Applied EcoSystems, Inc.
Environmental Management, Consulting & Field Services

Quality Assurance Project Plan (QAPP)

RACER Flint West 12990
Glenwood Avenue and Stevenson Street
Flint, Michigan

April 1, 2021
Project # 11-4312-102

Applied EcoSystems, Inc.
G-4300 South Saginaw Street, Burton, Michigan 48529
Phone: (810) 715-2525   Fax: (810) 715-2526
www.AppliedEcoSystems.com

USEPA ID Number: MID 005 356 654
Revision Number 1 April 2021
Prepared by: Applied EcoSystems, Inc.
Prepared for: RACER Trust
Page Count: 463

Approved By: David Favero Date: 04/01/2021
Dave Favero
RACER Trust Project Manager

Approved By: Date: 04/01/2021
Michael Smith
Applied EcoSystems Senior Technical Manager

Approved By: Rodney Abke Date: 04/01/2021
Rodney Abke
Applied EcoSystems Project Manager

Approved By: Date: 04/01/2021
Robert Houghton
Applied EcoSystems QA Assurance Officer

Approved By: John Laverty Date: 04/01/2021
John Laverty
Merit Project Manager

Approved By: Barbara Ball Date: 04/01/2021
Barbara Ball
Merit QA Manager

Approved By: Susan Schafer Date: 04/01/2021
Susan Schafer
Eurofins Project Manager

Approved By: Date: 04/01/2021
Mark Loeb
Eurofins QA Manager

Approved By: Digitally signed by BRANDON PURSEL
Date: 2021.04.05 15:25:46 -05'00' Date:
Brandon Pursel
U.S. EPA Project Manager

Approved By: Digitally signed by ZACHARY SASNOW
Date: 2021.04.05 13:43:01 -05'00' Date:
Zachary Sasnow
U. S. EPA Region 5 QA Coordinator

QAPP Distribution List

Name/Organization	*Number of Copies*
Brandon Pursel – USEPA Region 5	1 (Electronic)
Zachary Sasnow - USEPA Region 5 (QA)	1 (Electronic)
David Favero – RACER	1 (Electronic)
Michael Smith – Æ	1 (Electronic)
Rodney Abke – Æ	1 (Electronic)
Barbera Ball - Merit	1 (Electronic)
John Laverty – Merit	1 (Electronic)
Susan Schafer – Eurofins	1 (Electronic)
Mark Loeb – Eurofins	1 (Electronic)

TABLE OF CONTENT

FIGURES

TABLES

APPENDICES

Æ	Applied EcoSystems, Inc.
ASTM International (ASTM)	
RBCA	ASTM Risk-Based Corrective Action
Buildings, Structures, and Materials	
AST	Aboveground Storage Tank
HVAC	Heating, Ventilation, and Air Conditioning Systems
LUST	Leaking Underground Storage Tank
ROW	Right-of-Way
UST	Underground Storage Tank
Federal Agencies	
USEPA	Environmental Protection Agency
FEMA	Federal Emergency Management Agency
USDA	United States Department of Agriculture
USGS	United States Geological Survey
Federal Environmental Regulations, Programs, and Databases	
FOIA	Freedom of Information Act
RCRA	Resource Conservation and Recovery Act
Hazardous Substances and Petroleum Products	
PCBs	Polychlorinated Biphenyls
PNAs	Polynuclear Aromatics - also known as Polycyclic Aromatic Hydrocarbons (PAHs)
TMBs	Trimethylbenzenes
GP	Gasoline Indicator Parameters
ULGP	Unleaded Gasoline Indicator Parameters
LGP	Leaded Gasoline Indicator Parameters
VOCs	Volatile Organic Compounds
CoCs	Constituents of Concern
GRO	Gasoline Range Organics
DRO	Diesel Range Organics
NAPL	Non-Aqueous Phase Liquid
LNAPL	Light Non-Aqueous Phase Liquid
QA/QC	Quality Assurance\Quality Control
Mapping, Instruments and Units of Measurement	
bgs	Below Ground Surface
Sqft	Square feet
GIS	Geographic Information System
msl	Mean Sea Level
PID	Photoionization Detector
ppb	Parts Per Billion
ppb(v)	Parts Per Billion by Volume
ppm	Parts Per Million
ppm(v)	Parts Per Million by Volume
µg/kg	Micrograms per Kilogram
µg/L	Micrograms per Liter
Michigan-Specific	
NREPA	Natural Resources and Environmental Protection Act

