contaminated by metal ions.	• Wash the suppressor membrane with an alkaline magnesium EDTA solution (→ page 15). If the problem remains the suppressor needs to be changed. • Run a clean-up procedure on the separator column. Follow the manufacturers instructions. Disconnect the column from the system before starting the clean-up.
• The baseline is drifting.	• The system has not stabilised yet. • Leakage in the flow system, temperature variations, debris on the column filters.	• Wait until the baseline has stabilised (Note: This can take a relatively long time). • Choose the simplest action first. Try also shutting off all pumps one by one. The injector can be a tricky source off error (→ page 8).
• Negative peaks.	• High background. • The cables between the detector and the recorder/integrator are connected with opposite polarity (signal to ground & vv).	• Check the regenerant flow, and if the regenerant cartridge has been consumed. • Make sure that – and + out from the detector connects to the corresponding terminals on the recorder/integrator. Possibly switch the cords between – and +.
• High backpressure.	• The column inlet filter is clogged. • The injector needs service or is placed in a position between *Load* and *Inject*.	• Disconnect the column. Compare with normal backpressure in SOP. • If the pressure remains when the column is disconnected the injector is the source. Check the position of the handle and perform service if necessary (→ page 8).

Title: Total Organic Carbon in Solids Using the LECO C632 Total Organic Carbon Analyzer [Methods SW846 9060 Mod, 9060A Mod and PSEP-TOC]

Approvals

Signatures on File	
Stan Palmquist Date	Joe Schairer Date
Inorganic Department Manager	Health & Safety Manager / Coordinator
Terri Torres Date	Dennis Bean Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. 001 **Distributed To:** Lab Intranet

1.0 Scope and Application

1.1 This procedure describes the determination of total organic carbon in soils, sludge, and sediments using the LECO C632 TOC analyzer. The LECO instrument uses 0.20 gram quantities of sample, and so results are less prone to precision problems that are typical of the trace TOC instruments that use sample aliquots in the 10-100 mg range. The method referenced for this procedure is EPA Method 9060.

1.2 The reporting limit (RL) is 0.2% carbon or 2,000 mg/kg.

1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.2.1 in the Quality Assurance Manual

2.0 Summary of Method

The sample is treated with 6N (1:1) HCL or 5% phosphoric Acid to drive off inorganic carbonates and then dried to remove moisture and acid. Organic carbon in the sample is converted to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is measured by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

3.0 Definitions

Total Organic Carbon (TOC):

The carbon measured as a result of oxidation of the sample after the removal of inorganic carbon.

4.0 Interferences

4.1 Oily samples will cause erratic results. This is minimized by homogenization of the sample.

4.2 This procedure is applicable to samples that can be thoroughly homogenized into a fine powder.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Spent crucibles must be allowed to cool to room temperature prior to disposal.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
5% Phosphoric Acid	Irritant Corrosive	1 mg/L TWA	Severe Chemical burns. Pain with skin contact, ingestion or inhalation. Can cause permanent damage to lungs. Maybe fatal if swallowed or inhaled.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- LECO C632 Analyzer
- Oven - The temperature must be sufficient to drive off water and acid and dry the samples

6.2 Computer Software and Hardware

- Computer with a minimum 1GB memory, Pentium 4 processor, 80 G hard drive or equivalent or as recommended by instrument manufacturer.
- LECO's proprietary computer interface and computer data handling system
- LIMS system: TALS version 1.0 or higher

6.3 Supplies

- Porcelain Combustion Boats
- Small Beakers
- Spoons or spatulas
- Miscellaneous volumetric glassware
- Compressed gas duster cans
- Aluminum weighing dishes
- 20 ml disposable scintillation vials
- Mortar and pestle

7.0 Reagents and Standards

7.1 Phosphoric, 5%.

Add 5.9 ml of 85% H_3PO_4 to 100 mL of deionized (DI) water
(Either the HCl or the Phosphoric acid can be used to remove the inorganic carbon.)

7.2 6N Hydrochloric Acid (1:1)

Slowly and carefully and with stirring, add 500 mL of concentrated HCL to 500 mL of deionized (DI) water. Allow to cool before use.

7.3 TOC Calibration Standard (MS/MSD/CCV)

Low Level: Calcium Carbonate; 12.00%C
High Level: Potassium Biphthalate, 47.05%C

7.4 TOC Initial Calibration Verification (ICV) This standard is from a different source than that of 7.2.

Low Level: Calcium Carbonate; 12.00%C
High Level: Potassium Biphthalate, 47.05%C

7.5 TOC Calibration Standard (LCS)

This standard is purchased from ERA. The true value will be dependent on the lot received.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Soils	Glass	3 Grams	Cool 0-6°C	14 Days for PSDDA/PSEP/SMS 28 days for all other. Sediments may be frozen extending holding time for up to 6 months.	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Seattle SOP TA-QA-0620, Quality Control Program.

9.1.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in

SOP TA-QA-0610. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

A batch is a group of no greater than 20 samples excluding QC samples (LCS, MS, MSD, Method Blanks), which are processed similarly, with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3 Method Blank (MB)

One method blank (MB) must be processed with each batch. The method blank consists of a solid blank matrix (typically Ottawa Sand) containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

Acceptance Criteria: The method blank should not contain any analyte of interest above one-half the reporting limit.

Corrective Action: If the analyte level in the method blank exceeds one-half the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data must be taken in consultation with the client and must be addressed in the project narrative.

If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

If all samples associated with a blank greater than the RL are greater than 10 times the blank value, the samples may be reported with an NCM to qualify the high blank value.

9.4 Laboratory Control Sample (LCS)

One LCS must be processed with each batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

The LCS for TOC in soils is performed by analyzing a 0.20 g aliquot of an ERA CRM (see Section 7.5). The LCS is prepared by slowly add 5% Phosphoric Acid and watch for the sample to fizz. If there is no fizzing then the sample is ready to be dried in the oven. If the sample fizzes then more 5% Phosphoric Acid needs to be added. Continue adding 5% Phosphoric Acid until the fizzing stops. (1:1 HCl can also be used)

Acceptance Criteria: The LCS recovery must fall within the established control limits certified by the vendor. The control limits are maintained in the LIMS.

Corrective Action: If any analyte is outside established control limits, the system is out of control, and corrective action must occur. Corrective action

will be re-preparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD) Samples

One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) that is prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to an MS/MSD pair. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked.

The MS and MSD for the automated method are prepared by placing 0.10g of the soil sample to be spiked into a porcelain boat and adding an identical weight of calcium carbonate. These are mixed and combusted as a sample with the weight of the soil (0.10 g) used as the sample weight in the sample table. The mass of the calcium carbonate used is typed into the “description” field of the LECO software run log.

Acceptance Criteria: The recovery of the analyte in the MS and MSD must fall within +-20% of the true value.

Corrective Action: If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch.

If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed.

9.6 Duplicate Sample Analysis

A duplicate pair is required with each analytical batch and must be within 50% RPD. Note that the control limits only apply to samples with results greater than 5 times the RL. The process of establishing control limits is described in more detail in the QC SOP TA-QA-0620.

Corrective Action: If the RPD is greater than 50% the sample should be reanalyzed if within holding time and sufficient sample is remaining.

Note: Samples analyzed under the PSEP protocol require one sample per batch of 20 to be analyzed in triplicate. *Triplicate = 6 burns total for the sample chosen for triplicate; sample – 2 burns, duplicate (DU) – 2 burns and triplicate (TRL) – 2 burns.*

Note: Samples analyzed for the USACE require analysis in quadruplicate for all samples.

9.7 <u>Instrument QC</u>

9.8 Initial Calibration Verification (ICV)

The ICV standard is analyzed immediately following the ICAL. The ICV is a second-source calcium carbonate standard with a true value of 12% carbon. The analyte recovery must fall within the 80-120% range. If it is outside the acceptance limits, check the equipment and standards, correct any problems, and then recalibrate.

9.9 Continuing Calibration Verification (CCV)

The calibration is checked at the beginning of an analytical sequence (ICV), after every ten samples (CCV), and at the end of the sequence (CCV) by measuring a CCV standard.

The CCV is calcium carbonate with a true value of 12% carbon.

The CCV recovery must be within the 80-120% range. If it is outside the acceptance limits, check the equipment and standards, correct any problems, recalibrate, and rerun all samples analyzed since the last successful CCV.

9.10 Initial and Continuing Calibration Blank (ICB and CCB)

System cleanliness is checked at the beginning of an analytical sequence (ICB), after every ten samples (CCB), and at the end of the sequence (CCB) by analyzing a blank.

The ICB/CCB for the automated method is a solid sample matrix.

Results must be less than the reporting limit. If the blank result is greater than the reporting limit, check for carry-over from high level samples, clean the system, recalibrate, and rerun all samples analyzed since the last successful CCB.

9.11 Test for Selection Efficiency

Once a year or as part of a new analyst's demonstration of capability, the efficiency of inorganic carbon removal for a solid matrix will be checked by splitting a sample containing at least 10K mg/Kg TOC into two portions, adding to one portion an inorganic carbon level similar to that of the sample. The TOC for both portions will be determined and the values compared. If the TOC values don't agree within ±20% RPD (for TOC concentrations at least 5 times the RL), adjust the sample volume or the amount of acid added to the sample to obtain complete removal of the inorganic carbon.

9.12 Any extra QC that is analyzed in a batch or sequence must be evaluated using the same criteria as the corresponding QC above

10.0 Procedure

One time procedural variations are allowed only if deemed necessary in the professional judgment of supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.1 Sample Preparation

10.1.1 Place a 2-3 gram sample in a dry weight tin. Slowly add 5% Phosphoric Acid and watch for the sample to fizz. If there is no fizzing then the sample is ready to be dried in the oven. If the sample fizzes then more 5% Phosphoric Acid needs to be added. Continue adding 5% Phosphoric Acid until the fizzing stops. (1:1 HCl can also be used)

10.1.2 Heat the samples in an oven maintained at 70℉ ± 2° F until they appear dry.

10.1.3 After drying, the samples should be homogenized, and ground to uniform consistency using a clean mortar and pestle. Clean the mortar and pestle by dusting with the compressed air duster and then wiping with a clean KimWipe. Leave out any extraneous artifacts, i.e., glass shards, large twigs, leaves, etc.

10.2 Instrument Operating Conditions

10.2.1 Instrument operating parameters are defined in the instrument's maintenance logbook. The absolute response of the daily ICV is evaluated and tracked in the logbook.

10.3 Calibration

10.3.1 Calibration should be performed whenever a ICV or CCV fails QC criteria or following major instrument maintenance. The calibration typically will be good for up to six months.

10.3.2 Instrument and furnace should be left on at all times. Be sure that the furnace is reheated to 1350℃ before beginning analysis.

10.3.3 If the furnace has been shut down due to maintenance or a power failure, ramp the temperature up slowly to 600℃ to minimize the ther mal stresses on the combustion tube.

10.3.4 Turn on the compressed air to the autosampler and the oxygen to the combustion analyzer.

10.3.5 Check that the incoming oxygen pressure is 20-40 psi and the combustion pressure is <15 psi.

10.3.6 An initial calibration is performed annually, or as needed. based on the instrument performance and maintenance.

10.3.7 Initial Calibration: The LECO analyzer is calibrated with calcium carbonate, a solid with a true value of 12% carbon and blanks.

10.3.7.1 Analyze three blanks

10.3.7.2 Analyze a six point standard curve (0.050g, 0.075g, 0.100g, 0.150g, 0.200g and 0.250g) with the 12% carbon standard.

10.3.8 The results are plotted in a calibration curve area vs. concentration (see corporate SOP CA-Q-S-005, Calibration Curves).

Acceptance Criteria:	The absolute value of the correlation coefficient (r) must be 0.995 or greater. The correlation coefficient can be determined by subtracting the RMS Error from the ICAL report from 1.
Corrective Action:	If the correlation coefficient is less than the acceptance limit, recheck instrument conditions and calibration standards. Samples cannot be analyzed until the initial calibration is successful.

10.4 Sample Analysis

10.4.1 Weigh approximately 0.20 g of homogenized and dried sample into a new, compressed air dusted, tared porcelain weigh boat. Spread the sample evenly throughout the boat. With the cursor in the "mass" column, push the read button on the balance to add the weight of the sample to the LECO software run log.

10.4.2 Load the samples into the auto sampler. After the samples are loaded, use the software to begin analysis.

10.4.3 Unless there are special project requirements, all instrument and batch QC is analyzed as a single analysis, while all samples are analyzed as two replicates (or "in duplicate"). For the QC sample, the sample duplicate and triplicate are substituted for the two replicates.

10.4.4 Sample results should be less than 20% carbon so that they use the calibrated low-range IR cell. Sample results of greater than 20% carbon should be reanalyzed with a smaller aliquot. (This equates to about 2.5 to 3 million counts, right around the high point on the curve)

10.4.5 Samples and standards are measured in the following sequence:

ICV
ICB
MB
LCS
LCSD (IF NEEDED)
QC SAMPLE
QC DUPLICATE
QC TRIPLICATE (IF NEEDED)
QC MS
QC MSD
2-4 SAMPLES (FOR A TOTAL OF 10 SAMPLES)
CCV
CCB
10 SAMPLES
CCV
CCB

10.5 Data Review

First and second level data reviews are recorded on the Wet Chemistry Data Review Checklist.

10.5.1 Upon completion of the analytical run, the primary analyst must review all data for compliance with criteria documented in Sections 9.0 and 10 and evaluate control charts according to SOP TA-QA-0600. The primary analyst will enter the data into TALS upon completion of their initial review and update the status.

10.5.2 The Supervisor (or designate) must perform a secondary peer review of the data as entered into TALS. Upon satisfactory completion of this review, the Supervisor (or designate) will update the status of the data set to second level reviewed, indicating the data is ready for reporting to the client.

10.6 Instrument Maintenance

The level of gasses must be checked before each analysis to insure they do not need to be replaced. All maintenance and repairs need to be documented in the instrument's maintenance logbook. The logbook must include the instrument name, serial number for each major component (e.g., GC, auto sampler) and the date of start-up. When an instrument is not capable of analyzing samples, it needs to be tagged "Out of Service". Logbook entries must include a description of the problem and what actions were taken to

address the problem. After an instrument has undergone maintenance or repairs, the system is evaluated using a CCV or ICAL. If the evaluation is successful, the analyst documents in the logbook that the "System returned to control as indicated by a passing CCV" (or ICAL, MB, etc as may be the case). Raw data counts are recorded in the maintenance logbook for each passing ICV.

10.7 Troubleshooting

If you are experiencing low recovery of QC samples check the desiccant. If it starts to appear solid or if there is a color change it will need to be changed per manufactures instructions.

If samples will not run make sure to check the temperature setting for the furnace to insure it is set correctly.

11.0 Calculations / Data Reduction

11.1 Calibration Curves

Detailed calibration equations can be found in the corporate SOP CA-Q-S-005 "Calibration Curves".

11.2 Accuracy

$$\textbf{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\textbf{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.3 Precision (RPD)

$$\textbf{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.4 Concentration =

$$\text{mg/kg or L} = \frac{C \times V \times D}{W}$$

Where:

C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor
W = Weight/Volume of sample aliquot extracted (grams or mLs)

NOTE: TOC analysis should not be dry weight corrected. TOC samples are dried prior to analysis. If a client requires the true dry weight correction at 104C (PSEP) then the total solids should be analyzed twice, once at 70C and once at the normal 104 C and both reported to the client.

11.5 Control limits are stored in and accessed from LIMS.

11.6 The detection limit for this method will vary based on the results of detection limit studies performed. Samples less than the method detection limit are reported as ND. Please refer to LIMS for current reporting limit information.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure (see SOP TA-QA-0602). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

Analyst initial and continuing Demonstration of Capabilities (DOC) are performed before any client samples are analyzed and are updated annually. See SOP TA-QA-0617 for details.

12.3 Training Requirements

See SOP-TA-QA-0608 for detailed training requirements.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Waste Disposal SOP TA-EHS-0036.

14.2 The following waste streams are produce when this method is carried out:

14.2.1 Acidic waste: Is bulked into the Metals Digest Waste Stream which is sent out for waste water treatment.

14.2.2 Porcelain Combustion Boats: Are dispose of into the "Dirt Samples and Debris" waste stream which is sent out for incineration.

14.2.3 Foreign soil waste and materials contaminated during sample preparation are collected for autoclaving and disposal per SOP TA-QA-0531.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition and all promulgated updates, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, January 2005, Method 9060,Total Organic Carbon, Revision 0, September 1986.

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition and all promulgated updates, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, January 2005, Method 9060A, Total Organic Carbon, Revision 1, November 2004.

15.3 Puget Sound Estuary Protocols, Conventional Sediment Variables, Total Organic Carbon, March 1986.

15.4 Puget Sound Estuary Protocols, Conventional Sediment Variables, Recommended Guidelines for measuring Organic Compounds in Puget Sound Water, Sediment and Tissue Samples, April 1997.

16.0 Method Modifications:

Item	Method	Modification
1	SW 9060	Method 9060 is designed for water samples and requires quadruplicate analysis to overcome potential precision problems. This procedure is exclusively for soil samples, and the LECO instrument is designed for soil analysis. The sample aliquots are 10-100 times larger than are practical with most other non-dispersive IR instruments, and so the precision is acceptable with duplicate analyses.
2	SW 9060	Method 9060 requires the use of a blender to homogenize samples. Since this procedure is for soils, the samples are ground to a uniform consistency.