EGLE	Michigan Department of Environment, Great Lakes and Energy and its predecessors below:	
	MDEQ	Michigan Department of Environmental Quality
	MDNRE	Michigan Department of Natural Resources and Environment
RRD	Remediation and Redevelopment Division	
RC	Restrictive Covenant	
CAP	Corrective Action Plan	
LARA	Michigan Department of Licensing and Regulatory Affairs	
RBSL	Risk Based Screening Levels	
	DW/DWP	Drinking Water/Drinking Water Protection
	DC	Direct Contact
	F/E	Flammability/Explosivity Limit
	GSI/GSIP	Groundwater-Surface Water Interface/Groundwater-Surface Water Interface Protection
	PI	Particulate Inhalation
	VIA	Volatilization to Indoor Air
	RIASL	Recommended Interim Action Screening Levels
	SSVIC	Site-Specific Vapor Intrusion Criteria
	VOA	Volatilization to Outdoor Air
MI 10 Metals	Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Mercury, Selenium, Silver, and Zinc	
CSM	Conceptual Site Model	

1.0 Introduction

The following outlines the scope of the Resource Conservation and Recovery Act (RCRA) Corrective Action investigations, monitoring and other associated sampling and analyses, to be performed in accordance with the requirements of the RCRA Administrative Order on Consent (AOC) (effective September 29, 2011) between the United States Environmental Protection Agency (USEPA) and RACER for the Flint West Site.

This Quality Assurance Project Plan (QAPP) presents the organization, objectives, planned activities, and specific quality assurance/quality control (QA/QC) procedures associated with the specific investigation phases and monitoring activities for the Flint West Site. Protocols for sample collection, sample handling and storage, chain-of-custody (COC) procedures, and laboratory and field analyses are described or specifically referenced to related investigation documents.

This QAPP addresses the QA/QC elements in the USEPA's QA-R5 document (March 2001) and other relevant guidance documents. The QA/QC procedures described in this QAPP are consistent with USEPA guidance in general.

1.1 Introduction

1.1.1 Project Objectives and Decision Statement

The primary objectives for data collection activities include:

- Collect sufficient data to monitor groundwater quality and the effectiveness of proposed remedial response activities.
- TCE-impacted groundwater. Performance groundwater monitoring will be conducted to monitor the effectiveness of the remedial activities and determine when/if additional injections may be warranted.

The Decision Statement for the project scope is as follows:

- Determine whether interim or final remedial actions are necessary and/or have been completed to control current unacceptable risks, if any, to human health or the environment.
- Provide data for the development of a study of appropriate corrective measures (if warranted) to control current and future unacceptable risks to human health and the environment.

Associated specific objectives for field and laboratory data collection are discussed in Section 1.4 of this plan.

1.1.2 Project Status/Phase

The project status and investigation approach are presented in the Work Plans, subsequent amendments or sampling programs submitted as necessary, and periodic status reports.

1.1.2 QAPP Preparation Guidlines

As previously noted, this QAPP has been prepared to present the project specific QA/QC elements in EPA's QA-R5 document (March 2001).

1.2 Facility Description

1.2.1 Site Location and Zoning

The Site is an irregular-shaped parcel encompassing approximately five acres of land within the City of Flint, Genesee County, Michigan.

The Site is zoned as located within a Heavy Manufacturing District (G) per the City of Flint zoning map. Properties to the north and east are also zoned G. Properties to the south are zoned Light Manufacturing District (F) and properties to the west are zoned Community Business (D-3) per the City of Flint Zoning Map.

1.2.2 Geology

1.2.2.1 Regional Conditions

The surface topography of the Site generally slopes to the northwest toward the Flint River. Review of the Flint North, Michigan USGS 7.5-minute Topographic Map indicates that the Site is approximately 720 feet above msl, per the North American Datum 29 (NAD29).

Regional geology in the vicinity of the Site is characterized as medium-textured glacial till, gray, grayish brown or reddish brown, nonsorted glacial debris. This matrix is dominantly loam and silt loam texture, with variable amounts of cobbles and boulders. The matrix occurs as ground moraine, till plain or undifferentiated ground moraine-end moraine complexes and includes small areas of coarser or finer-textured tills as well as small areas of outwash.

According to the USDA National Cooperative Soil Survey website,[1] the surface soils consist of Urban land-Udorthents. These deposits are described as loamy till on dry loamy drift plains associated with recessional moraines.

According to the 1987 Bedrock Geology of Michigan map[2], the bedrock below the Site is the Saginaw Formation. This bedrock is a medium to coarse grained sandstone with some layers of shale, coal and limestone, and is early Pennsylvanian age.

1.2.2.2 Site Conditions

Based on borings and excavations conducted at the Site, subsurface lithology consists of sandy glacial tills consisting primarily of silty sand and clay layers in the upper approximately 20 feet to

---

[1] *Web Soil Survey*, Unites States Department of Agriculture, Natural Resources Conservation Service website, http://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx

[2] *1987 Bedrock Geology of Michigan*, Department of Environmental Quality, Geological Survey Division, 1:500,000 scale, November 12, 1999

30 feet below grade with shallow groundwater perched on a clay layer. (Note that Site elevation varies approximately 8 feet to 10 feet due to the retaining wall).

1.2.3 Groundwater Conditions

1.2.3.1 Regional Groundwater and Surface Water Conditions

The lithology shown on water well records to the northwest is similar to the geology encountered beneath the Site. The soils described in these logs are varying layers of silty sandy and clay. The uses of these wells are listed as “unknown.” Static water levels are listed at approximately 70 feet below surface and the wells are screened between 80 and 100 feet below surface down to a water-bearing sand.

The Site and surrounding properties are connected to the City of Flint municipal water supply. According to EGLEs GeoWebface[3] website, the Site is not within a wellhead protection area.

The nearest surface water is the Flint River, which is located approximately 560 feet northwest of the Site.

1.2.3.2 Site Groundwater Conditions

The depth to groundwater ranges from approximately eight to 17 feet below grade, the saturated thickness above the clay ranges from about 10 feet to 15 feet, and groundwater flow in this unit is generally to the northwest toward the Flint River. Bedrock was encountered at approximately 20 feet below grade on the north portion of the Site. Groundwater velocity is estimated to range from approximately 0.0017 ft/day to 0.17 ft/day based on the gradient calculated using the July 2019 gauging data (0.018 ft/ft), the range of hydraulic conductivity values for silty sand (0.0284 ft/day to 2.84 ft/day), and an effective porosity of 0.30.

1.3 Site History

Prior to its redevelopment in 1929, the Site was a residential area. The Site was used as a mechanic shop and was eventually turned into an assembly line manufacturing plant that produced intake and exhaust engine valves. Processes that have been conducted at the Site at Building 9 include: forging, plating, degreasing/parts cleaning, process wastewater collection and transport, lubrication, grinding/forming, welding, forming, heat treating and recycling, soluble lubricating oils treatment and recycling, and tumbling. Since initial Site construction, additional construction activities occurred twice at the Site; the first was an addition in 1971 and the second was the construction of an overhead roof which was added to the north storage area in 1986.