17.0 Attachments

None

18.0 Revision History

- Revision 4, dated 26 September 2016
  - Changed MSDS to SDS, section 5.2
  - Added detail for triplicate analysis, section 9.6
- Revision 3, dated 29 September 2015
  - Added recording of raw data counts of passing ICVs, section 10.6
- Revision 2, dated 22 September 2014
  - Added computer hardware and software, section 6.2
  - Added supplies, section 6.3
  - Added clarification to holding time requirements, section 8.0
  - Added requirement to record weight of spike for MS/MSD, section 9.5
  - Added detail on cleaning Mortar and pestle, 10.1.3
  - Clarified when calibration should be performed, section 10.3.1
  - Updated calibration from five points to six points, section 10.3.6.2
  - Updated analysis sequence, section 10.4.5
  - Added checking gas levels to section 10.6
  - Added troubleshooting section, 10.7
  - Added details on true dry weight at 104C to section 11.4
  - Updated waste streams, section 14.2
- Revision 1, dated 29 July 2013
  - Added 5% Phosphoric Acid to multiple sections of the SOP
  - Changed the weight of sample used for the MS/MSD in section 9.5
  - Updated waste streams, section 14.2
- Revision 0, dated 6 July 2012
  - Initial release.

Title: Determination of Fixed Gases (Reformed Gases) in Air Samples using Gas Chromatography

[Methods ASTM D-1946 / EPA 3C / ASTM D-1945 / ASTM D-3588]

Approvals (Signature/Date):

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1. SCOPE AND APPLICATION

1.1. This standard operating procedure (SOP) is applicable to the gas chromatographic analysis of air or vapor samples for fixed gas compounds using thermal conductivity detectors (Front TCD/Aux TCD).

1.2. This SOP is restricted for use by experienced analysts or those under the supervision of analysts experienced in sample preparation, use of gas chromatography (GC), and interpretation of chromatograms.

1.3. Analytes, Matrix, and Reporting Limits (RLs)

1.3.1. Target analytes and RLs are listed in Attachment 1. Note that RLs are subject to change based on annual LOQ/LOD studies.

1.3.2. Applicable matrices – ambiant air, indoor air

1.4. This SOP also describes the calculations used to report Natural Gas composition (ASTM D1945) and "Heat Value and Relative Density of Gaseous Fuels" (ASTM D-3588). To calculate these values, results from Method TO-3 (WS-GCA-0018) are also required.

1.5. When undertaking projects for Department of Defense (DoD) and/or Department of Energy (DOE) the relevant criteria in QA Policy WS-PQA-021 must be checked and incorporated.

2. SUMMARY OF METHOD

2.1. An air or vapor sample is injected with a gas-tight syringe into a sample loop or by directly connecting a canister to the sample line and onto HaySep and Mol Sieve columns. The system automatically adjusts the sample loop to one atmosphere before injection. Oxygen (O2), nitrogen (N2), and methane (CH4) are the first to pass through the HaySep and are then directed onto the Mol Sieve. After they have eluted onto the Mol Sieve, the Mol Sieve is isolated. Carbon dioxide (CO2) is next to elute from the HaySep, bypassing the isolated Mol Sieve, then goes to the TCD. Carbon monoxide (CO) is last to elute from the HaySep, bypassing the isolated Mol Sieve, then goes to the TCD. Ultra high purity (UHP) helium (He) is used as the carrier gas.

2.2. Hydrogen (H2) and Helium (He) may also be analyzed. UHP N2 is used as the carrier gas. After the elution of these compounds from the HaySep onto the Mol Sieve, the HaySep is back-flushed to vent. H2 and He elute from the Mol Sieve and are detected by the TCD.

3. DEFINITIONS

3.1. Note that “must” and “shall” in this SOP denote required activities.

3.2. Air Sample Bag: Commonly referred to as FlexFilm or Tedlar bag, in 1.0-L or 3.0-L volume, that is constructed of proprietary material (e.g., SKC or ESS).

3.3. Fixed gases: Fixed gases are a group of atmospheric gases which include N2, O2, CO2, CO, CH4, H2, and He.

3.4. Part per million volume to volume (ppmv or ppm v/v): Concentration expressed as part of gaseous (vapor) volume of pure target compound contained in a million part of gaseous volume of sample. One ppmv is equal to 1/10000 of a % v/v.

Note: This reporting unit is NOT equivalent to the common ppm unit used in soil or water analysis.

3.5. Passivated canister: Commonly referred to as SUMMA canister, SilcoCan, or T.O.-Can in 1.0-liter, 1.8-liter, 6-liter, or 15-liter volume.

3.5.1. SUMMA canister: A spherical stainless steel container, which interior has been specially treated by a process (SUMMA passivation) that renders all surfaces inert to VOCs.

3.5.2. SilcoCan: A sampling canister manufactured by Restek Corporation using the Restek Silcosteel® process to coat the interior of the canister with fused silica, rendering it inactive to most VOCs.

3.5.3. T.O.-Can: A spherical stainless steel container (which is the equivalent of a SUMMA canister) that is manufactured by Restek Corporation using a proprietary electropolishing process and extensively cleaned using an ultrasonic method that ensures a high-quality passivated surface that maintains the stability of VOCs during storage.

3.6. Percent by volume (% v or % v/v): Concentration expressed as percentage of gaseous (vapor) volume of pure target compound contained in a gaseous volume of sample; also known as mole percent.

3.7. Standard Dry Air: The laboratory bases its analysis/calculations on the following composition:

Nitrogen	78.1%
Oxygen	20.9%
Argon	0.918%
Carbon dioxide	0.034%
% Total	100.000%

3.8. Standard molar volume = 24.45 L/mol at standard conditions (i.e., room temperature of 25°C and standard pressure of 1 atmosphere).

3.9. Standard pressure = 1.0 atmosphere or 14.6 pounds per square inch absolute (psia) or 0 inches of mercury or 0 pounds per square inch gauge (psig), based on laboratory elevation and average barometric pressure.

Note: Full vacuum (0 psia) = -30 inches of mercury vacuum.

3.10. Vacuum/Pressure Gauge: Device used to measure the vacuum or pressure in a passivated canister. Units of measure range from -30 to 0 inches of mercury (for vacuum) to 0 to 30 psig (for positive pressure). All pressure units are converted to psia.

3.11. Further definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

3.12. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

4. INTERFERENCES

4.1. The analytical system is relatively free of interferences due to the multiple column configuration and limited number of similar compounds. Compounds of interest are well separated and there are no major baseline upsets to complicate correct peak integration.

4.2. Contamination may occur in the sampling systems if sample containers are not properly cleaned prior to use.

4.3. Air sample bags should also be shown to be free of contamination at levels one-half the RL for all target analytes.

4.4. All other sampling equipment including pumps, flow controllers, and filters must be thoroughly cleaned and checked for leaks to ensure that the filling apparatus will not contaminate samples.

4.5. The potential for result bias due to carry-over exists. When carry-over is suspected, the sample must be re-analyzed.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Sacramento Addendum to the Corporate EH&S Manual (WS-PEHS-002) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems

associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toed, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Pressurized gas equipment is used in this procedure. Be sure all valves and gauges are operating properly and that no equipment is over-pressurized. After changing cylinders, check all gas line connectors for leaks, with soapy water. Release of high pressure gas can cause rapid suffocation.

Danger: H_2 is a flammable high pressure gas. It can form explosive mixtures with air. It may ignite if the valve is opened to air.

5.1.2. When pressurizing canisters, safety glasses must be worn. If pressure from a canister must be released during this process, a face shield must also be worn.

5.1.2.1. Passivated canisters should never be pressurized over 40 psig.

5.1.3. Pressurized gas cylinders must be securely retained. The use of a face shield is required when changing regulators or disconnecting / connecting cylinders..

5.1.4. Air sample bags must not be pressurized, as seam splitting will occur.

5.1.5. Air sample bags may be used for standard preparation. These must be handled with care and must not be over-filled to prevent them from rupturing. Make sure the valves are closed tightly when not in use.

5.1.6. In order to prevent contamination of the laboratory air by the samples, the vent line must be connected to the system outlet and the fume hood must be turned on.

5.1.6.1. The effluents from the sample splitters for the GC must be vented to a fume hood or at a minimum, must pass through a charcoal filter.

5.1.7. The GC oven contains elevated temperature zones. These zones must be cooled prior to an analyst or technician working on the unit. Temperature appropriate gloves must be worn when working with hot or cold items.

5.1.8. Due to high voltage risk, power to the GC must be turned off or disconnected before work can be done on the instrument.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. There are no materials with a health rating of 3 or 4 used in this method **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methane	Flammable at 5% to 15% in air; Asphyxiate	PEL – Simple Asphyxiant	Exposure via inhalation of the gas. Signs and symptoms of acute exposure may include rapid respiration, muscular incoordination, fatigue, nausea, vertigo, unconsciousness, and death.
Helium	Simple Asphyxiate	Oxygen depletion	Exposure via inhalation of the gas. Rapid respiration, muscular incoordination, fatigue, dizziness, nausea, vomiting, unconsciousness, and death.
Nitrogen	Simple Asphyxiate	Oxygen depletion	Exposure via inhalation of the gas. Rapid respiration, muscular incoordination, fatigue, dizziness, nausea, vomiting, unconsciousness, and death.
Hydrogen	Flammable, Simple Asphyxiate	Oxygen depletion	Exposure via inhalation of the gas. Rapid respiration, muscular in-coordination, fatigue, dizziness, nausea, vomiting, unconsciousness, and death.
Carbon Monoxide	Flammable, poisonous, odorless, Asphyxiate.	Simple Asphyxiant	Exposure via inhalation of the gas. Acts on blood causing damage to central nervous system. Can be fatal even with adequate oxygen. Can form explosive mixtures with air. Symptoms of exposure include shortness of breath, headache, confusion, nausea, dizziness, and unconsciousness.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. Agilent 7890A (or similar) GC equipped with a Front TCD and an Aux TCD

6.1.2. Automated data system capable of archiving instrument runs

6.1.2.1. Chemstation is the data acquisition system.

6.1.2.2. Chrom version 2.1 is the data processing system.

6.2. Supplies

6.2.1. Chromatographic grade stainless steel and/or nickel tubing and chromatographic grade stainless steel connective fittings (Valco, SwageLok, or equivalent)

6.2.2. Stainless steel chromatographic packed columns – HaySep N 1.8 m X 1/8" X 2.0 mm 60/80; Mol Sieve 5A 1.8 m X 1/8" X 2.0 mm 45/60

6.2.3. Assortment of gas-tight syringes from 0.01-mL to 2.0-L volume for standard preparation (Hamilton, SGE, or equivalent)

6.2.4. Pressure regulators for carrier gas, Front TCD/Aux TCD, and standards – single-stage, stainless steel diaphragm

6.2.5. Stainless steel vacuum/pressure gauge capable of measuring from -30 inches of mercury to 30 psig, or transducer and process meter capable of measuring from 0 psia to 50 psia

6.2.6. 7-micron filters (Nupro or equivalent)

6.2.7. Air sample bag, 1- or 3-L (SKC or equivalent)

6.2.8. Passivated canister, 1.0-L, 1.8-L, 6-L or 15-L (SIS, Restek, Anderson Instruments, Rasmussen, or equivalent)

7. REAGENTS AND STANDARDS

All reagents must be ACS reagent grade or better unless otherwise specified.

7.1. Reagents

7.1.1. UHP He for carrier gas, TCD reference gas, sample preparation, and standard preparation

7.1.2. UHP H_2 for detector combustion and the reduction catalyst

7.1.3. Zero-grade air for detector combustion and the oxidation catalyst

7.1.4. UHP N2 for carrier gas, TCD make-up gas, TCD reference gas, sample preparation, and standard preparation

7.2. Primary Gas Standards

7.2.1. Primary gas standards (CH_4, CO_2, CO, N_2, He, H2, and O_2) are available in various concentrations as mixtures or pure components, and analytically certified by the supplier (Scott-Marrin, Scott Specialty, or equivalent).

7.2.2. Dilutions of primary gas standards are made on a volume/volume basis using serial dilution methodologies. UHP N_2 or UHP He is used as the diluent gas.

7.3. Working gas standards

7.3.1. Working gas standards are prepared in passivated canisters or air sample bags by making dilutions of the primary gas standards. See Attachment 3 for the nominal concentration levels used in the initial calibration (ICAL).

7.3.2. Working Gas Standard Prepared in Canisters - To prepare a working gas standard, an aliquot of the primary gas standard or of the pre-mixed primary gas standard is transferred to a clean and evacuated passivated canister. The aliquot is metered in by measuring the vacuum of the canister as the aliquot is being transferred. The ratio of the final canister pressure and the pressure transferred is the dilution factor. The canister is pressurized with UHP N2 or UHP He and is then allowed to equilibrate.

7.3.3. Working Gas Standard Prepared in Air Sample Bags - To prepare a working gas standard, an aliquot of the primary gas standard or of the pre-mixed primary gas standard is transferred to a clean air sample bag. The aliquot is transferred by direct injection with a volumetric gas-tight syringe. The air sample bag is filled with UHP N2 or UHP He to the appropriate volume using a volumetric gas-tight syringe. The air sample bag standard is then allowed to equilibrate.

7.3.4. To calculate the concentration of the standard prepared:

$$ppmv = C_{ps} \times P_i / P_f$$

Where:

C_{ps} = concentration of compound in primary gas standard, ppmv

P_i = aliquot of primary gas standard used in psia or in mL (if using air sample bag)

P_f = final pressure of canister in psia or final volume in mL (if using air sample bag)

7.4. The preparation of each standard is recorded in the Laboratory Information Management System (LIMS).

7.5. Expiration date for standards and reagents are based on vendor specification. If no vendor expiration date is assigned, the laboratory assigns an expiration date of two years from the date of receipt. Refer to TestAmerica SOP WS-QA-0017 for further information on standards and expiration dates. Expiration dates must be documented on the gas cylinders. Expiration of working standards is six months.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample container, preservation techniques, and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements:

Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Passivated Canister	2000 mL	None	30 days	EPA/625/R-96/010b, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air
Passivated Canister	2000 mL	None	30 days	Advisory – Active Soil Gas Investigations FINAL, April 30, 2012 (DTSC and LARWQCB)
Air Sample Bag	500 mL	None	72 hours	N/A

8.2. Passivated canisters used for sample collection must be certified clean (see SOP WS-QA-0032). A 7-micron filter should be placed on the inlet of the canister to protect the valve from particulates.

8.3. Samples should be shipped at room temperature, in packaging suitable to prevent puncture and exposure to light.

8.4. If air sample bags are to be shipped by aircraft, they should be filled about 75% full to allow for expansion during shipment.

8.5. The pressure of a canister should be recorded before and after sample collection in the field to help detect canister leakage and document proper sampling.

8.6. Samples are stored at room temperature.

8.7. When air sample bags are transferred to certified clean canisters within the 72 hour holding time, the holding time is extended to 30 days from date/time of sampling..

8.8. **Important Note:** The information in this section is the minimum laboratory requirements and is communicated to the client via the Sample Acceptance Policy delineated in the section of the QAM that discusses Handling of Samples.

9. QUALITY CONTROL

9.1. Batch

A batch is defined as a set of up to 20 client samples of the same matrix processed using the same procedures and the same lot(s) of reagents within the same time period. A batch must contain a Laboratory Control Sample (LCS) and a Method Blank, but they do not count towards the maximum 20 samples in a batch.

9.1.1. Rerun of the same client sample is counted as part of the 20 in a batch (i.e., a client sample analyzed twice in the same batch must be counted as two client samples).

9.1.2. Field quality control (QC) samples (e.g., trip blanks, equipment blanks, and field duplicates) count as client samples; therefore, they add to the batch count.

9.1.3. Laboratory QC samples, including duplicates and clean canister blanks (screen cans), do not add to the batch count.

9.1.4. In some cases, an LCS Duplicate may be required by a client or program to provide batch precision. In that instance, the acceptance criteria and corrective actions appropriate for the LCS are applied.

9.1.5. The batch must be analyzed sequentially using the same instrument and instrument configuration within the same calibration event. That is, the same calibration curve, calibration factors, or response factors must be in effect throughout the analysis.

9.1.6. Refer to the laboratory's QC Program document (WS-PQA-003) for further details of the batch definition.

9.2. Laboratory Control Sample

For each batch of samples, an LCS must be analyzed after the calibration standard and before the method blank and samples. The LCS is spiked with all the target analytes at concentrations within the calibration range of the method.

9.2.1. If any analyte is outside established recovery and precision control limits, the system is out of control and corrective action must occur. Corrective action typically includes reanalysis of the LCS or the batch. See also the troubleshooting guidelines in Section 11.5.

9.2.1.1. Repeated failures are an indication of a systematic deficiency that must be corrected.

9.2.1.2. For instances when the analytical system is still in control (i.e., analytical system performance is otherwise nominal and no systematic deficiencies are indicated), corrective action is defined as re-analyzing the LCS and/or LCSD after documenting and correcting the exact condition that caused the failure. Such failure may be due, but not limited, to poor standard preparation, low standard pressure, closed standard valve, incorrect or broken sample line used, detector turned off, or low GC supply gas pressure.

9.2.1.3. For instances when the analytical system is not in control (i.e., analytical system performance indicates a systematic deficiency or other defect requiring instrument maintenance or repair), corrective action is defined as the performance of instrument maintenance or repair. After maintenance or repair, the entire batch must be re-analyzed starting with a new initial calibration (ICAL) or a new continuing calibration verification (CCV), depending on whether maintenance or repair was performed.

9.2.2. The LCS/LCSD that failed acceptance criteria should be further evaluated as follows as per the QC program document (QA-PQA-003).

9.2.3. If the batch is not reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. Acceptable reasons for not reanalyzing include evaluation of sporadic marginal exceedances (ME), or an elevated recovery (indicating a high bias) with samples non-detect for the failing analyte. Refer to the QC program document (WS-PQA-003) for more details regarding evaluation and acceptance of out of control LCS data.

9.2.4. Current LCS/LCSD control limits are stored in the LIMS. Control limits are subject to change based on periodic evaluation of LCS/LCSD control charts by Quality Assurance personnel, in accordance with the procedures detailed in policy WS-PQA-003.

9.3. Method Blank

For each batch, an acceptable method blank must be analyzed. The method blank is analyzed after the calibration standards and LCS and prior to client samples. The method blank is typically UHP He collected in either a passivated canister or an air sample bag, or may be obtained directly from the laboratory's He supply line. The method blank for H2 and He analysis is UHP N2. The method blank for CH4 (FID), C2H4, C2H6, and C2H2 analysis is UHP He.