The Site building underwent decommissioning and demolition activities in 1996, and all manufacturing process machines have been removed. At the time of demolition, all machinery and wooden floor blocks were removed, the Site was cleaned and filled, trenches and sumps were capped with concrete, and hazardous and non-hazardous materials were containerized for disposal or recycling.

---

[3] EGLE GeoWebFace http://www.deq.state.mi.us/GeoWebFace/#

Subsurface investigations and corrective actions have been conducted on the Site primarily to address historical releases of Chlorinated Volatile Organic Compounds (CVOCs). No significant source mass was found in unsaturated soils. The highest remaining concentrations of trichloroethene are in the saturated unit and underlying clay in the central portion of the Site and in the immediately adjacent GCP walking path.

Groundwater was first analyzed for PFAS in samples collected in January 2018. Several PFAS compounds, including Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS), were detected in groundwater samples from monitoring wells MW-111S, and MW-112S. PFAS compounds have subsequently been detected in all monitoring wells except MW-102S, MW-104S, MW-105S, and MW-108S. The Michigan Department of Environment, Great Lakes and Energy (EGLE) established drinking water Maximum Contaminant Levels (MCLs) in August 2020 for seven PFAS compounds including PFOA and PFOS. Concentrations of PFOA and/or PFOS exceeding these MCLs have been detected in groundwater samples from MW-100S, MW-101S, MW-103S, MW-106SR, MW-107S, MW-109S, MW-110S, MW-111S, MW-112S, MW-113S, MW-114S. In December 2020, EGLE established drinking water MCLs for five additional PFAS compounds. No other PFAS compounds exceeded MCLs.

1.4 Project Objectives and Intended Data Use

The investigative and corrective action activities include the sampling and analysis of environmental media for the presence of organic and inorganic constituents based on historical operations at the Site. The field and laboratory parameters are summarized in Table 1.1. This table may be updated when sampling programs are modified, or when remedial alternatives are proposed.

1.4.1 Target Parameter List

The investigative and corrective action activities include the sampling and analysis of environmental media for the presence of organic and inorganic constituents based on historical operations at the Site. The field and laboratory parameters are summarized in Table 1.1. This table may be updated when sampling programs are modified, or when remedial alternatives are proposed.

1.4.1.1 Field Parameters

Concurrent with sample collection, several field parameters will be determined by the field sampling personnel. Field parameter measurements will be dependent upon the requirements of the applicable sampling program.

For aqueous samples (surface water and groundwater), at a minimum, the following parameters will be determined with field testing equipment: pH, specific conductivity, temperature, turbidity, dissolved oxygen, and oxidation/reduction potential (ORP).

For soils and solid matrices, field parameters will include visual observations, odor identification, and volatile organic compound (VOC) screening using a calibrated photoionization detector (PID) equipped with an 11.7-eV lamp.

Although field monitoring equipment is not available for screening of PFAS, soils will be screened in the field for VOCs using a calibrated PID as VOCs are constituents of concern for the Site and PID readings may provide information on impacted soils and/or preferential contaminant migration zones. The samples will be placed in sealed plastic bags, and the tip of the PID will be inserted into the bag to obtain a reading of VOCs that volatilize into the air headspace in the bag. The PID has a detection level of one part per million (ppm) VOCs.

1.4.1.2 Laboratory Parameters

VOCs, specifically TCE, and select metals (arsenic, chromium, hexavalent chromium, copper, lead, selenium and zinc) are the primary target analytes. Other possible target parameters include PFAS, additional metals, sulfate/sulfide, and general/physical parameters. The basis for the selected parameter list is provided in the Work Plans.

Table 1.2 presents the estimated quantitation limits (EQL) for each compound or analyte. Method detection limit (MDL) studies have been performed by Merit Laboratories, Incorporated (Merit) in accordance with the procedures established in the Federal Register, Title 40, Part 136, July 1, 2015. MDLs are updated on an annual basis; the most recent results will be furnished upon request. Merit will be used as primary project laboratory network.