9.3.1. The Method Blank must <u>not</u> contain any analyte of interest $\geq$ RL (or $\geq$1/2 RL, as dictated by the QSM or project-specific requirements. Otherwise, the Method Blank is further evaluated and corrective actions must be performed,

as stated below. See troubleshooting guidelines in Section 11.5.

9.3.1.1. Repeated failures are an indication of a systematic deficiency that must be corrected.

9.3.1.2. For instances when the analytical system is still in control (i.e., analytical system performance is otherwise nominal and no systematic deficiencies are indicated), corrective action is defined as re-analyzing the method blank after documenting and correcting the exact condition that caused the failure. Such failure may be due, but not limited, to sub-ambient method blank pressure, closed method blank container valve, incorrect or broken sample line used, detector turned off, or low GC supply gas pressure.

9.3.1.3. For instances when the analytical system is not in control (i.e., analytical system performance indicates a systematic deficiency or other defect requiring instrument maintenance or repair), corrective action is defined as the performance of instrument maintenance or repair. After maintenance or repair, the entire batch must be re-analyzed starting with a new ICAL or a new CCV, depending on whether maintenance or repair was performed.

9.3.2. Re-analyze the Method Blank once to determine if an error or an anomaly occurred during sample analysis. If the re-analysis is acceptable, then the Method Blank can be considered in control.

9.3.3. If there are no results greater than the RL in the samples or if the results in the samples are greater than 10X the Method Blank level, the data may be reported with qualifiers. In this case, the elevated Method Blank result is not believed to impact data quality. The anomaly must be reported in an NCM.

9.3.4. If there are results greater than the RL in the samples and if these results are less than 10X the Method Blank level, the samples must be re-analyzed.

9.3.4.1. If re-analysis is not possible due to limited sample volume or other constraints, the Method Blank is reported and all associated samples are flagged. The client must be consulted. The anomaly must be reported in an NCM. The laboratory Project Manager (PM) must record the client's decision in the NCM.

10. CALIBRATION

10.1. For details of the calculations used to generate the regression equations, and how to use the factors generated by these equations, refer to CA-Q-P-003, "Calibration Curves & Selection of Calibration Points".

10.2. Initial Calibration

10.2.1. Instruments must be calibrated at initial setup and as needed thereafter, and at least annually. More frequent calibrations must be performed if project-specific requirements dictate.

10.2.2. Prior to sample analysis, an ICAL curve consisting of a minimum of five points at different concentrations is analyzed to determine the linear working range of the analytical system for each target analyte. The lowest calibration level for each target analyte must be at or below the RL. The highest calibration level is considered to represent the upper range of the analytical system for the corresponding target analyte.

10.2.3. The acceptability of the calibration curve for each target analyte is determined by evaluating the percent relative standard deviation (%RSD) of the average CF or RF calculated from the different calibration levels, or by evaluating the correlation coefficient (r) or the coefficient of determination (r2) of the curve.

10.2.3.1. For calibration by average RF, the calibration is deemed acceptable for a given analyte if the %RSD is ≤ 25 (or ≤ 20 for EPA 3C analysis). Peak area is used for this determination.

10.2.3.2. A calibration curve based on linear regression fit is acceptable if r ≥ 0.995 and a minimum of six points is required.

10.2.3.3. A calibration curve based on quadratic (second-order) fit is acceptable if r2 ≥ 0.990 and a minimum of six points is required.

Note: The data acquisition system used for this GC analysis requires forcing the analytical curve through zero. Otherwise, all detections below the lowest point of the calibration curve will not be quantitated.

10.2.4. If the %RSD, r, or r2 does not meet the required acceptance criteria, the corresponding curve is considered invalid and corrective action must be performed. See troubleshooting guidelines and techniques in Section 11.5.

10.2.4.1. Repeated failures are an indication of a systematic deficiency that must be corrected.

10.2.4.2. For instances when the analytical system is still in control (i.e., analytical system performance is otherwise nominal and no systematic deficiencies are indicated), corrective action is defined as re-analyzing the specific calibration level(s) after documenting and correcting the exact condition that caused the failure. Such failure may be due, but not limited, to poor standard preparation, low standard pressure, closed standard container valve, incorrect or broken sample line used, detector turned off, or low GC supply gas

pressure.

10.2.4.3. For instances when the analytical system is not in control (i.e., analytical system performance indicates a systematic deficiency or other defect requiring instrument maintenance or repair), corrective action is defined as the performance of instrument maintenance or repair. After maintenance or repair, all calibration levels must be re-analyzed and re-evaluated to determine if the %RSD, r, or r2 meets acceptance criteria.

10.2.5. A new ICAL is required when situations like, but not limited to, the following are encountered:

- After changes are made to the original ICAL instrument configuration
- After replacement of analytical columns
- After replacement of detectors

10.2.6. The analyst may elect to drop points from the calibration curve to improve subsequent quantitation, in accordance with Policy CA-T-P-002, Selection of Calibration Points.

10.2.7. Initial Calibration Verification (ICV)

Each new multi-point calibration must be verified using a second-source standard. The second-source standard, as quantitated against the new calibration curve, must have recoveries between 80% and 120% for each target analyte. If these criteria are not met, the following corrective actions must be performed:

- Rerun the second-source check standard.
- Re-prepare or acquire a new standard.
- Evaluate instrument conditions or perform maintenance or repair, if needed.
- Re-analyze a new ICAL.

10.2.8. An acceptable ICAL and ICV is documented using a GC Initial Calibration Curve Review Checklist (see Attachment 6). This checklist is submitted to the Department Manager, or designee, for second-level review and signature. Only after successful completion of first and second-level reviews may the analysis be reported from the new ICAL.

10.3. Continuing Calibration Verification

10.3.1. A batch may be started after an approved ICAL and ICV have been completed.

10.3.2. An opening CCV standard is analyzed at the onset of each batch, or every 24-hour shift, whichever comes first, to verify the linearity of the ICAL. The CCV will contain each analyte of interest, on each applicable detector, a different source from that used in the ICV. The system is considered in control if the percent difference (%D) between the RF of the analyte in the CCV and the average RF of the analyte in the ICAL is ± 20 (for both ASTM D1946 and EPA 3C analysis).

10.3.3. If the CCV fails acceptance criteria, corrective actions must be performed. Per the NELAC Standard (Quality Systems, June 5, 2003, Section 5.5.5.10e, pages 216 and 217 of 324) and TNI Standard (EL-V1M4-2009, Quality Systems for Chemical Testing, Section 1.7.2e, page 92), if routine corrective action procedures fail to produce a second consecutive (immediate) CCV within acceptance criteria, then either the laboratory has to demonstrate acceptable performance after corrective action with two consecutive CCVs, or a new ICAL must be generated. See troubleshooting guidelines in Section 11.5.

10.3.3.1. Repeated failures are an indication of a systematic deficiency that must be corrected.

10.3.3.2. For instances when the analytical system is still in control (i.e., analytical system performance is otherwise nominal and no systematic deficiencies are indicated), corrective action is defined as re-analyzing the CCV after documenting and correcting the exact condition that caused the failure. Such failure may be due, but not limited, to poor standard preparation, low standard pressure, closed standard valve, incorrect or broken sample line used, detector turned off, or low GC supply gas pressure.

10.3.3.3. For instances when the analytical system is not in control (i.e., analytical system performance indicates a systematic deficiency or other defect requiring instrument maintenance or repair), corrective action is defined as the performance of instrument maintenance or repair. After maintenance or repair, the CCV (if this still meets the NELAC or TNI requirement stated in Section 9.2.4.3) may be re-analyzed. Otherwise, a new ICAL is required.

10.3.4. Following the last injected sample, the batch is closed with a passing CCV, which must also meet the same acceptance criteria as the opening CCV. Per the NELAC Standard (Quality Systems, June 5, 2003, Section 5.5.5.10c, page 216 of 324) and TNI Standard (EL-V1M4-2009, Quality Systems for Chemical Testing, Section 1.7.2c, page 92), acceptable opening and closing CCVs must bracket reportable samples.

10.3.4.1. If the closing CCV fails acceptance criteria, follow the corrective action procedures defined in Section 10.3.3.

10.3.4.2. If any target analyte or target group in the closing CCV exceeds acceptance criteria and the target analyte or target group was ND in the associated samples, no further corrective action is required. However, the nonconformance must be reported in an NCM.

10.3.4.3. If any sample result is reported from a batch where the closing CCV failed acceptance criteria, the CCV failure must be documented in an NCM. The NCM must indicate the reason why the sample results, in the best judgment of the analyst, are being reported under a failed closing CCV.

10.3.5. If sample analysis must be halted for more than an 8-hour hour period, an opening CCV must be analyzed prior to continuance of the batch, to ensure that instrument conditions have remained stable.

11. PROCEDURE

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file.

Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Sample Preparation

11.2.1. For air sample bag samples, the air sample bag is checked for damage and is analyzed as received. Air samples bags are analyzed from the bag or transferred to an evacuated can within 72 hours of sampling.

11.2.2. For air sample bag that needs to be transferred to a certified clean canister, please follow the procedure as outlined in WS-WI-0036. After the sample bag is transferred to a canister, the holding time is extended to 30 days as listed in Section 8.1.

11.2.3. For passivated canister samples, the initial pressure is checked by attaching the process meter line connector to the passivated canister. The process meter line connector must be rinsed before use, with the pressurization gas (UHP N_2

or UHP He, if requested) by physically holding it against the gas outlet and flushing for 10 seconds, as this avoids possible carry-over concerns from high concentration samples. With the process meter line connector attached, the passivated canister valve is opened briefly and the pressure is recorded. If the pressure is less than 6 psig, the passivated canister is pressurized to 10 psig with the pressurization gas. The initial and final pressure must be recorded in the Canister Pressurization Logbook (see Attachment 7) and in the individual Canister Field Data Record (see example form in SOP WS-QA-0032).

11.2.3.1. If there is an associated analytical test (e.g., EPA TO-14A or EPA TO-15) to the sample that requires use of a mass flow controller to measure injected sample volume, the passivated canisters should be pressurized with UHP N2 only.

11.2.3.2. If UHP N2 is used, then the final GC results must be corrected for N2 content (see Section 11.7).

11.2.3.3. If N2 is also a target analyte, a back calculation/correction factor is used (see Section 11.7 and 12.8.9).

11.2.4. When the passivated canister vacuum/pressure is increased, a dilution factor is calculated and is applied to the results. The calculation is provided in Section 12.8.6.

11.2.5. Pressurizing canister sample with UHP He is an option, if requested by clients. Pressurizing samples with UHP He will eliminate the error associated with N2 correction. EPA TO-14A or EPA TO-15 analysis on samples pressurized with UHP He will require a flow correction factor.

11.2.6. If the canister was previously padded with UHP He, this must be documented as indicated in SOP WS-WI-0038 Section 7.3.7.

11.3. Calibration

11.3.1. Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration must be documented.

11.3.2. Refer to Section 10 for details regarding instrument calibration.

11.4. Sample Analysis

The calibration standards and the sample QC are analyzed in the same manner as client samples. After the calibration standards are analyzed and evaluated (Section 10), the sample QC is analyzed and evaluated (Section 9), all prior to client sample analysis.

11.4.1. Recommend instrument conditions are presented in Attachment 2. If, after instrument maintenance or repair, these parameters change, then the updated parameters must be listed in the instrument maintenance log. The appropriate QC is performed prior to analysis of samples to verify method performance.

11.4.2. For analysis using EPA 3C, all samples must be analyzed in duplicate. The results are acceptable when the peak areas for two consecutive injections agree within 5% of their average (<10% difference between the sample runs). Note that only client samples are analyzed in duplicate. All calibration and sample QC are analyzed once.

11.4.2.1. If the duplicate runs exceed the acceptance criteria, run the sample one more time to confirm that the excessive variation is due to the sample matrix/container and not the analytical system. Otherwise, perform corrective action based on the investigated cause of the variation. See similar corrective actions defined in Section 9.

11.5. Troubleshooting Guidelines and Techniques

11.5.1. Low pressure in canisters containing the standards or problems with carrier/detector gas supply: Always confirm that adequate pressure remains in the canisters and that the instrument gas supplies are sufficient before working on the instrument hardware.

11.5.2. Low Response: Causes are typically leaking detector.

11.5.3. Baseline Noise: Check for supply gas contamination and leaking fittings. Carrier gas filters may need to be changed, including the pencil filters inside the GC. Sample carry-over or contamination may also be an issue and baking the system while flushing sample lines will remove most carry-over.

11.5.4. Valve Switching Issues: Excessive baseline disruptions can be caused by valve actuation when the columns are not properly balanced. Balance the columns by adjusting the carrier restrictors so that head pressure does not change when the column is taken offline.

11.5.5. Instrument Issues: If data loss or error messages are encountered, consult the instrument troubleshooting guidance found in the operator's manual. The manual is in the help section of the GC software.

11.6. Maintenance or Repair of Analytical Instruments or Support Equipment

11.6.1. When analytical instruments or support equipment require repair or maintenance, they shall be taken out of operation or otherwise isolated, and tagged as 'out-of-service' until such a time as the repairs or maintenance have been made and the instrument or support equipment can be demonstrated as operational by calibration and/or verification or other tests to demonstrate acceptable performance. Details on the tag-out procedures to be followed may be found in the section of the QAM that discusses Equipment and Calibrations.

11.6.2. Schedule for routine maintenance of analytical instruments may be found in Attachment 4.

11.6.3. All maintenance or repair must be documented in the Instrument Maintenance Logbook (see example in Attachment 8).

11.7. Monochrom

11.7.1. Monochrom is used for samples being analyzed for D3588/EPA 3C. Samples being analyzed by these methods need to be run through Monochrom for specific calculations needed for those methods. Refer to the Monochrom manual located on the intranet for specific instructions on how to use the Monochrom program.

12. CALCULATIONS/DATA REDUCTION

12.1. After the analytical run has ended, a real-time review of the data is performed to determine if a successful analysis has been achieved. Peaks which exceed the upper calibration range and/or which exceed the signal output of the detector must be diluted and re-analyzed.

12.2. The chromatogram/data is reviewed to determine if the proper dilution has been performed. If the sample was analyzed at the proper dilution, the chromatogram/data is evaluated to determine if proper peak identification and integration was performed.

12.3. A target compound is identified by comparison of the sample analyte RT with that of the standards analyzed within the corresponding batch.

12.4. When a compound has been identified, that compound will be quantitated based on its RF from the ICAL, the integrated area of the peak as determined by the instrument data system, the dilution factor, and the N_2 correction (if applicable).

12.4.1. The data system automatically quantitates the sample results. If a canister sample was pressurized before analysis, the results must be multiplied by the DF (see Section 12.8.7). Correction for N2 (if applicable) must also be performed (see Section 12.8.9).

12.4.2. If, in the best judgment of the analyst, the instrument data system integration is incorrect, then the analyst may manually integrate the peak. See Section 12.7.

12.5. The laboratory reviews the total or summation of the fixed gases reported as part of the data validation process. The review is a secondary check to confirm that valid data acquisition occurred during analysis. The assessment of 95-100% v/v criteria can provide useful information when the analysis is for the full list of fixed gases, but is not required when a subset of compounds is analyzed or reported. If the total fixed gases result is below this range, it is possible that the difference is due to the amount of non-analyzed components in the sample. This case must be investigated. Screening data, NMOC data, subsequent H_2 and He analysis, sulfur compounds analysis, and/or other information should be considered. If the sample containers were pressurized with UHP N_2, then they should be evaluated for error associated with UHP N_2 pressurization. Samples that do not meet the required total fixed gases acceptance criteria and which deviation is not yet accounted for, must be re-analyzed at least once.

12.5.1. An investigation of the deviation from the total or summation acceptance criteria may result into transducer recalibration, instrument maintenance, and/or instrument recalibration. Samples must be re-analyzed after the condition has been remedied. The area supervisor, or designee, should be notified as soon as possible when re-analysis is expected to be outside the sample holding time.

12.5.2. Every time the acceptance criteria for the total or summation of fixed gases result are not met, the deviation and the resulting investigation must be reported in an NCM. The same reporting procedure must be followed for unexplained deviation.

12.6. Second-column confirmation for the results is not required due to the unique separation properties of the multiple column analytical system and the limited possibilities of non-analyte interference.

12.7. All manual or re-integration of chromatograms must be documented in accordance with TestAmerica Corporate SOP CA-Q-S-002. Documentation includes, at a minimum, before and after copies of the chromatograms with a reference to the reason for re-integration, dated, and initialed. All manual integrations must undergo a secondary-level review.

12.8. Calculations

12.8.1. Calculation for RF

$$RF = \frac{\text{Peak Area in Standard}}{\text{Concentration of Standard}}$$

12.8.2. Calculation for RPD

$$\text{RPD} = \frac{\left|\text{Value A - Value B}\right|}{\text{Average of Values}} \times 100$$

12.8.3. Calculation for %RSD

$$\%\text{RSD} = \frac{\text{Std. Dev of RFs}}{\text{Mean of RFs}} \times 100$$

12.8.4. Calculation for %D

$$\%D = \frac{RF\ ICAL - RF\ CCV}{RF\ ICAL} X 100$$

12.8.5. Calculation for %Rec

$$\%\ \text{Re}\,c = \frac{Amount\ cpd.\ recovered}{Amount\ cpd.\ spiked}\ X\ 100$$

12.8.6. Calculation for Pressure DF

$$DF = \frac{Y_a}{X_a}$$

Where:

X_a = absolute canister pressure before dilution (initial pressure)

Y_a = absolute canister pressure after dilution (final pressure)

12.8.7. Calculation for determining concentration of compound in sample, using average RF

$$\text{Conc. Compound} = \frac{\text{Area Compound}}{\text{Ave RF for Compound}} \times \text{DF}$$

12.8.8. Reporting units are typically % v/v for ASTM D-1946 and EPA 3C analysis. If results are to be reported in units of ug/L (also mg/m³), use the following equation:

$$\text{Result (ppmv)} \times \frac{\text{Molecular weight of compound}}{24.45} = \text{ug/L}$$

Note: 24.45 is the volume of ideal gas at 25° C and 1 atmosphere
1% v/v = 10000 ppmv

12.8.9. Calculation for N_2 results in samples pressurized with N_2:

Total amount of N_2:

$$T_{N2} \text{ (as analyzed)} = S_{N2}(I/F) + 100((F-I)/F)$$

Where:

T_{N2} is the result % v/v of N_2 as analyzed (no DF applied)
S_{N2} is the N_2 in the sample (no DF applied)
I and F are the initial pressure and the final pressure, respectively, of the sample during pressurization (psia)
100 is the percent concentration of N_2 added

Rearranging,

$$S_{N2} = (T_{N2} - 100((F-I)/F))F/I$$

Or, in final form with the DF applied:

N_2 reported, % v/v = N_2 total (as analyzed, with DF) – [100 x (DF-1)]

12.9. No conversion of the analytical results to standard conditions is made.

12.10. Calculations for D1945 (Natural Gas)

This calculation is performed automatically by Monochrom.

Before performing the calculations for D1945, the following parameters must be determined:

D1946	TO3	EPA 15_16
CO2, O2, N2, CH4, CO, H2, He	Ethane, Propane, Butane, Pentane, C5 Range, C6 Range, C7 Range, C8 Range, C9 Range, C10+ Range	H2S (optional)

12.10.1. Results for each of the above parameters are normalized by first summing the raw % v/v results for each parameter to determine the total %. The values are then normalized:

$$\text{Normalized Result} = \frac{\text{Raw Result} \times 100}{\text{Total \%}}$$

When the normalized results are summed, they should equal 100%.

Non-detect values are presumed to be 0 for the purposes of this calculation.

12.11. Calculations for D3588

This calculation is performed automatically by Monochrom.

Before performing the calculations for D3588, the following parameters must be determined, and the normalization as described above performed.

D1946	TO3	EPA 15_16
CO2, O2, N2, CH4, CO, H2, He	Ethane, Propane, Butane, Pentane, C5 Range, C6 Range, C7 Range, C8 Range, C9 Range, C10+ Range	H2S (optional)

12.11.1. Three properties are determined for D3588 – Ideal Gross Heating Value, Ideal Net Heating Value, and Specific Gravity. For each property, the contribution from the measured values is calculated by using the property constant and the normalized result:

$$\text{Contribution} = \frac{\text{Normalized Result} * \text{Property Constant}}{100}$$

Units for Gross Heating Value and Net Heating Value are btu/cubic ft.

Parameter	Gross Heating Value Constant	Net Heating Value Constant	Specific Gravity
Carbon Dioxide	0	0	1.5196
Oxygen	0	0	1.1048
Nitrogen	0	0	0.96723
Methane	1010	909.4	0.55392
Carbon Monoxide	320.5	320.5	0.968
Ethane	1769.7	1618.7	1.0382
Propane	2516.1	2314.9	1.5226
n-Butane	3262.3	3010.8	2.0068
n-Pentane	4008.9	3703.9	2.4912
C5 Balance	4008.9	3703.9	2.4912
C6 CPDS	4755.9	4403.9	2.9755
C7 CPDS	5502.5	5100.3	3.4598
C8 CPDS	6248.9	5796.2	3.9441
C9 CPDS	6996.5	6493.6	4.4284
>/= C10 CPDS	7742.9	7189.9	4.9127
Hydrogen Sulfide	637.1	586.8	1.1767
HYDROGEN	324.2	273.93	0.6960
Helium	0	0	0.13820

12.11.2. Once individual values are calculated, the results for each property are summed and reported.

12.12. Technical Data Review

Technical data review is performed in accordance with Policy WS-PQA-012, and is documented utilizing review checklists. Examples of appropriate review checklists are found in Attachments 5 and 6.

12.12.1. One aspect of technical review is to ensure that the test instructions are clear, and that all project-specific requirements have been understood and followed. If directions to the analyst are not clear, the analyst must consult the Department Manager or the appropriate PM, who must clarify the instructions.

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

13.2. Method Detection Limit

The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOP WS-QA-0006. MDLs are available in the Quality Assurance Department.

13.3. Initial Demonstration

The laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for air, soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.3.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be less than or equivalent to the CCV/LCS samples.

13.3.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these to the laboratory generated QC Limits.

13.4. If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

14. POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed,

preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Expired standards will be part of the Lab Pack waste stream. They will be identified as expired, stored under the manufacturer's recommended conditions, and then packed for disposal as outlined in SOP WS-EHS-0001.

15.1.1. Gas standards in non-returnable, non-refillable cylinders, such as Scotty® Transportables, are slowly vented in the fume hood. Once empty, they are turned over to the Hazardous Waste Specialist and damaged (e.g. a hole drilled into the cylinders so they cannot be reused, then they are disposed or recycled.

15.1.2. Gas standards in returnable, refillable cylinders are returned to the manufacturer.

15.2. Air sample bags are slashed in a hood and allowed to completely vent, then placed into an orange high VOA lab trash can. When the can is full or after no longer than one year, tie the plastic bag liner shut and put the lab trash into the appropriate steel collection drum for the incinerator in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment..

16. REFERENCES/CROSS REFERENCES

16.1. ASTM D 1946-90 (Re-approved 2000), Standard Practice for the Analysis of Reformed Gas by Gas Chromatography.

16.2. EPA 3C, Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from stationary sources, 40 CFR Chapter 1, Part 60, Appendix A.

16.3. TestAmerica Sacramento QAM, current revision

16.4. TestAmerica Corporate Environmental Health and Safety Manual CW-E-M-001, current revision

16.5. Advisory – Active Soil Gas Investigations, January 28, 2003 (DTSC and LARWQCB)

16.6. EPA/600/R-04/003, 2003 NELAC Standard, June 5, 2003

16.7. The NELAC Institute (TNI) Standard 2009, Volume 1, Management and Technical Requirements for Laboratories Performing Environmental Analysis

16.8. TestAmerica Corporate SOP CA-Q-S-005, Calibration Curves (General), current revision

16.9. TestAmerica Corporate SOP CA-Q-S-002, Manual Integrations, current revision

16.10. TestAmerica Corporate SOP CA-Q-S-006, Detection Limits, current revision

16.11. TestAmerica Sacramento Safety SOP WS-EHS-0001, Sample and Chemical Waste Characterization, Collection, Storage and Disposal, current revision.

16.12. ASTM D 1945-03 (Re-approved 2010), Standard Test Method for Analysis of Natural Gas by Gas Chromatography

16.13. ASTM D 3588-98 (Re-approved 2011), Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels.

17. METHOD MODIFICATIONS

17.1. ASTM D-1946

17.1.1. The method uses a calibration method in which a separate standard is run closely approximating each sample's concentration for target analytes. TestAmerica Sacramento uses the more widely accepted method of initial multi-point and continuing calibrations to define linear response.

17.1.2. TestAmerica Sacramento does not normalize sample results to 100%, unless required by the client. Normalizing assumes a zero contribution of all other components not analyzed (e.g., H2, He, hydrogen sulfide, etc.), and can affect results significantly.

17.1.3. Commercially-prepared standards that have the industry standard analytical uncertainty of 2-5% are used.

17.1.4. Standards may be prepared in N_2 as well as in He.

17.1.5. The method specifies use of a TCD.

17.1.6. Due to the multi-detector, multi-valve configuration of TestAmerica Sacramento's analytical instrument for fixed gases analysis, one or more sample loops, not necessarily equal to 0.5 mL, may be used.

17.2. EPA 3C

17.2.1. The method specifies use of at least three concentration levels for the multi-point calibration, spanning the range of suspected sample concentrations. TestAmerica Sacramento uses a minimum of five-point calibration on each applicable detector for all standard analyte components, to define the reporting range.

17.2.2. TestAmerica Sacramento does not use correction for moisture content. This would require additional client measurements to be supplied, and at most would result in a 2-3% correction in reported values.

17.2.3. TestAmerica Sacramento does not use correction for temperature at sampling. As the laboratory supplies fully evacuated sample containers for sampling, any field temperature does not affect results. Laboratory temperature is constant for sample pressurization and analysis.

17.2.4. The method specifies that "helium must be used to prepare calibration gases" so that detector response is consistent. TestAmerica Sacramento also uses UHP N2, UHP helium, or zero-grade air to prepare calibration gases. Detector response is unaffected by the diluent gas since the analytical system separates the diluent gas from the standard components prior to detection. Furthermore, sample injection size is determined by a sample loop and not a mass flow controller.

17.2.5. The method specifies that if two consecutive sample injections do not agree within 5% of their average, then run additional samples until consistent area data are obtained. TestAmerica Sacramento requires that only at least one additional injection be analyzed. Refer to Section 11.4.5.

18. ATTACHMENTS

18.1. Attachment 1: Target Analytes and Reporting Limits

18.2. Attachment 2: GC Conditions – Agilent 7890A

18.3. Attachment 3: Nominal ICAL Concentrations

18.4. Attachment 4: Schedule for Routine Maintenance of Analytical Instrument

18.5. Attachment 5: Example GC Initial Calibration Curve Review Checklist

18.6. Attachment 6: Example GC Technical Data Review Checklist

18.7. Attachment 7: Canister Pressurization Logbook (Example Page)

19. REVISION HISTORY

19.1. WC-GCA-0020, Revisioni`.1.4. Effective 11/23/2016

19.1.1. Section 7.8 – Added “When air sample bags are transferred to certified clean canisters, the holding time is extended to 30 days. “

19.1.2. Section 11.2.1 – Added to end of paragraph: “Air samples bags are analyzed from the bag or transferred to an evacuated can within 72 hours of sampling.”

19.1.3. Added Section 11.2.2 – “For an air sample bag that needs to be transferred to a certified clean canister, please follow the procedure as outlined in WS-WI-0036. After the sample bag is transferred to a canister, the holding time is extended to 30 days as listed in Section 8.1.”

19.1.4. /Added Section 11.2.6 – “If the sample was previously padded with UHP He, this must be documented as indicated in SOP WS-WI-0038, Section 7.3.7.

19.1.5. Editorial changes.

19.2. WS-GCA-0020, Revision 1.3, Effective 06/09/2016

19.2.1. Changed Section 11.7.1 Monochrom only used for Method 3C analytes.

19.2.2. Editorial changes.

19.3. WS-GCA-0020, Revision 1.2, Effective 07/25/2014

19.3.1. Added references to D3588 and D1945 in the title and Section 16.

19.3.2. Sections 12.10 and 12.11 were inserted to support the calculations for D3588 and D1945.

19.3.3. Editorial Changes.

19.4. WS-GCA-0020 Revision 1.1, Effective 05/28/2014

19.4.1. Changed Section 2.1 to include – “Carbon monoxide (CO) is last to elute from the HaySep, bypassing the isolated Mol Sieve, then goes to the TCD. Ultra high purity (UHP) helium (He) is used as the carrier gas.

19.4.2. Updated Table in Section 5.2 to include Carbon Monoxide.

19.4.3. Editorial changes.

19.5. WS-GCA-0020, Revision 1, Effective 6/19/2013

19.5.1. Included reference to Chrom as the data processing software in Section 6.1

19.5.2. Change references to SOP LA-QAS-002 and LA-SRA-002 to refer to the appropriate Sacramento SOPs (WS-QA-0017 and WS-QA-0032, respectively).

19.5.3. The first sentence of Section 12.5 has been revised from “The laboratory acceptance criteria for the total or summation of the fixed gases reported must be equal to or greater than 95% v/v, not to exceed 105% v/v.” to “The laboratory reviews the total or summation of the fixed gases reported as part of the data validation process. The review is a secondary check to confirm that valid data acquisition occurred during analysis. The assessment of 95-100% v/v criteria can provide useful information when the analysis is for the full list of fixed gases, but is not required when a subset of compounds is analyzed or reported.”

19.5.4. Inserted “required” into the last sentence of Section 12.5.

19.5.5. Replaced Attachments 5, 6, and 7 with Sacramento-specific examples.

19.5.6. Removed Attachment 8 (example maintenance logbook).

19.5.7. Updated Attachment 3 with current calibration concentrations.

19.5.8. Inserted section 9.1.4, “In some cases, an LCS Duplicate may be required by a client or program to provide batch precision. In that instance, the acceptance criteria and corrective actions appropriate for the LCS are applied.”

19.6. WS-GCA-0020, Revision 0, Effective 04/01/2013

19.6.1. This is the first version of this SOP.

Attachment 1: Target Analytes and Reporting Limits

Compound	RL, % v/v[1]
Carbon Dioxide	0.50
Carbon Monoxide	0.010
Methane	0.50
Nitrogen	1.0
Oxygen	0.20
Helium	0.10
Hydrogen	0.010

Attachment 2: GC Conditions – Agilent 7890A

Fixed Column Oven: 100°C
FID: Oven 250°C, FID Range = 12, Time Constant = Slow
TCD: Oven 130°C, Filament 210°C, Range = 0.5, Polarity = positive, Time constant = slow
Reduction Catalyst: 380°C
Sample Lines and A/S valve at 80°C
Valve Ovens at 120°C
Fixed FF = 20 mL/min, BF = 30 mL/min w/ He reference at 20 mL/min
H_2/He FF=20 mL/min, BF = 20 mL/min w/ N_2 reference at 20 mL/min
FID H_2 20 mL/min + 10 mL/min Red Cat H_2
FID Air = 300 mL/min
Initial time t = 0, all events off
0.01 min: Sample flow starts
1.7 min Sample flow stops with 0.2 min before loop vent
2 min Sample loop injection
3.05 min Mol Sieve Column Isolation
3.5 min H_2/He stripper BF for 4 min relay event time
6.5 min Fixed BF
6.7 min Fixed Mol Sieve in line
Additional events include catalyst recharge and sample advance pre-purge

[1] Note that RLs are subject to change based on annual MDL studies.

Attachment 3: Recommended Nominal ICAL Concentrations (%v/v)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9
Carbon Dioxide	0.01	0.02	0.05	0.2	1.0	5	10	50	100
Carbon Monoxide	0.01	0.02	0.05	0.2	1.0	5	10	50	100
Methane - TCD	0.50	1.0	5.0	10	50	-	-	-	-
Nitrogen	1.0	10	30	80	100	-	-	-	-
Oxygen	0.2	1.0	10	20	30		-	-	-
Helium	0.02	0.1	0.2	1.0	10	50	-	-	-
Hydrogen	0.010	0.1	0.5	1.0	10	50	-	-	-

Attachment 4: Schedule for Routine Maintenance of Analytical Instrument

Frequency	Maintenance Item
Daily	Check for sufficient supply of carrier and detector gases. Check for correct column flow and/or inlet pressures. Check temperatures of injectors and detectors. Verify temperature programs. Check baseline level with analysis of blanks. Inspect chromatogram to verify symmetrical peak shape and adequate resolution between closely eluting peaks.
Quarterly	Oxidation and Reduction Catalysts: Perform leak checks. Replace/condition when poor response is observed.
As needed	All Detectors: Clean when baseline indicates contamination or when response is low. Perform periodic leak checks (quarterly). Replace/condition traps (when poor response or disappearance of reactive or poorly trapped compounds). Bake trap to correct for high background. Replace gas supply. Clean moisture filters. Bake column.

Attachment 5: Example GC Initial Calibration Curve Review Checklist

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sacramento

GCA ICAL Review Checklist

Instrument ID: _____ Method: _____

Work List ID: _____ Analysis Batch(es): _____

Analytes Included in this ICAL: _____

ICAL Review	1st Level	2nd Level	N/A
1. Method locked in Chrom.		X	
2. ICAL is set as most recent method in Chrom.		X	
3. RTC Marker included for and RT TO3 windows set correctly.			
4. Standards used in ICAL are current.			
5. No analytes have saturated peaks.			
6. All peaks correctly identified and within retention time windows.			
7. Manual Integrations reviewed and appropriate.			
8. All analytes meet %RSD or linear regression requirements.			
9. Any levels dropped are reviewed and appropriate.			
10. ICV meets requirements and is run after the ICAL.			
11. RFs are calculated correctly. Perform Manual calculation.			
12. ICAL meets requirements stated in SOP.			
13. Chromatograms are uploaded/reviewed in TALs.			
14. ICAL is locked in TALs.	X		

Curve Valid for:	Yes	No	Criteria
Standard SOP			RSD ≤20%, r≥ 0.995 (intercept <1/2RL for 8081,8082, NQ) and (<RL for 8330) and r>0.990 (intercept <RL for 8015), ICV≤15%, PEM ≤15%
DOD QSM V3,V4, V5			RSD ≤20%, r≥ 0.995, ICV≤20%, PEM ≤15%

1st Level Reviewer: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Comments: _____

_____

_____

_____

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Attachment 6: Example GC Technical Data Review Checklist

TestAmerica
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Sacramento

Air GC Data Review Checklist

Job Number(s): _____ Instrument/Work List ID(s): _____

TALS Analytical Batch(es): _____ ICAL Batch(es): _____

☐ TO3 ☐ TO12 ☐ 1946/3C ☐ EPA 15/16

Review Items	--- Level 1 --- Yes	No	N/A	Level 2
Initial Calibration				
1. Is ICAL locked in Chrom and in TALS?				
2. If RRF used for ICAL, did it meet acceptance criteria? ☐ 20% (8000 series) ☐ ≥ 0.990 (EPA 1516) ☐ 30% (TO-12)				
3. Is ICV properly linked in TALS for Tier 4 jobs ?				
Continuing Calibration				
1. Did %Drift (%D) meet method criteria (30% TO-12) (15% EPA 15/196) (20% QSM TO-3/1946)?				
2. Are compounds within retention time windows?				
3. Does CCV frequency meet criteria (10 samples QSM) or every 20 samples (standard work)?				
4. RTC present for TO3 analytes?				
Client Samples & QC Sample Results				
1. Was the correct analysis performed & were project instructions followed?				
2. Were preparation and analysis completed within holding times?				
3. Are preparation weights/volumes entered correctly?				
4. Have Chromatograms been uploaded/reviewed?				
5. Are positive results within calibration range?				
6. Are any dilutions due to matrix? (Requires NCM if "yes.")				
7. Are all positive results within RT windows, both columns if 2 required?				
8. Are target constituents in LCS/LCSD within control limits?				
9. All target analytes in MB < RL (< ½ RL for DoD)? (Requires NCM if "no.")				
10. Do results (e.g. dilutions) make sense?				
11. Are all manual integrations appropriate and documented properly?				
12. Are nonconformances documented as NCMs?				
13. Are all QC samples properly linked in TALS?				
14. Have all flags been reviewed for appropriateness?				
15. Are all Chrom graphics and reports reviewed/uploaded in the analytical batch?				
16. Has QC checker been run?				
17. NCM numbers:				

1st Level Reviewer: _____ Date: _____

2nd Level Reviewer: _____ Date: _____

Comments: _____

_____

_____

q:\forms\checklists\gca-002_air gc_review 2014-07-16.doc GCA-002 07/16/2014 RKE

Attachment 7: Canister Pressurization Logbook (Example Page)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sacramento

Canister Pressurization Log

Date	Sample ID	Can #	Initial Press. (psig)	Initial Press. (psia)	Final Press. (psig)	Final Press. (psia)	Gauge ID	Initial	Comments
							A B		
							A B		
							A B		
							A B		
							A B		
							A B		
							A B		
							A B		
							A B		
							A B		
							A B		

A = Gauge CD5437; B = Gauge _____

[Calculation: psig + 14.7 = psia]

QA-813 r1 GEC 7/21/2014

PAGE 1

Reviewed by /Date: _____

APPENDIX E FIELD DATA SHEETS

Stantec	Field Report	ESPA-301 Page 1 of 1 Rev. 2.2 Jan 2014

BC & OFFICE	DATE	PAGE	CLIENT
	PROJECT NO.	TASK NO.	SUBCONTRACTOR

TO:	LOCATION	
	WEATHER	TEMP.