1.5 Sampling Locations

The Proposed Scopes of Work and Work Plans, and subsequent amendments or sampling programs provide a summary and rationale for the sample locations at the Site. It is possible, however, that depending on the nature of encountered field conditions, sampling locations may change. The person responsible for making such decisions will be the Æ Project Manager whose responsibilities are described in Section 2 of this QAPP. Any change of the sampling strategy will only be implemented after approval from the RACER Project Manager. Current sample collection activities include: soil/water investigative sampling, groundwater monitoring, and corrective action activities.

1.6 Project Schedule

The schedule and projected milestones are presented in the Work Plans.

2.0 Project Organization And Responsibilities

The RACER Project Manager with assistance from the designated Æ Project Manager, will have the primary responsibility for the implementation of investigation and monitoring activities. The project laboratories listed in Appendix A will perform the analyses of environmental samples collected at the Site. Note, Eurofins Environment Testing America (Eurofins) is subcontracted by Merit Laboratories for methane analysis only. This section defines the roles and responsibilities of the individuals who will perform the investigation, monitoring, and subsequent activities.

Figure 1 provides the organization chart for the project team. All personnel on the organization chart will be provided and are expected to follow procedures in the final copy of the QAPP.

2.1 Management Responsibilities

Management responsibilities are as follows:

Brandon Pursel (U.S. EPA RCRA Corrective Action Project Manager)

The Regulatory Agency Project Manager has the overall general responsibility for oversight of all phases of the Investigative and Corrective Action activities.

Dave Favero – RACER Project Manager

The RACER Project Manager is responsible for implementing the project and has the authority to commit the resources necessary to meet project objectives and requirements. The RACER Project Manager's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully. The RACER Project Manager will provide the major point of contact will control matters concerning the project and will represent the project team at regulatory agency meetings. The Project Manager will approve project objectives and schedules. The RACER Project Manager will oversee project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task.

Michael Smith - Æ Senior Technical Manager

The Æ Senior Technical Manager will provide final review of significant work products and may participate in technical meetings with USEPA or other agencies. The Æ Senior Technical Manager will ensure that overall technical quality is maintained. The Æ Senior Technical Manager will be actively involved in the direction of the project.

Rodney Abke - Æ Project Manager

The Æ Project Manager has overall responsibility for ensuring that the project meets individual Work Plans and objectives. The Æ Project Manager will:

1. Acquire and apply technical and other resources as needed to ensure performance within budget and schedule restraints.
2. Review work performed on each task to ensure quality, responsiveness, cost effectiveness, and timeliness.

3. Be responsible for the preparation and quality of interim and final reports.
4. Communicate with RACER about the progress of the project.

The Æ Project Manager is responsible for managing the implementation of all Work Plans and other RCRA activities and coordinating the collection of data pertaining to investigations or monitoring stages. The Æ Project Manager also reviews, understands and provides approval of the QAPP.

2.2 Quality Assurance Responsibilities

The QA team will consist of a QA Officer and the Æ Project Manager. QA responsibilities are described as follows:

Robert Houghton - Æ Quality Assurance Officer

The Æ QA Officer reports directly to the Æ Project Manager and will be responsible for ensuring that all QA/QC procedures are being followed. The Æ QA Officer will be responsible for overseeing the review of all field and laboratory data. Additional responsibilities include:

1. Assuring the application and effectiveness of the QAPP by the analytical laboratory and the project staff
2. Conducting internal QA/QC of the investigation activities
3. Providing input to the Æ Project Manager as to corrective actions required resulting from the above-mentioned evaluations
4. Preparation and review of data validation and audit reports
5. Approval of the QAPP

The Æ QA Officer will be assisted by data validation staff in the evaluation and validation of field and laboratory generated data. The Æ QA Officer will monitor the performance of the laboratory to ensure that the Data Quality Objectives (DQOs) for the project are met.