CHRONOLOGY OF FIELD ACTIVITIES/ISSUES/OBSERVATIONS

EQUIPMENT USED:	SUBCONTRACTOR HOURS:	STAFF HOURS:
MILEAGE:	REVIEWED BY:	
cc:	PREPARED BY:	

Stantec	Variance / Time Delay Form	ESPA-302	
		Page 1 of 1	
		Rev. 2.2	Jan 2014

Site Name _____

Location _____

Stantec Project No. _____

The purpose of this form is to document variances from the Work Plan scope or design specifications and/or document instances of time delays. Fax or deliver to the Stantec project office with the daily report. Please print legibly.

Variance / Time Delay Began	Variance / Time Delay Ended	Duration of Variance / Time Delay
_____	_____	_____
Date & Time	Date & Time	

Description of Variance

Work Plan Task / Spec Section _____

Reason for Delay AND/OR Variance

Stantec Personnel _____
Print

Signature _____ **Date** _____

Stantec	Waste Management Form	ESPA-303
		Page 1 of 1
		Rev. 2.2 Jan 2014

Project Name _____ **Project Manager** _____

Site Location _____ **Project Number** _____

Date of Generation	Manifest/ Container No.	Waste Type	Type of Waste Container	No. of Containers	Volume of Waste	Company Responsible for Transportation	Date of Off-Site Transpor-tation	Disposal Facility	Waste Characterization Submitted To	Date of Submittal	Date of Disposal

PROJECT: LOCATION: PROJECT NUMBER:	WELL / PROBEHOLE / BOREHOLE NO:

Stantec

ESPA-304/20

DRILLING / INSTALLATION:	
STARTED COMPLETED:	
DRILLING COMPANY:	
DRILLING EQUIPMENT:	
DRILLING METHOD:	
SAMPLING EQUIPMENT:	
NORTHING (ft):	EASTING (ft):
LAT:	LONG:
GROUND ELEV (ft):	TOC ELEV (ft):
INITIAL DTW (ft):	WELL DEPTH (ft):
STATIC DTW (ft):	BOREHOLE DEPTH (ft):
WELL CASING DIA. (in):	BOREHOLE DIA. (in):
LOGGED BY:	CHECKED BY:

Time & Depth (feet)	Graphic Log	USCS	Description	Sample	Time Sample ID	Measured Recov. (feet)	Blow Count	Headspace PID (units)	Depth (feet)
5									5
10									10
15									15

PROJECT:
LOCATION:
PROJECT NUMBER:

WELL / PROBEHOLE / BOREHOLE NO: ESPA-304/40

DRILLING / INSTALLATION:
STARTED COMPLETED:
DRILLING COMPANY:
DRILLING EQUIPMENT:
DRILLING METHOD:
SAMPLING EQUIPMENT:

NORTHING (ft): EASTING (ft):
LAT: LONG:
GROUND ELEV (ft): TOC ELEV (ft):
INITIAL DTW (ft): WELL DEPTH (ft):
STATIC DTW (ft): BOREHOLE DEPTH (ft):
WELL CASING DIA. (in): BOREHOLE DIA. (in):
LOGGED BY: CHECKED BY:

Time & Depth (feet)	Graphic Log	USCS	Description	Sample	Time Sample ID	Measured Recov. (feet)	Blow Count	Headspace PID (units)	Depth (feet)
5									5
10									10
15									15
20									20
25									25
30									30
35									35

Stantec	Test Pit Record	ESPA-309	
		Page 1 of 1	
		Rev. 1.2	Jan 2014

CLIENT: _____ **LOCATION:** _____

PROJECT NO.: _____ **DATUM:** _____

DATE: _____ **WATER LEVEL (ft bgs):** _____

LOGGED BY: _____ **PIT DEPTH (ft bgs):** _____

APPROVED BY: _____ **TEST PIT NO. TP-**_____

DEPTH (ft bgs)	ELEVATION (ft)	Soil Description	STRATA PLOT	WATER LEVEL	SAMPLE TYPE	SAMPLE Number	OTHER TESTS	UNDRAINED SHEAR STRENGTH – skf (20, 40, 60, 80) / WATER CONTENT & ATTERBERG LIMITS (w_P, w, w_L) (10 20 30 40 50 60 70 80 90)
0								
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								

Non-Degreed Professional (User) requiring gINT: _____

Office Location / BC #: _____

1.0 PURPOSE & APPLICABILITY

The purpose of this document is to request the approval of gINT use by professionals without a civil/geotechnical engineering or geology degree. The step-by-step procedures described in the **gINT Use By Professionals Without A Civil/Geotechnical Engineering Or Geology Degree SOP** will allow personnel to acquire and use gINT for professionals without an appropriate degree.

We are requesting gINT be added to the above referenced individual's software package. We have read and understand the **gINT Use By Professionals Without A Civil/Geotechnical Engineering Or Geology Degree SOP**.

User Name	_____	User Signature	_____	Date	_____
BCML Name	_____	BCML Signature	_____	Date	_____
Licensed Reviewer Name	_____	Licensed Reviewer Signature	_____	Date	_____
Licensed Reviewer License #	_____				

At the end of a field work day, the field notebook should contain a detailed record of events, activities, developments, and personnel involved in the site work in the form of signed and dated entries as a legal record. As such, it must be complete and in sufficient detail that, if necessary, a person not at the site could reconstruct the day's events. Information that should be entered in the field notebook each day includes, as applicable:

- Date, including year.
- Project name, number, and location.
- Purpose of visit.
- A list of Stantec, client, agency, and subcontractor personnel on site.
- Relevant weather conditions (especially significant precipitation events, temperature, wind speed and wind direction) and significant changes throughout the day.
- Times during the day recorded in military time to mark events or significant milestones.
- Any unusual circumstances, observations, or occurrences.
- Communications with client or agencies, property owners, or managers.
- Subcontractor progress and/or problems and results of subcontractor inspections.
- Notes regarding any changes to or deviations from the FSP, QAPP, or HASP, with the rationale for changes.
- Observations such as species identifications or evidence of biological stress,
- Sampling or monitoring instruments used and all equipment calibrations.
- Results of measurements, such as sampler flow rate checks, VOCs, DO, temperature, pH, animal, or plant counts, etc. Record all non-detected values using the "less than" symbol and detection limit (*e.*g., <10 ppmv). Record all units of measure clearly.
- Equipment repairs or maintenance.
- Time of occurrence and nature of any equipment or mechanical malfunctions.
- A list of samples collected, noting sample number, sampling depths, analyses to be conducted, shipping date, time, and destination.
- Identification of quality assurance samples (blanks, duplicates, replicates, etc.).
- Chain-of-custody form numbers associated with each batch of samples shipped.
- Calculations (e.g., determination of monitoring well volumes, or ichthyoplankton net depth and sample volume).
- List of all photographs taken, giving a description of the subject matter, orientation of view, time, photographer's name, and image number.
- Initial each page and sign and date the field notebook on the last page for each day.
- "X" out any unused space on each page of the notebook.
- Strike out and initial any changes to the field notes.

Field Supplies Checklist

ESPA-602

Page 1 of 1

Rev. 2.2 Jan 2014

	PLANNING MATERIALS
	Proposal/work plan
	Existing report data
	Cross-sections
	Site plan
	Phone list
	Access agreement
	ROW permit
	Shipping airbills
	NOTE-TAKING SUPPLIES
	Field notebook OR Field Report
	Aluminum clipboard
	Borehole logs/well diagrams
	Munsell color chart
	Surveying forms
	Sampling data forms
	O&M data forms
	Permanent markers
	Pencils
	Ruler
	Camera/film/digital storage
	Camera charger/batteries
	Protractor
	Calculator
	HEALTH & SAFETY SUPPLIES
	Health & Safety certifications
	HASP
	PPE card
	NIOSH Pocket Guide
	Hard hat
	Steel-toed boots
	Safety glasses
	Water resistant boots
	Reflective vest
	Insulated coveralls
	Rain suit
	Respirator and canisters
	Work gloves
	Nitrile gloves
	Latex gloves
	Viton gloves
	Tyvek suits
	Saranex suits
	Boot covers
	Vehicle safety light
	Barricades
	Traffic cones
	First aid kit/eyewash kit
	Face shield

	DISPOSABLE SUPPLIES
	Paper towels
	Aluminum foil
	Spray paint
	Trash bags
	Non-phosphate detergent
	Distilled water
	Cleaning brushes
	Funnel
	Ziploc® bags
	Duct tape
	Stakes
	Flagging
	Cooler
	Ice and/or blue ice
	Table/chair
	Sample tube cutter
	Socket set
	Pipe wrenches
	Screw drivers
	Knife
	Electrical tape
	Stainless trowel
	100-foot surveyor's tape
	Measuring wheel
	25-foot steel measuring tape
	Rock hammer
	Sledge hammer
	Pry Bar
	Shovel
	Hand auger
	Post hole digger
	Broom
	Snow shovel
	Flashlight
	Hand mirror
	METERS
	Water level meter
	Interface probe
	DO meter
	Eh meter
	pH meter
	Conductivity meter
	PID or FID
	Draeger pump & tubes
	O_2/CO_2 Meter
	Calibration solutions
	HACH kits
	Electrical multimeter
	Pitot tube kit
	Anemometer
	Magnehelic gauges
	Flow meter
	Cathodic protection meter

	SAMPLING EQUIPMENT
	Peristaltic pump
	Flexible tubing
	Tubing
	Flow-through cell
	1-inch bailers
	2-inch bailers
	4-inch bailers
	Stainless steel bailer
	Cotton string
	5-gallon buckets
	Purge trailer
	Sample vials
	Sample bottles
	Sample jars
	Air sampling tubes
	Metals filters
	Water/gasoline paste
	LABELS
	COCs
	COC seals
	Sample labels
	Drum waste labels
	Sample labels
	Drum waste labels
	SPECIALIZED EQUIPMENT
	Laptop
	Data logger/transducer
	Air compressor
	Air pump
	Pipe fittings
	Knockout drum
	Hoses
	Concrete mix
	Blower
	Generator
	Drill & bits
	Car battery
	Metal detector
	Auto level, tripod & rod
	Slug

Order for Fine-Grained Soil Logging Descriptions

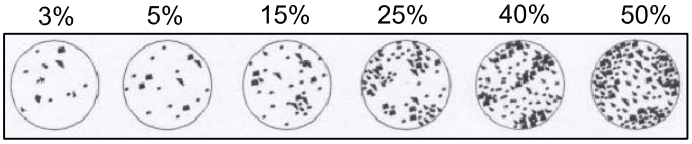
Item 1	Group name, grain size distribution	See page 2: Group name can include modifiers trace; little; some; with; "-y"; e.g.; silty; See grain size distribution table below for Item 1
Item 2	Group Symbol	See page 2
Item 3	Color	Munsell color codes; shade; secondary and primary color names
Item 4	Particle-size range	Gravel: fine or coarse; sand: fine, medium, or coarse
Item 5	Plasticity of fines	Non-plastic; low; medium; high
Item 6	Consistency	Very soft; soft; firm; hard; very hard
Item 7	Moisture Condition	Dry; moist; wet
Item 8	Odor	No; slight; moderate; strong
Item 9	Staining	No; hydrocarbon; iron oxide
Item 10	Structure	Stratified; laminated; fissured; slickensided; lensed and homogeneous
Item 11	Comments	Odor type; reaction with HCl; roots; mica; gypsum; surface coatings on coarse grains; caving or sloughing of hole; drilling difficulties; dry strength; dilatancy; toughness; etc.

PART OF ITEM 1 Grain Size Distribution

Term	Criteria	Description
Trace	0 to 5%	Minor fractions for both fine- and coarse-grained materials
Little	6 to 10%	Minor fractions for both fine- and coarse-grained materials
Some	11 to15%	Minor fractions for both fine- and coarse-grained materials
With	16 to 25%	Minor fractions for both fine- and coarse-grained materials
"-y"	26 to 49%	Suffix for minor fractions for only fine-grained material, e.g., silty

ITEM 5 Plasticity

Term	Criteria
Non-plastic	A 1/8 inch (3 mm) thread cannot be rolled at any water content.
Low	The thread can barely be rolled and the lump cannot be formed when drier than the plastic limit.
Medium	The thread is easy to roll and not much time is required to reach the plastic limit. The thread cannot be rerolled after reaching the plastic limit. The lump crumbles when drier than the plastic limit.
High	It takes considerable time rolling and kneading to reach the plastic limit. The thread can be rerolled several times after reaching the plastic limit. The lump can be formed without crumbling when drier than the plastic limit.



ITEM 6 Consistency

Term	Criteria
Very Soft	Thumb will penetrate soil more than 1 in. (25 mm)
Soft	Thumb will penetrate soil about 1 in. (25 mm)
Firm	Thumb will indent soil about 1/4 in. (6 mm)
Hard	Thumb will not indent soil, but readily indented with thumbnail.
Very Hard	Thumb will not indent soil.

ITEM 7 Moisture Condition

Term	Criteria
Dry	Absence of moisture, dusty, dry to touch
Moist	Damp, but no visible water
Wet	Visible free water, usually soil is below the water table

ITEM 10 Structure

Term	Criteria
Stratified	Alternating layers of varying material or color with layers at least 6 mm thick; note thickness
Laminated	Alternating layers of varying material or color with layers less than 6 mm thick; note thickness
Fissured	Breaks along definite planes of fracture with little resistance to fracturing
Slickensided	Fracture planes appear polished or glossy, sometimes striated
Blocky	Cohesive soil that can be broken down into small angular lumps, which resist further breakdown
Lensed	Inclusion of small pockets of different soils, such as small lenses of sand scattered through a mass of clay; note thickness
Homogeneous	Same color and appearance throughout

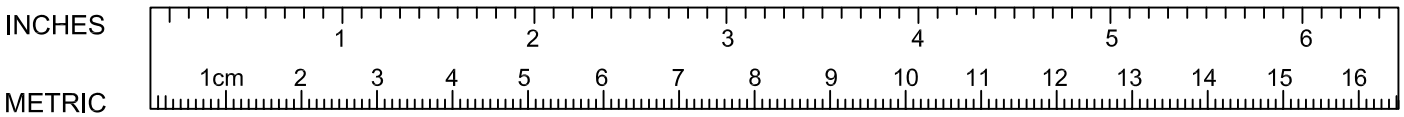
PART OF ITEM 11 Reaction with HCl

Term	Criteria
None	No visible reaction
Weak	Some reaction, with bubbles forming slowly
Strong	Violent reaction, with bubbles forming immediately

PART OF ITEM 11 Identification of Inorganic Fine-Grained Soils from Manual Tests

USCS	Dry Strength	Dilatancy	Toughness
ML	None to low	Slow to rapid	Low or thread cannot be formed
CL	Medium to high	None to slow	Medium
MH	Low to medium	None to slow	Low to medium
CH	High to very high	None	High

REFERENCES:
AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) D–2488–00 "STANDARD PRACTICE FOR DESCRIPTION AND IDENTIFICATION OF SOILS (VISUAL–MANUAL PROCEDURE)"
UNITED STATES BUREAU OF RECLAMATION (2002). ENGINEERING GEOLOGY FIELD MANUAL, 2ND EDITION, 2002: 563pp. GOVERNMENT PRINTING OFFICE ISBN 0–16–067623–1.



REPRODUCE ONLY AT 100% TO PRESERVE SCALES

PART OF ITEM 1 Flow Chart for Identifying Inorganic Fine-Grained Soil (50% or more fines)

GROUP SYMBOL				GROUP NAME
CL	<30% plus No. 200	<15% plus No. 200		Lean clay
		15-25% plus No. 200	% sand ≥% of gravel	Lean clay with sand
			% sand <% of gravel	Lean clay with gravel
	≥30% plus No. 200	% sand ≥% of gravel	<15% gravel	Sandy lean clay
			≥15% gravel	Sandy lean clay with gravel
		% sand <% of gravel	<15% sand	Gravelly lean clay
			≥15% sand	Gravelly lean clay with sand
ML	<30% plus No. 200	<15% plus No. 200		Silt
		15-25% plus No. 200	% sand ≥% of gravel	Silt with sand
			% sand <% of gravel	Silt with gravel
	≥30% plus No. 200	% sand ≥% of gravel	<15% gravel	Sandy silt
			≥15% gravel	Sandy silt with gravel
		% sand <% of gravel	<15% sand	Gravelly silt
			≥15% sand	Gravelly silt with sand
CH	<30% plus No. 200	<15% plus No. 200		Fat clay
		15-25% plus No. 200	% sand ≥% of gravel	Fat clay with sand
			% sand <% of gravel	Fat clay with gravel
	≥30% plus No. 200	% sand ≥% of gravel	<15% gravel	Sandy fat clay
			≥15% gravel	Sandy fat clay with gravel
		% sand <% of gravel	<15% sand	Gravelly fat clay
			≥15% sand	Gravelly fat clay with sand
MH	<30% plus No. 200	<15% plus No. 200		Elastic silt
		15-25% plus No. 200	% sand ≥% of gravel	Elastic silt with sand
			% sand <% of gravel	Elastic silt with gravel
	≥30% plus No. 200	% sand ≥% of gravel	<15% gravel	Sandy elastic silt
			≥15% gravel	Sandy elastic silt with gravel
		% sand <% of gravel	<15% sand	Gravelly elastic silt
			≥15% sand	Gravelly elastic silt with sand

NOTE: Percentages are based on estimating amounts of fines, sand, and gravel to the nearest 5%.

PART OF ITEM 1 Flow Chart for Identifying Organic Fine-Grained Soil (50% or more fines)

GROUP SYMBOL				GROUP NAME
OL/OH	<30% plus No. 200	<15% plus No. 200		Organic soil
		15-25% plus No. 200	% sand ≥% of gravel	Organic soil with sand
			% sand <% of gravel	Organic soil with gravel
	≥30% plus No. 200	% sand ≥% of gravel	<15% gravel	Sandy organic soil
			≥15% gravel	Sandy organic soil with gravel
		% sand <% of gravel	<15% sand	Gravelly organic soil
			≥15% sand	Gravelly organic soil with sand

NOTE: Percentages are based on estimating amounts of fines, sand, and gravel to the nearest 5%.

ITEM 2 Group Symbols

Grain Size	Soil Type	USCS	Pattern	Group Description
Fine-Grained Soils; More Than Half is Smaller Than Number 200 Sieve (0.003" or 0.0075 mm)	Silts And Clays	ML		Inorganic silts and very fine sands, rock flour, silty or clayey fine sands, or clayey sands with slight plasticity
		CL		Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, lean clays
		MH		Silt of high plasticity, elastic silts
		CH		Inorganic clays of high plasticity; fat clays
Highly Organic Soils		PT		Peat or other highly organic soils
		OL		Organic soil with few coarse grains
		OH		Organic soil with coarse grained material

Order for Coarse-Grained Soil Logging Descriptions

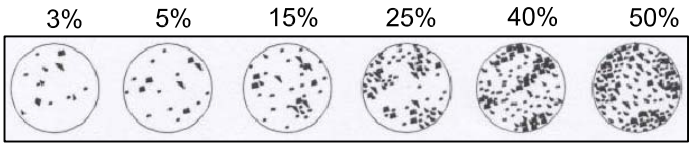
Item 1	Group name, grain size distribution	See page 2: Group name can include modifiers trace; little; some; with; "-y"; e.g., silty; See grain size distribution table below for Item 1
Item 2	Group Symbol	See page 2
Item 3	Color	Munsell color codes; shade, secondary, and primary color names
Item 4	Particle-size range	Gravel: fine or coarse; sand: fine, medium, or coarse
Item 5	Density	Very loose; loose; medium dense; dense; very dense
Item 6	Moisture Condition	Dry; moist; wet
Item 7	Odor	No; slight; moderate; strong
Item 8	Staining	No; hydrocarbon; iron oxide
Item 9	Structure	Stratified; laminated; fissured; slickensided, etc.
Item 10	Cementation	Weak; moderate; strong
Item 11	Particle Angularity	Angular; subangular; subrounded; rounded
Item 12	Gradation	Weak; moderate; strong See Page 2
Item 13	Mineralogy	Argillaceous; calcareous; carbonaceous; dolomitic; feldspathic; ferruginous; lithic; dolomitic; micaceous; manganese; pyritic; quartz; sideritic; siliceous
Item 14	Comments	Odor type; reaction with HCl; roots; mica; gypsum; surface coatings on coarse grains; caving or sloughing of hole; drilling difficulties; dry strength; dilatancy; toughness; etc. See Page 2

PART OF ITEM 1 Grain Size Distribution

Term	Criteria	Description
Trace	0 to 5%	Minor fractions for both fine- and coarse-grained materials
Little	6 to 10%	Minor fractions for both fine- and coarse-grained materials
Some	11 to15%	Minor fractions for fine-grained materials
With	16 to 25%	Minor fractions for fine-grained materials
"-y"	26 to 49%	Suffix for minor fractions for only fine-grained material, e.g., silty

ITEM 4 Grain Size

Term	Size (mm)	Size (Inches)	Scale size
Cobbles	75 to 300	3 to 12	Fist-size to basketball
Coarse gravel	19 to 75	3/4 to 3	Thumb-size to fist-size
Fine gravel	4.75 to 19	3/16 to 3/4	Pea-size to thumb size
Coarse sand	2.0 to 4.75	1/16 to 3/16	Rock salt-size to pea-size
Medium sand	0.0425 to 2.0	1/64 to 1/16	Sugar-size to rock salt-size
Fine sand	0.0075 to 0.0425	0.003 to 1/64	Flour-size to sugar-size
Silt/Clay	<0.0075	<0.003	Flour-size and smaller



ITEM 5 Density

Term	SPT N (blows/ft)	Field Test
Very Loose	0 to 4	-
Loose	5 to 10	Easily penetrated with 1/2-inch rod pushed by hand
Medium dense	11 to 30	Easily penetrated with 1/2-inch rod driven with a 5-pound hammer
Dense	31 to 50	Penetrated with 1/2-inch rod driven with a 5-pound hammer
Very dense	>50	Penetrated only 2/3 with 1/2-inch rod driven with a 5-pound hammer

ITEM 6 Moisture Condition

Term	Criteria
Dry	Absence of moisture, dusty, dry to touch
Moist	Damp, but no visible water
Wet	Visible free water, usually soil is below the water table

ITEM 9 Structure

Term	Criteria
Stratified	Alternating layers of varying material or color with layers at least 6 mm thick; note thickness
Laminated	Alternating layers of varying material or color with layers less than 6 mm thick; note thickness
Fissured	Breaks along definite planes of fracture with little resistance to fracturing
Slickensided	Fracture planes appear polished or glossy, sometimes striated
Blocky	Cohesive soil that can be broken down into small angular lumps, which resist further breakdown
Lensed	Inclusion of small pockets of different soils, such as small lenses of sand scattered through a mass of clay; note thickness
Homogeneous	Same color and appearance throughout

ITEM 10 Cementation

Term	Criteria
Weak	Crumbles or breaks with handling or little finger pressure
Moderate	Crumbles or breaks with considerable finger pressure
Strong	Will not crumble or break with finger pressure

ITEM 11 Particle Angularity

Term	Criteria
Angular	Particles have sharp edges and relatively planer sides with unpolished surfaces
Subangular	Particles are similar to angular criteria, but have rounded edges
Subrounded	Particles have nearly planar sides, but have well-rounded corners and edges
Rounded	Particles have smoothly curved sides and no edges

REFERENCES:
AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) D-2488-00 "STANDARD PRACTICE FOR DESCRIPTION AND IDENTIFICATION OF SOILS (VISUAL-MANUAL PROCEDURE)"
UNITED STATES BUREAU OF RECLAMATION (2002). ENGINEERING GEOLOGY FIELD MANUAL, 2ND EDITION, 2002: 563pp. GOVERNMENT PRINTING OFFICE ISBN 0-16-067623-1.

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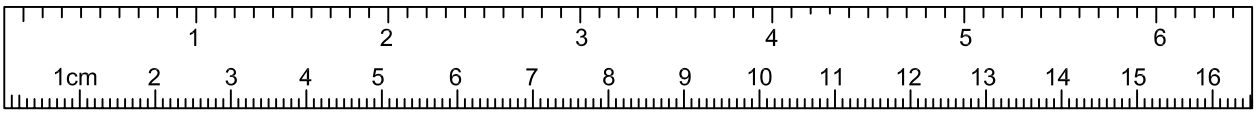
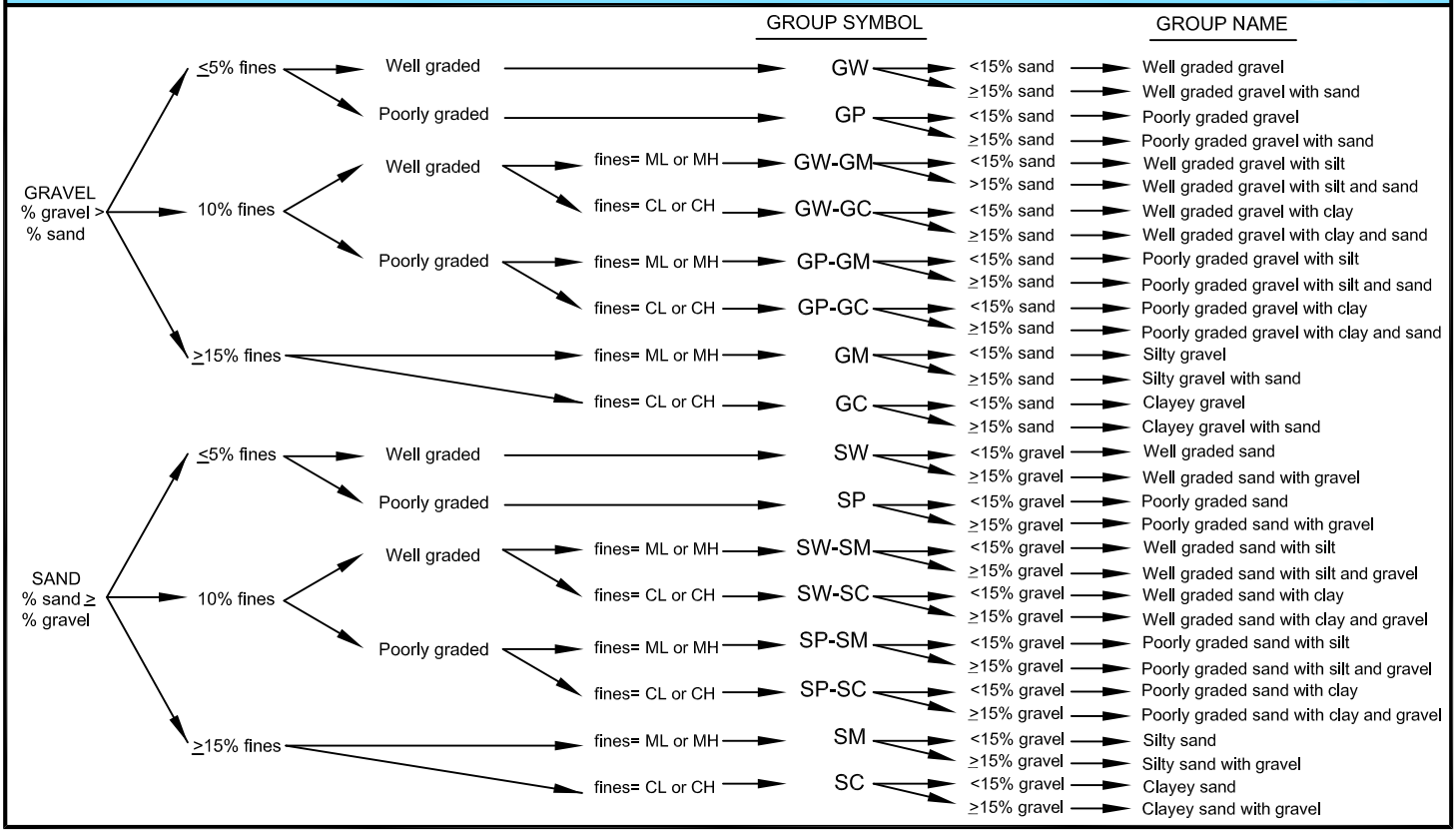


METRIC

REPRODUCE ONLY AT 100% TO PRESERVE SCALES

PART OF ITEM 1 Flow Chart for Identifying Coarse-Grained Soils (less than 50% fines)



NOTE: Percentages are based on estimating amounts of fines, sand, and gravel to the nearest 5%.

ITEM 2 Group Symbols

Grain Size	Soil Type		USCS	Pattern	Group Description
Coarse Grained Soils More Than Half Is Larger Than Number 200 Sieve (Fines) (0.003" or 0.0075mm)	Gravels More Than Half Coarse Fraction Is Larger Than Number 4 Sieve (3/16" or 4.75mm)	Clean Gravels With Little Or No Fines	GW		Well graded gravels, gravel-sand mixtures
			GP		Poorly graded gravels, gravel-sand mixtures
		Gravels With Over 15% Fines	GM		Silty gravels, poorly graded gravel-sand-silt mixtures
			GC		Clayey gravels, poorly graded gravel-sand-clay mixtures
	Sands More Than Half Coarse Fraction Is Smaller Than Number 4 Sieve (3/16" or 4.75mm)	Clean Sands With Little Or No Fines	SW		Well graded sands, gravelly sands
			SP		Poorly graded sands, gravelly sands
		Sands With Over 15% Fines	SM		Silty sands, poorly graded sand-silt mixtures
			SC		Clayey sands, poorly graded sand-clay mixtures

ITEM 12 Gradation

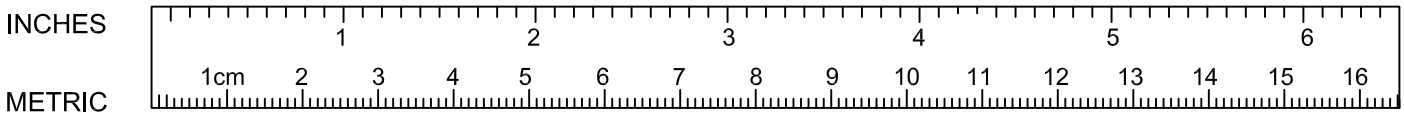
Term	Criteria
Well graded	Sand/gravel has a wide range of grain size (3 sieve sizes) and substantial amounts of intermediate particle sizes
Poorly graded	Sand/gravel predominantly of one grain size
Moderately graded	Sand/gravel has moderate range of grain sizes (2 sieve sizes)
Gap gradation	Sand/gravel consists of a wide range of grain sizes with some intermediate sizes obviously missing

PART OF ITEM 14 Reaction with HCl

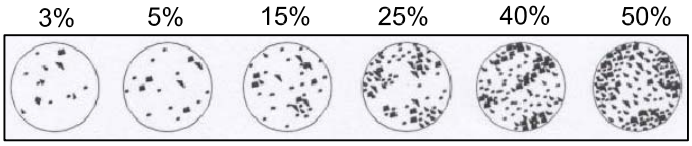
Term	Criteria
None	No visible reaction
Weak	Some reaction, with bubbles forming slowly
Strong	Violent reaction, with bubbles forming immediately

Order for Rock Logging			
Item 1	Rock type	Sedimentary	Conglomerate; breccia; sandstone; wacke; siltstone; claystone; mudshale; clayshale; iron formation; bituminous coal; boundstone; grainstone; packstone; wackestone; mudstone; halite; gypsum; anhydrite; dolomite; chert
		Igneous	Granite; aplite; rhyolite; diorite; granodiorite; rhyodacite; dacite; monzonite; syenite; felsite; latite; trachyte; trachyandesite; andesite; gabbro; basalt; peridotite; lamprophyre; diabase; pyroclastic breccia; lapilli tephra; coarse ash tuff; fine ash tuff; obsidian; volcanic glass; pumice; scoria; cinders
		Metamorphic	Amphibolite; gneiss; schist; mylonite; argillite; slate; phyllite; fault breccia; carbonaceous; pyritic; feldspathic; sideriditic; micaceous
Item 2	Mineralogy		Quartz; siliceous; argillaceous; ferruginous; dolomitic; lithic; calacareous; carbonaceous; pyritic; feldspathic; sideriditic; micaceous
Item 3	Color	Hue	10R; 2.5YR; 5YR; 7.5YR; 10YR; 2.5Y; 5Y
		Value	2.5/; 3/; 4/; 5/; 6/; 7/; 8/; N2/; N3/; N4/; N5/; N6/; N7/; N8/
		Chrome	0, 1, 2, 3, 4, 6, 8 (there is no 5 nor 7)
		Shade	Strong; very light; light; dark; very dark; very pale; pale; dusky; very dusky; weak
		Secondary color	Brownish; reddish; grayish; greenish; bluish; yellowish; pinkish; olive
		Primary color	Brown; black; red; gray; white; green; blue; blue green; olive; yellow; pink; purple
Item 4	Texture/Grain size	Granular	Coarse
		Crystalline	Crystalline; medium crystalline; finely crystalline; very finely crystalline; microcrystalline
Item 5	Field Strength		Extremely soft; very soft; soft; medium hard; hard; very hard; extremely hard
Item 6	Moisture		Dry; moist; wet; dripping; flowing
Item 7	Odor		No; slight; moderate; strong
Item 8	Staining		No; hydrocarbon; iron oxide
Item 9	Structure Thickness		Very thickly; thickly; medium; thinly; very thinly
Item 10	Structure		Uniform; bedded; foliated; banded
Item 11	Primary Sedimentary Structure		Interbedded; horizontal; rhythmic; crossbedded; inclined; ripple; flaser; wavy; lenticular; flow banded; graded
Item 12	Secondary Sedimentary Structure		Disturbed; rooted; bioturbated; fossilliferous
Item 13	Bedding Angle		0, 15, 30, 45, 60, 75, 90
Item 14	Fracture/Joint spacing		Very close; close; medium; wide; very wide
Item 15	Discontinuity	Contact	Conformable; unconformable; sharp; gradational; erosional
		Type	Bedding fracture; cleavage fracture; fault; incipiant fracture; induced fracture; joint
		Aperture Observation	Calcite coating; chlorite coating; clean; gypsum coating; infilled; soil infilling; surface staining; veneer
		Infilling	Calcite; chlorite; clay; gypsum; talc; mica
		Persistance	Continuous in cores; discontinuous; very high; high; medium; low; very low
		Planarity	Planar; stepped; stepped to undulating; undulating; undulating to planar
		Roughness	Rough; rough to smooth; rough to striated; smooth; smooth to striated; striated
		Surface Appearance	Matte; polished
Item 16	Weathering		Freshly; slightly; moderately; highly; completely
Item 17	Geological Formation		User defined
Item 18	Local Name		User defined
Item 19	Comments		Unusual field observations, such as Rock Quality Designation (RQD), odor type. Discontinuities including: dip, direction, waviness wavelength, waviness amplitude, joint roughness, coefficient, aperture, termination, wall strength, seepage rating, water flow, and other comments

REFERENCES:
AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) D-2488-00 "STANDARD PRACTICE FOR DESCRIPTION AND IDENTIFICATION OF SOILS (VISUAL-MANUAL PROCEDURE)"
UNITED STATES BUREAU OF RECLAMATION (2002). ENGINEERING GEOLOGY FIELD MANUAL, 2ND EDITION, 2002: 563pp. GOVERNMENT PRINTING OFFICE ISBN 0-16-067623-1.