Zachary Sasnow - Regulatory Agency Quality Assurance Officer

The Regulatory Agency QA Officer may review this QAPP. Additional Regulatory Agency responsibilities for the project may include:

1. Conducting external performance and system audits of the RFI laboratories
2. Reviewing and evaluating field and analytical laboratory procedures

2.3 Laboratory Responsibilities

Laboratory Project Manager

The Laboratory Project Manager will report directly to the Æ QA Officer and will be responsible for ensuring all resources of the laboratory are available on an as-required basis. The Laboratory Project Manager will also be responsible for the approval of the final analytical reports and approval of the laboratory's ability to adhere to the QAPP.

Laboratory Operations Manager

The Laboratory Operations Manager will report to the Laboratory Project Manager and will be responsible for coordinating laboratory analysis, supervising in-house COC reports, scheduling sample analyses, overseeing data review, and overseeing preparation of analytical reports.

Laboratory QA Officer

The Laboratory QA Officer will have sole responsibility for review and validation of the analytical laboratory data generated as part of the RFI. The Laboratory QA Officer will sign all final laboratory data reports provided from the analysis of the project samples and will provide Case Narrative descriptions of any data quality issues encountered during the analyses conducted by the laboratory. The Laboratory QA Officer will also define appropriate QA procedures, overview QA/QC documentation, and approve this QAPP.

Laboratory Sample Custodian

The Laboratory Sample Custodian will report to the Laboratory Operations Manager and will be responsible for the following:

1. Receiving and inspecting the incoming sample containers
2. Recording the condition of the incoming sample containers
3. Signing appropriate documents
4. Verifying COC and its correctness
5. Notifying the Laboratory Project Manager and Laboratory Operations Manager of sample receipt and inspection
6. Assigning a unique identification number and customer number and entering each into the sample receiving log
7. Initiating transfer of samples to lab sections
8. Controlling and monitoring access/storage of samples and extracts

Laboratory Technical Personnel

The laboratory technical staff will have the primary responsibility in the performance of sample analysis and the execution of the QA procedures developed to determine the data quality. These activities will include the proper preparation and analysis of the project samples in accordance with the contract laboratory's Quality Assurance Manual and associated Standard Operating Procedures (SOPs).

One or more of the following laboratories may provide laboratory services in support investigation and correct action conducted at the Site:

Merit Laboratories Incorporated/East Lansing, Michigan

Data Validation Staff

The data validation staff will be independent of the laboratory and familiar with the analytical procedures performed. The validation will include a review of each validation criterion as prescribed by the guidelines presented in Section 9.2.2 of this document, based on the phase of

Corrective Action activity, and be presented in a formal written report for submittal to the Æ Project Manager.

2.4 Field Responsibilities

Æ Field QA Officer

The Æ Field QA Officer is responsible for the overall operation of the field team and reports directly to the Æ Project Manager. The Æ Field QA Officer works with the project Health and Safety Officer to conduct operations in compliance with the project health and safety plan (HASP). The Æ Field QA Officer will facilitate communication and coordinate efforts between the Æ Project Manager and the field team members. Other responsibilities include:

1. Developing and implementing field-related work plans, ensuring schedule compliance, and adhering to management-developed project requirements
2. Coordinating and managing field staff, including sampling and drilling
3. Performing field system audits
4. Overseeing QC for technical data provided by the field staff
5. Preparing and approving of text and graphics required for field team efforts
6. Coordinating and overseeing technical efforts of subcontractors assisting the field team
7. Identifying problems in the field, resolving difficulties in consultation with the Æ Project QA Officer, and Æ Project Manager/Coordinator, and implementing and documenting corrective action procedures
8. Will review and understand the QAPP
9. Participating in preparation of the final reports

Field Team Personnel

Field Team Personnel involved in the project scope will be responsible for:

1. Performance of field activities as detailed in various Work Plans and in compliance with the DQO outlined in this QAPP for the specific activity being conducted.