REPRODUCE ONLY AT 100% TO PRESERVE SCALES



APPENDIX F FIELD SOPS

1.0 PURPOSE & APPLICABILITY

The purpose of this document is to define the standard operating procedure (SOP) for collecting soil samples when drilling with hollow-stem augers, direct push, and hand auger methods. The ultimate goal of the sampling program is to obtain samples that meet acceptable standards of accuracy, precision, comparability, representativeness, and completeness. All steps that could affect tracking, documentation, or integrity of samples have been explained in sufficient detail to allow different sampling personnel to collect samples that are equally reliable and consistent.

This procedure provides descriptions of equipment, field procedures, sample containers, decontamination, documentation, decontamination, storage, holding times, and field quality assurance (QA) and quality control (QC) procedures necessary to collect soil samples.

While the Project Quality Assurance Project Plan (QAPP) is intended to be strictly followed, it must be recognized that field conditions may force some modifications to the SOP. Any modification to the procedure shall be approved by the Project Manager or Task Leader in advance. Where SOP modification is planned sufficiently in advance, regulatory agency concurrence will be sought prior to conducting the specific activity. When direct contact with regulatory agency staff is not possible, or unscheduled delays will result, such as during field activities, regulatory agency will be notified of deviations from the SOPs, in writing, as soon as possible after the occurrence.

2.0 DEFINITIONS

HASP	Health and Safety Plan
OSHA	Occupational Safety and Health Administration
PID	Photoionization Detector
PPE	Personal Protective Equipment
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
QAPP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
USCS	Unified Soil Classification System
VOA	Volatile Organic Analysis
VOCs	Volatile Organic Compounds

3.0 HEALTH AND SAFETY CONSIDERATIONS

Refer to the site-specific Health and Safety Plan (HASP) for health and safety considerations applicable to soil sampling.

Many hazards should be considered during the soil sampling activities, careful consideration of these hazards by the project team is essential. Some of the hazards include the following:

- Proper utility clearance must be performed in accordance with the Pre-Drilling/Excavation Checklist and Utility Clearance Log. There must be a minimum clearance of five (5) feet in addition to the diameter of the drilling augers. Client-specific requirements may be more restrictive.

- Traffic control may be required depending on the proximity of soil sampling activities to the roadway. Traffic control plans should be carefully evaluated to adequately delineate the work zone and provide the necessary safety factors.

- Personal protective equipment (PPE) including hard hats, high visibility traffic vest, gloves, hip boots or chest waders and other appropriate clothing;

- Heat and cold stress;

- Biological hazards such as insects and spiders. Appropriate clothing is required such as long-sleeved shirts and long pants.

- Bloodborne pathogens. Some of our sites may have syringes and other drug paraphernalia that must be carefully avoided.

- Chemical exposure on sites with open contamination. Respiratory protection may be necessary. Proper selection of respiratory protection is essential and an understanding of its limitation (i.e., negative pressure respiratory protection does not supply oxygen in an oxygen-deficient atmosphere). Staff should familiarize themselves with exposure limits for contaminants of concern.

- Use of air monitoring instrumentation will likely be necessary. We must be careful to make sure that our instrumentation is appropriate for the airborne contaminants of interest and that our staff understands the limitations of the instrumentation. Staff must also understand and perform calibration including zeroing with zero gas cylinders and appropriate other calibration gases.

- Decontamination of equipment and personnel must be properly designed and constructed to be sure that contamination is kept within the boundaries of the exclusion zone;

- Noise and proper use of hearing protection devices such as ear plugs and muffs.

- Emergency action plan must be carefully coordinated in advance between Stantec, our subcontractors, the client, and emergency responders.

All of these risks and others must be discussed with our subcontractors and clients to be sure they are properly addressed. Once the issues have been addressed at a project management level, they must be communicated to the staff that will actually perform the work. Details of procedures, instrument measurements and calibration, and other activities must be recorded in the field log and/or on data collection forms.

4.0 QUALITY ASSURANCE PLANNING CONSIDERATIONS

Soil sampling shall be done by personnel familiar with the common sources of random and systematic error so appropriate decisions can be made in the field. Some of the

common phenomena which may degrade the sample quality collected from the well point are listed below.

- **Volatilization.** Volatilization occurs when the sample is in contact with air for an extended time. Typically volatilization occurs if the sample undergoes excessive disturbance during sampling or if air pockets exist at the top of the container. Limiting disturbance during sampling, filling sample containers in order of volatility, and tight capping of bottles immediately after filling will minimize these errors.

- **Adsorption/desorption.** This is the gain or loss of chemicals through exchange across surfaces. Adsorption may occur when the sample comes in contact with large surface areas such as the sampling container. Thorough decontamination of sample collection containers/monitoring equipment probes along with expedient transfer from the sample container to the labrotory container minimizes sorption effects.

- **Chemical reaction.** Dissolved chemical constituents may change due to reactions such as oxidation, hydrolysis, precipitation, etc. Proper preservation and adherence to holding times minimize these reactions.

- **Sample contamination.** Sample contamination is the most common source of errors and can result from several factors, including incomplete decontamination, contact with other samples, and contact with the atmosphere. Careful attention to decontamination, handling, and container sealing minimizes sample contamination.

5.0 RESPONSIBILITIES

The Project Manager or Task Leader will be responsible for assigning project staff to complete soil sampling activities. The Task Leader will also be responsible for assuring that this and any other appropriate procedures are followed by all project personnel.

The project staff assigned to the soil sampling will be responsible for completing their tasks according to this and other appropriate procedures. All staff will be responsible for reporting deviations from the procedure or nonconformance to the Task Leader, Project Manager or Project QA/QC Officer.

6.0 TRAINING AND QUALIFICATIONS

Only qualified personnel shall be allowed to perform this procedure. At a minimum, Stantec employees qualified to perform soil sampling will be required to have:

- Read this SOP.

- Read project-specific QAPP.

- Indicated to the Task Leader that all procedures contained in this SOP are understood.

- Completed the Occupational Safety and Health Administration (OSHA) 40-hour training course, and/or annual 8-hour refresher course, as appropriate.

- Coordinated any proposed sampling activites with the laboratory to ensure proper sampling procedures.
- Previously performed soil sampling activities generally consistent with those described in this SOP.

Stantec employees who do not have previous experience with soil sampling will be trained on site by a qualified Stantec employee, and will be supervised directly by that employee until they have demonstrated an ability to perform the procedures.

7.0 REQUIRED MATERIALS

The following is a typical list of equipment that may be needed to perform soil sampling:

- Auger rig or direct-push unit with appropriate equipment for sampling, or hand auger.
- Continuous soil sampler (2-½-inch x 18-inch or 2-foot split-spoon sample tube) or direct-push clear acetate or polyvinyl chloride PVC tube (typically 4-foot long).
- Photoionization detector (PID) or other air monitoring instrumentation as required by the HASP.
- 4-mil-thick plastic sheeting or aluminum foil.
- Tape measure.
- Unified Soil Classification System (USCS) based on the Visual-Manual Procedures in ASTM Standards D 2487-00 and D 2488-00.
- 5035 sample containers with lids.
- Terra-cores™ or similar coring sampling device, if required.
- Sample labels.
- Stainless steel trowels, putty knives or similar soil working tool.
- Penetrometer (if available).
- Waterproof marking pens, such as the Staedtler Lumocolor.
- Coolers (with ice) for sample storage and shipment.
- Sample data forms/clip board.
- Decontamination supplies (Alconox™ [or similar detergent], brush, bucket).
- Nitrile gloves, or other specified chemical resistant gloves.
- Work gloves.

- Camera and film or disks.
- Blank soil borehole logs or a field-logging PDA.
- Personal safety gear (hard hat, steel-toed boots, ear plugs, safety glasses, etc.).

8.0 METHODS

8.1 Hollow-Stem Auger/Direct Push Sampling

Make sure that all equipment and meters have been calibrated to the equipment specifications and the results have been recorded in the field log.

The top five (5) feet of the boreholes will be cleared via air knife, vacuum excavation, ground penetrating radar, hand auger, tile probe or some combination of these methods.

Shallow soil boreholes are typically drilled with hollow-stem augers or geoprobe and sampled at the intervals specified in the work plans. Sampling shall be done in advance of the lead auger to minimize cross-contamination. Samples for laboratory analysis shall be taken with a continuous soil sampler. Standard blow counts shall be recorded for driving the sampler 6 and 12 inches (ASTM Method D 1586-99) if sampler is hammer driven.

Upon retrieval of the sample, the sample will placed on a clean surface (or lined with disposable aluminum foil or plastic sheeting) and will be screened with a PID for locating potential elevated PID readings. If applicable, a representative grab sample will be collected along with a headspace sample and placed into the appropriately labeled sample container. The sample containers shall be placed in self-sealing plastic or bubble bags in a cooler with ice or frozen ice packs for storage until they are delivered to the analytical laboratory.

The following method is to be used for headspace screening:

- The portion (for headspace screening) should be placed into an appropriately sized re-sealable Ziploc® or equivalent bag;
- Seal and label the bag with the borehole identification and the depth of the sample;
- Allow the bag to equilibrate for approximately ten (10) minutes; and
- Insert the probe tip of the PID into the bag. Obtain a measurement using the PID.

The remainder of the sample shall be logged in accordance with the USCS and recorded on the boring logs according to the following procedure:

1. As much information as possible is to be shown in the heading of each log. This includes, but is not limited to:

   - Project name and project identification number;
   - Identification of borehole;

- Name of drilling company;
- Make, model, type, and size of drilling and sampling equipment used;
- Date and time of start and end of drilling
- Name of geologist(s) logging boring;
- End of boring depth; and,
- Depth to water (if encountered).

2. Each log is to begin with a description of the surface, (i.e., native, paved with asphalt, paved with concrete, and such). If any concrete is cut to open the hole, the thickness will be noted.

3. Every foot will be accounted for, with no gaps. If an interval is not sampled it will be noted. If an attempt is made to sample an interval, but there is no recovery, it will be noted.

4. Complete construction details are to be detailed for each well on a standard well construction form. Construction details should include:

   - A description of the type and length of casing i.e., 20' of 2" inner diameter (ID) Schedule 40 PVC casing;
   - Length and depths of the top and bottom of the screened interval;
   - Screen slot size;
   - Depths of the top and bottom of the filter pack;
   - Filter pack materials and sand size;
   - Depths and types of bentonite seals;
   - Detail of the use of grout; and,
   - Detail of the surface completion (i.e., stick up, flush-mounted).

5. The number of bags of sand, bentonite, and grout used will be counted. These numbers will be compared daily with the driller's daily report.

Soil cuttings will be stockpiled on 4-mil thick plastic sheeting or drummed. The cuttings and other investigation-derived waste will be managed in accordance with the work plan or client-specific directives.

When sampling for volatile organic compounds (VOCs), use USEPA Method 5035. Method 5035 requires ample preservation in the field at the point of collection. The preservative used for the low concentration soil method (0.5 to 200 µg/kg) is sodium bisulfate and the preservative used for the medium/high concentration soil method (>200 µg/kg) is methanol. This field collection and preservation procedure is intended to prevent loss of VOCs during sample transport, handling, and analysis. The holding time for VOC analysis is 14 days.

1. Use the lab provided plunger style sampler (T-handle, syringe with tool, or terra-core™ sampler) to collect a 5g soil sample.

2. Unscrew the lid of the lab provided pre-preserved sodium bisulfate volatile organic analysis (VOA) vials and inject the 5g soil sample.

3. Tightly seal the VOA vial.
4. Repeat this step with the second sodium bisulfate VOA vial.
5. Then, repeat with the methanol preserved VOA vial.
6. Collect a soil sample in the 4-ounce wide mouth glass jar provided by the lab.
7. Make sure sample containers are labeled and bagged in plastic or bubble bags.
8. Ice the samples.

8.2 Hand Auger Sampling

Shallow soil boreholes less than five (5) feet in depth can be collected using a hand auger. The auger will be advanced until the desired sampling depth is reached. The auger will be removed from the boring, the sample will be extracted from the hand auger and field screened (as appropriate), and representative grab samples will be collected and placed into the appropriate labeled sample container. Decontamination of the auger and extensions will occur after each sample.

Boreholes will be abandoned by backfilling with bentonite chips and hydrating with potable water.

8.3 Excavation

Excavations and test pits will be excavated using a backhoe provided by the subcontractor. The dimensions of individual excavations will vary depending on the strength and stability of the trench walls and the specific purpose of the trench. Excavations greater than four (4) feet deep will not be entered by any personnel unless shoring is performed or the sides are stepped back to the proper angle per OSHA requirements.

When starting an excavation, the backhoe operator will first remove the topsoil or cover (if any) and place it in a discrete mound at least five (5) feet from the edge of the excavation. The excavation will be continued in approximately 6-inch cuts with the backhoe using a horizontal scraping motion rather than a vertical scooping motion. If a visibly-stained or otherwise chemically-affected soil interval is encountered, the affected excavated soils will be placed on 4-mil thick plastic sheeting.

8.3.1 Excavation Sampling

Samples will be collected from the backhoe bucket using a stainless steel trowel or similar. The top layer of soil will be removed prior to collecting the sample. The soil will then be placed in the appropriately labeled sample container and placed inside a chilled cooler.

8.3.2 Excavation Backfilling

The soils will be replaced in the excavation at their original depths to the extent

practicable so that the soil from the bottom of the trench will be placed on the bottom, and the topsoil will be replaced on the top. The backhoe will be used to backfill and compact the excavation.

Upon completion and subsequent backfilling of each excavation, four corners will be marked with a wooden stake for surveying. If appropriate, a fifth stake will be placed above the location where a soil sample was collected. The points may be surveyed, as needed.

8.4 Decontamination Methods

8.4.1 Sampling Equipment Decontamination

The following steps will be used to decontaminate sampling equipment:

- Ensure that the decontamination process has been carefully designed to be sure that the solutions used are appropriate for the chemicals of interest.
- Ensure that the decontamination area is properly constructed to keep contamination within the contamination reduction and exclusion zones.
- Ensure that the decontamination area is properly constructed to contain the rinse solutions and solids.
- Personnel will dress in suitable safety equipment to reduce personal exposure.
- Smaller equipment that will not be damaged by water will be placed in a wash bucket containing an Alconox™ (or equivalent) solution and scrubbed with a brush or clean cloth. Smaller equipment will be rinsed in water. Change rinse and detergent waters between boreholes, as needed.
- For larger drilling equipment the soil and/or other material will be scraped off with a flat-bladed scraper, and placed within a deconcontamination (decon) pad. The decon pad will be constructed in a predetermined location, and equipment shall be cleaned with a pressure washer using potable water. Care will be taken to adequately clean the insides of the hollow-stem augers, and cutter heads.
- Equipment that may be damaged by water will be carefully wiped clean using a sponge and detergent water and rinsed in or wiped down with distilled water. Care will be taken to prevent any equipment damage.

Following decontamination, equipment will be placed in a clean area or on clean plastic sheeting to prevent contact with potentially contaminated soil.

Following decontamination, drilling equipment will be placed on the clean drill rig and moved to a clean area. If the equipment is not used immediately, it will be stored in the designated secure, clean area.

8.4.2 Excavation Decontamination

Decontamination protocols must be carefully designed and constructed to deal with the chemicals of interest and ensure that the rinse solutions and solids are contained within the contamination reduction zone.

The backhoe bucket will be decontaminated prior to excavating each excavation. The entire backhoe, bucket, and tires will be decontaminated at the conclusion of the trenching operation. Decontamination will involve using a steam cleaner with an Alconox™ solution or pressure washer and rinsing using a steam cleaner or pressure washer with potable water. Backhoe decontamination will take place at the decontamination area located adjacent to the maintenance building or at another appropriate location.

The sampling equipment will be decontaminated prior to collecting each sample. Decontamination will consist of washing the equipment with a scrub brush in a bucket with an Alconox™ solution (or equivalent) and rinsing the equipment in a bucket filled with tap water. The date and time of decontamination of the backhoe and sampling equipment will be recorded in the field book and/or data collection forms.

8.5 Sample Containers, Storage, and Holding Times

Refer to the Project Sampling and Analysis Plan (SAP) for project specific instructions on proper containers, storage of samples and allowable holding times.

9.0 QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

Refer to the QAPP and SAP for specific quality control checks and acceptance criteria.

10.0 DOCUMENTATION

A borehole log will be completed for each hollow-stem auger or direct-push borehole. The field notebook and/or data collection forms will contain the following information:

- Project name and number.
- Drilling company's name.
- Date drilling started and finished.
- Type of auger and size (ID & OD).
- Type of equipment for air monitoring (PID or FID).
- Air monitoring calibration and measurements.
- Well completion and graphic log.
- Driller's name.
- Geologist's or engineer's name.

- Type of drill rig.
- Borehole number.
- Surface elevation (if available).
- Stratigraphic description with depth.
- Classification of the soils according to the USCS.
- Water levels and light non-aqueous phase liquid levels, if applicable.
- Drilling observations.
- Map of borehole or monitoring well location.

In addition, proper documentation will include observance of the chain of custody procedures as described in the Project QAPP and SAP.

Additional information regarding field documentation for borehole logging for fine- and coarse-grained soils and rocks is provided in Stantec checklists ESPA-603 through ESPA-605.

ACCEPTANCE

Author

James M. Kerr, Jr.	J. M. Kerr, Jr.	6/1/2016
Printed Name	Signature	Date

Quality/Technical Reviewer

Angus McGrath		6/1/2016
Printed Name	Signature	Date

Independent Reviewer

John W. McInnes		6/1/2016
Printed Name	Signature	Date

1.0 PURPOSE & APPLICABILITY

The purpose of this document is to define the standard operating procedure (SOP) for decontamination procedures. The ultimate goal of the decontamination procedure is to prevent cross-contamination between samples and sample areas and to protect workers from hazardous materials.

This procedure gives descriptions of equipment and field procedures necessary to perform decontamination.

This procedure may apply to all sampling by Stantec personnel or their subcontractors by the aforementioned sampling methods.

It must be recognized that field conditions may force some modifications to the SOP. Any modification to the procedure shall be approved by the Project Manager or Task Leader in advance and sufficiently documented so that the reason for the deviation can be clearly articulated to our clients and regulators, as necessary. Where SOP modification is planned sufficiently in advance, regulatory agency concurrence will be sought prior to conducting the specific activity.

2.0 DEFINITIONS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
OSHA	Occupational Safety and Health Administration
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure
WP	(Project) Work Plan

3.0 HEALTH AND SAFETY CONSIDERATIONS

Consideration of Health and Safety risks prior to performing this work is paramount. This risk review may be performed by modifying a generic or an existing Job Safety Analysis in the HASP. Following is a short list of the items for consideration. Careful review of these items and other site-specific conditions by the project team is essential.

- Traffic guidance and control. Even plans developed by outside traffic control contractors need to be carefully evaluated to make sure they are protective of our staff and contractors.
- Personal protective equipment, including hard hats, high-visibility traffic vest, gloves, appropriate clothing.
- Heat and cold stress.
- Biological hazards such as insects and spiders. Appropriate clothing is required such as long-sleeved shirts and long pants.

- Blood borne pathogens. Some of our sites may have syringes and other drug paraphernalia that must be carefully avoided.

- Chemical exposure on sites with open contamination. Respiratory protection may be necessary. Proper selection of respiratory protection is essential and an understanding of its limitation (i.e., negative pressure respiratory protection does not supply oxygen in an oxygen-deficient atmosphere). Staff should familiarize themselves with exposure limits for contaminants of concern.

- Use of air monitoring instrumentation will likely be necessary. We must be careful to make sure that our instrumentation is appropriate for the airborne contaminants of interest and that our staff understands the limitations of the instrumentation. Staff must also understand and perform calibration including zeroing with zero gas cylinders and appropriate other calibration gases.

- The exclusion and contaminant reduction zones must be properly designed and constructed so that contamination from decontamination activities of equipment and personnel is kept within this area.

- Noise and proper use of hearing protection devices such as ear plugs and muffs.

- Emergency action plan must be carefully coordinated in advance between Stantec, our subcontractors, the client, and emergency responders.

All of these risks and others must be discussed with our subcontractor and clients to be sure they are properly addressed. Once the issues have been addressed at a project management level, they must be communicated to the staff that will actually perform the work. Details of procedures, instrument measurements and calibration, and other activities must be recorded in the field log and/or on data collection forms.

4.0 RESPONSIBILITIES

The Project Manager or Task Leader will be responsible for assigning project staff to complete decontamination activities. The Task Leader will also be responsible for assuring that this and any other appropriate procedures are followed by all project personnel.

The project staff assigned to the decontamination tasks will be responsible for completing their tasks according to this and other appropriate procedures. All staff will be responsible for reporting deviations from the procedure or nonconformance to the Task Leader, Project Manager, or Project QA/QC Officer.

Only qualified personnel shall be allowed to perform this procedure. At a minimum, Stantec employees qualified to oversee decontamination will be required to have:

- Read this SOP;

- Read project-specific QAPP;

- Indicated to the Task Leader that all procedures contained in this SOP are

understood;

- Completed the OSHA 40-hour training course and 8-hour refresher course, as appropriate; and,
- Previously performed decontamination activities generally consistent with those described in this SOP.

5.0 TRAINING/QUALIFICATIONS

Stantec employees who do not have previous experience with decontamination will be trained on site by a qualified Stantec employee, and will be supervised directly by that employee until they have demonstrated an ability to perform the procedures.

6.0 REQUIRED MATERIALS

The following is a typical list of equipment that may be needed to perform decontamination:

- Paper towels;
- Aluminum foil;
- Trash bags;
- Non-phosphate detergent (e.g., Alconox™);
- Distilled or deionized water (where available);
- Spray bottles;
- Cleaning brushes;
- 5-gallon buckets, purge tank, trailer, drums and drum labels or waste containers;
- Nitrile gloves, or other specified chemical resistant gloves;
- Work gloves; and,
- Personal protective equipment (hard hat, steel-toed boots, etc.).

7.0 DECONTAMINATION METHODS

Reusable field instrumentation and sampling equipment will be decontaminated prior to their first use, and between each well/sampling location in which they are used. Two types of decontamination procedures will be employed, depending on the level of visual or otherwise known contamination to which the instrumentation is exposed. Pre-use decontamination will follow the first decontamination protocol listed below.

Decontamination will be performed on all non-dedicated sampling equipment that may contact potentially contaminated soil or water, including water level probes, fiberglass tapes, Teflon bailers, and non-dedicated pump hoses. Clean nitrile gloves (or other appropriate material depending upon the chemicals involved) or powder less surgical gloves are to be worn during decontamination.

Each piece of sampling equipment will also be decontaminated between each well. The decontamination procedure for most equipment will be as follows:

- Disassemble equipment (i.e., bladder pump).
- Wash equipment in Alconox™ (or equivalent) and water solution using a brush or clean cloth to ensure emoval of all contaminants.
- Rinse equipment in fresh tap water. Re-rinse with de-ionized water or distilled water.
- Dry equipment with paper towel and place in clean place, if appropriate.

The effectiveness of these decontamination procedures will be verified by vigorous QA/QC protocols, including blanks, duplicates, and spikes.

Reusable instrumentation/equipment that has signs of visible NAPL or has potentially come in contact with NAPL-impacted material will be decontaminated in the following manner:

1. The instrumentation/equipment will be thoroughly rinsed with tap water to remove sediment and debris, after caked on material has been physically removed.
2. The instrumentation and sampling equipment will be thoroughly washed with a mixture comprised of approximately two (2) tablespoons of Alconox™ (or similar low phosphate cleaning agent) per 1-gallon of de-ionized water. A stiff bristle scrub brush will be used if necessary to provide thorough cleaning.
3. The instrumentation/equipment will be triple-rinsed with unused distilled or de-ionized water where available.

The effectiveness of the above decontamination procedures will be demonstrated through the periodic use of equipment blanks. A more detailed discussion of the proposed use of equipment blanks is provided in the FSP

Drill rigs or Geoprobes used on site will be thoroughly decontaminated prior to their arrival at the site and prior to initiation of any drilling activities. The rig and its equipment will be thoroughly examined to ensure that there are no significant fuel, hydraulic fluid, transmission oil, and/or motor oil leaks that could create a condition not previously in existence or exacerbate an existing condition.

Once the rig and its equipment have been thoroughly cleaned and inspected, subsequent decontamination efforts will focus only on those pieces of equipment which actually come into contact with soils or groundwater. No petroleum hydrocarbon based lubricants will be allowed on the drill stems or associated connections. Both the initial

comprehensive cleaning of the rig and subsequent decontamination procedures will be performed using either steam-cleaning equipment or high pressure hot water/detergent wash. In addition, casing centralizers and casing handling equipment, if used, will be cleaned prior to use in the construction of monitoring wells.

Decontamination wash solutions and rinsate will be collected and containerized in 5-gallon buckets, 55-gallon drums, or poly tanks. The collected rinsate will be disposed of appropriately.

8.0 QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

Refer to the Quality Assurance Project Plan for specific quality control checks and acceptance criteria.

9.0 DOCUMENTATION

A record will be maintained during the purging procedure that will contain at a minimum:

- Project name and number;
- Date, personnel;
- Decontamination procedures;
- Volume of rinsate fluid generated during decontamination; and,
- Disposal method of decontamination water.

The data shall be recorded on a log form or in field logs.

ACCEPTANCE

Author

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1.0 PURPOSE & APPLICABILITY

Accurate and thorough documentation of field work conducted by Stantec is a vitally important component of project operations. Field notes, and the validity of the records kept in them, comprise a significant portion of Stantec's work product. Field notes represent legal records of our services and require a corresponding level of care and professionalism regardless of the grade of the field note taker.

Field notebooks should be completed in the field and serve as a primary source of information enabling a third-party to easily reconstruct the chronology of field events, even if applicable field forms (i.e., chain-of-custody forms) are lost or destroyed.

This Field Notebook Standard Operating Procedure (SOP) has been prepared as guidance for collecting and managing field notes, such that these records are collected in a consistent manner throughout Stantec.

2.0 DEFINITIONS

COC	Chain-of-Custody
FSP	Field Sampling Plan
HASP	Site-Specific Health and Safety Plan
O&M	Operation & Maintenance
PPE	Personal Protective Equipment
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
QAPP	Quality Assurance Project Plan
WP	(Project) Work Plan

3.0 HEALTH AND SAFETY CONSIDERATIONS

Field notes should be used as a medium to describe all activities occurring at a site when Stantec is present with or without subcontractors or other contractors on site. Field notes should reflect the following information, at a minimum, concerning site health and safety observations:

1. Ambient site conditions (i.e., operating facility versus barren land).
2. Weather.
3. Traffic patterns.
4. Tailgate/Toolbox safety meeting time, place, and reference for notes.
5. HASP location and use.
6. Specific PPE used on site.
7. Sampling activities, types of media sampled, areas and times.

8. Contractors, visitors, and client representatives on site.

4.0 QUALITY ASSURANCE PLANNING CONSIDERATIONS

Field notebooks should document the project quality assurance standards, referencing one or more of the following:

1. A project-specific FSP, QAPP, or combined SAP.
2. A project WP or detailed proposal.
3. An O&M manual with written procedures.
4. An SOP for the specific tasks or task.
5. Forms or Checklists developed by a project team for a specific task.

The field notebook must not only record the daily quality assurance expectations for each task conducted but it should also reference the accepted standards of practice for both Stantec personnel and subcontractors in meeting these expectations.

5.0 RESPONSIBILITIES

With regard to field work documentation, the following are the minimum responsibilities for each position listed:

Project Manager – Responsible for:

- Ensuring project personnel performing field work understand the project quality assurance objectives and scope of work (i.e., SAP, QAPP, or WP and HASP).
- Managing resources (labor, equipment, materials, subcontractors) to be utilized, schedule, project number, project-specific field note requirements.
- Explaining expectations for communication with the home office (i.e., check-in phone calls, faxing or scanning field notes and forms).

Field Personnel – Responsible for:

- Reading and understanding project scope of work, schedule, and quality assurance documents prior to conducting field work.
- Maintaining copies of project documents, including the HASP.
- Diligently making routine entries in the field notebook concerning progress on site sampling activities, field conditions, and deviations from the planned scope of work

and activities of Stantec, its subcontractors, or other contractors/visitors to the site. Any other information relevant to the work being conducted shall also be recorded.

- Regular communication with the Project Manager throughout the day.

Health and Safety Officer – Responsible for:

- Periodic inspection of field notebooks for information relevant to potential site Health & Safety concerns, including use of PPE, monitoring instrument calibrations and use, and verification of training certificates from on-site personnel.

Project Quality Assurance Officer (if applicable) – Responsible for:

- Periodic inspection of field notebook(s) to ensure applicability of the field notebook for the project and the relevance of the notes collected.

- Management of field notebook in the field and project files in the home office following field work.

6.0 TRAINING/QUALIFICATIONS

Field personnel are expected to be experienced in the site-specific scope of work being performed through study and understanding of the project quality assurance standards prior to entering the field. While prior field experience on projects of similar scope and complexity is recommended, personnel maintaining the field notebook must record routine observations during field activities, and document non-routine events at the site in accordance with the project plans. Field personnel qualifications include legible penmanship, the ability to prepare clear illustrations and/or sketches of site features and activities, and the ability to responsibly manage field notebooks during and after field work.

7.0 REQUIRED MATERIALS

The following materials are required for proper field work documentation:

1. Field Notebook (e.g., Rite In The Rain, Composition, etc.) with numbered pages or Stantec field report forms.

2. Black or blue ink or indelible marking.

3. Wrist watch or clock.

4. Project Quality Assurance documents or forms.

5. Mobile telephone.

6. Communication log with pertinent contact information for key project (both Stantec and non-Stantec) personnel.

7. Site plan or map of area where work is to be conducted for reference purposes.

8.0 METHODS

The following protocol outlines a methodology to collect and manage field work documentation in a consistent manner throughout Stantec.

Multiple notebooks may be used for a project, perhaps concurrently, and the field note takers must coordinate with the Project Manager and Project Quality Assurance Officer (if applicable) to coordinate sequential numbering of field books.

1. Beginning of Project Day

The following entries should be made at the beginning of each project:

A. Note the project name, address and location, (i.e., off-site versus on-site, operable unit name, SWMU, etc.);

B. Note the governing documents including HASP, QAPP, WP, etc., for performing the work; and,

C. Note any specific activities planned for the day (e.g., drilling monitoring wells MW-1 through MW-4, removing a waste oil tank, completing a survey of sensitive habitat, or delineating a potential wetland, etc.).

2. Routine Events

The following entries should be made throughout each day, including:

A. Enter time (preferably at 15-minute increments) or starting and ending points (i.e., started drilling, completed well, etc.);

B. Enter description of location (well/borehole name, well being sampled, developed, tank being removed, area being cleared);

C. Enter description of equipment and materials in use and subcontractors working or on standby;

D. Note any specific activities to be completed for the day, and reference accompanying forms or attachments that need to be appended to the field note book in the order of occurrence. These might include:

- ❖ RMS-2 forms

- ❖ Tailgate meeting form;
- ❖ Subsurface clearance checklists;
- ❖ Equipment calibration;
- ❖ Borehole logs/well completion forms;
- ❖ Groundwater monitoring forms;
- ❖ Purge and sampling record;
- ❖ Chain-of-custody;
- ❖ Subcontractor (drillers/concrete cutters) daily reports;
- ❖ Equipment records; and,
- ❖ Supplies purchased (to be reported on expense report).

Or, for a construction/removal project:

- ❖ Air monitoring forms;
- ❖ Soil or rock tags;
- ❖ Bill-of-lading/waste manifests; and,
- ❖ Photographic log.

E. Note any variances to the project plan, project quality, or project delays;

F. Entries are to be made in ink and incorrect entries are to be changed only through strike-out, and then initialed by the note taker. Do not "scribble" or color over notes;

G. Notes must be factual, relevant and professional. No opinions or conjectures are appropriate. Observations and interpretations must be clearly distinguished within the context of the entry. Slang and editorial comments are inappropriate for field notebooks;

H. If photographs are taken, a photograph log should be maintained detailing the time the photo was taken, the name of the photographer, the direction of view in the photo, the content of the photo and any significant points to observe in photo; and,

I. Initial each page and sign and date the field notebook on the last page for each day.

3. Non-Routine/Significant Events

A. Enter time (exact military time);

B. Record full yet concise description of any non-routine occurrence, such as an incident (i.e., spill, fire, motor vehicle accident) or other events (e.g., EPA inspection) beyond the scope of the scheduled work; and,

C. As applicable, multiple photographs should be taken to document the variance or incident.

9.0 QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

Quality Control Checks are required at the following points during the field notebook documentation process:

1. Prior to entering the field, the Project Manager should ensure that field personnel have read the project quality assurance documents and that these are available for reference in the field;

2. At the end of each field day, personnel are responsible to forward copies of field notebook pages and supporting documentation to the Project Manager or designee;

3. At the completion of the phase of work and/or the end of the project, field notebooks must be assembled in the home office project file;

4. Working copies of field notebooks should be used within the home office rather than the original notebooks; and,

5. Use referenced Stantec forms, as attachments, described in Article 10.0, Documentation.

10.0 DOCUMENTATION

The following information (referenced in the field notebook), drawings and/or forms, as applicable, should be provided via facsimile or scan to the Project Manager daily (at a minimum) unless otherwise specified by the Project Manager:

- Photographs (i.e., color thumbnail digital photos).

- Equipment records.

- Revised maps and survey notes:

    - Corrections to existing site features (add new features; remove obsolete features), as applicable.
    - Placement of new wells/borings (with measured distances).
    - Preliminary groundwater elevation contour map based on new data.

- Subsurface clearance checklist from HASP.

- HASP acknowledgement form, updated as needed.

- RMS-2 forms

- Chain-of-custody record.

- Variance/delay form (ESPA-302).
- Waste management form (ESPA-303).
- Borehole logs and well completion diagrams (ESPA-304-20/40).
- Purging, monitoring, sampling, and development records (ESPA-305 and ESPA-306).

The following documentation list is provided for use with this field note documentation SOP:

- Field Report (ESPA-301).
- Variance/Time Delay Form (ESPA-302).
- Waste Management Form (ESPA-303).
- Borehole log and well construction detail template (ESPA-304-20/40).
- Field Note Checklist (ESPA-601).
- Field Supplies Checklist (ESPA-602).

ACCEPTANCE

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