3.0 Quality Assurance Objectives For Measurement Data

All Work Plans and subsequent amendments or sampling programs and associated QAPP are designed to produce data of the quality necessary to achieve the project objectives for the specific phase of the project and meet or exceed the minimum standard requirements for field and analytical methods. The overall QA objective for measurement data is to develop and implement procedures for field sampling, COC, lab analyses, and reporting that will provide results which are adequate for supporting the specific Corrective Action activity objectives and legally defensible in a court of law, as necessary. The QAPP program will include:

1. A mechanism for ongoing control of measurements and evaluation of data quality
2. A measure of data quality in terms of precision, accuracy, representativeness, completeness, and comparability

The following section is a general discussion of the criteria used to measure the field and laboratory analytical data quality. The laboratory SOPs and reference data provided in Appendix B and C, respectively, present the performance criteria for laboratory QC objectives.

3.1 Precision

3.1.1 Definition

Precision is defined as a quantitative measure of the degree to which two or more measurements are in agreement. Precision will be stated in terms of relative percent difference (RPD). The overall precision of measurement data is a mixture of sampling and analytical factors. Precision will be determined by collecting and analyzing field duplicate samples and by creating and analyzing laboratory duplicates from one or more of the field samples. The analytical results from the field duplicate samples will provide data on sampling precision. The results from the laboratory created duplicate samples will provide data on analytical precision.

3.1.2 Field Precision Sample Objectives

Field precision will be assessed through collection and measurement of field duplicates of investigation samples (excluding waste samples).

3.1.3 Laboratory Precision Sample Objectives

Laboratory duplicate analyses will be performed through the use of matrix spike/matrix spike duplicates (MS/MSD) for organic parameters and matrix duplicate (MD) analyses for certain inorganic parameters. The analytical data will be presented in summary table format. The precision criteria for laboratory MS/MSD/MD analyses are provided in the laboratory reference data provided in Appendix C.

3.2 Accuracy

3.2.1 Definition

Accuracy relates to the bias in a measurement system. Bias is the difference between the observed and the "true" value. Sources of error are the sampling process, field contamination, preservation techniques, sample handling, sample matrix, sample preparation, and analytical procedure limitations.

3.2.2 Field Accuracy Objectives

Sampling bias will be assessed by evaluating the results of field equipment rinsate and trip blanks. Field equipment rinsate and trip blanks will be collected as appropriate for each sampling effort.

Field equipment rinsate blanks will be collected by passing laboratory purified water over and/or through the respective decontaminated field equipment utilized during each sampling effort if the equipment will be reused to collect several samples. Field rinsate blanks will be analyzed for each target parameter for the respective sampling effort for which environmental media have been collected. (Note: If dedicated or disposable sampling equipment is used, equipment rinsate samples will not be collected as part of that field effort).

Trip blank samples will be prepared by the laboratory and provided with each cooler that includes VOC and/or PFAS analysis containers. Trip blank samples will be analyzed for each VOC and/or PFAS for which environmental media have been collected for analysis.

3.2.3 Laboratory Accuracy Sample Objectives

Analytical bias will be assessed through the use of known laboratory control samples (LCS) and Site specific MS sample analyses. LCS and MS/MSD sample analysis will be performed as prescribed by the analytical method SOPs. LCS analyses will be performed with each analytical batch of project samples to determine the accuracy of the analytical system.

The results of the LCS and MS/MSD analyses will be presented in a summary table reporting format and evaluated versus the acceptance criteria presented in the laboratory analytical reports. Current acceptance criteria are presented in the laboratory reference data provided in Appendix C.

The accuracy of organic parameter analyses also is monitored through the analysis of system monitoring or surrogate compounds. Surrogate compounds are added to each sample, standard, blank, and QC samples prior to the sample preparation and analysis. Surrogate compound percent recoveries provide information on the effect of the sample matrix on the accuracy of the analyses and are evaluated against the acceptance criteria presented in laboratory analytical reports. Current acceptance criteria are presented in the laboratory reference data provided in Appendix C.

3.3 Representativeness

3.3.1 Definition

Representativeness expresses the degree to which sample data accurately and precisely represents a characteristic of a population, a parameter variation at a sampling point, or an environmental condition. Representativeness is a qualitative parameter that is dependent upon the design of the sampling program. The representativeness criterion is satisfied by proper selection of sampling locations and quantity of samples collected.

3.3.2 Measures to Ensure Representativeness of Field Data

Representativeness will be addressed by describing sampling techniques and the rationale used to select sampling locations. Sampling locations may be biased (based on existing data, instrument surveys, observations, etc.) or unbiased (completely random or stratified-random approaches).

For this project, sampling will generally be biased; that is, sampling associated with the soil and groundwater will be based on the observed or known presence/absence of Site-specific contaminants, and/or Site knowledge of a release. If non-biased sampling is appropriate the approach will be identified in a specific Scope of Work or Work Plan. Specific sampling technique descriptions, which allow consistency, repetitiveness, and thus representativeness, are provided as SOPs in Appendix D.

3.3.3 Measures to Ensure Representativeness of Laboratory Data

Representativeness in the laboratory is ensured by using proper analytical procedures, and by analyzing field duplicate samples. By definition, field duplicate samples are collected to be representative of a given point in space and time. Thus, sample duplicates provide information relative to both precision and representativeness information.

3.4 Completeness

3.4.1 Definition

Completeness is a measure of the amount of valid (usable) data obtained from a measuring system compared to the amount that was expected to be obtained under normal conditions. The completeness goal for all data uses is that a sufficient amount of valid data be generated so that determinations can be made related to the intended data use with a high degree of confidence.

3.4.2 Field Completeness Objectives

Completeness is a measure of the amount of valid measurements obtained from all measurements taken in this project. Field completeness objective for this project will be 90 percent.

3.4.3 Laboratory Completeness Objectives

Laboratory data completeness objective is a measure of the amount of valid data obtained from all laboratory measurements. The evaluation of the data completeness will be performed at the conclusion of each sampling and analysis effort. Corrective actions such as revised sample handling procedures will be implemented if problems are noted.

The completeness of the data generated will be determined by comparing the amount of valid data, based on independent validation, with the total data set. The completeness objective will be 90 percent.

3.5 Comparability

3.5.1 Definition

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another.

3.5.2 Measures to Ensure Comparability of Field Data

Sample data should be comparable with other measurement data for similar samples and sample conditions. This goal is achieved through using SOPs to collect, preserve, store, and analyze representative samples and the reporting of analytical results. The field SOPs for the various activities to be conducted during Site investigations provide guidelines to generate reproducible results.

3.5.3 Measures to Ensure Comparability of Laboratory Data

Comparability of laboratory data also will be measured with the results from the analysis of Standard Reference Materials (SRM) obtained from either USEPA Cooperative Research and Development Agreement (CRADA) suppliers or the National Institute of Standards and Technology (NIST) (formerly National Bureau of Standards) for instrument initial and continuing calibration verification. The reported analytical data will be presented in standard units of mass of contaminant within a known volume or mass of environmental media.

- Solid Matrices - micrograms (µg) contaminant per kilogram (kg) for organic analyses, and milligrams (mg) contaminant per kg for inorganic analyses of media (Dry Weight)
- Aqueous Matrices - µg contaminant per liter (L) of media for organic analyses, ng per L of media for PFAS analyses, and mg per L for inorganic analyses

Additional guidance on analytical data reporting is contained in the laboratory SOPs.

3.6 Decision Rules

3.6.1 Definition

The decision rule is a statement that prescribes a course of action or non-action to be taken based on assumptions to test its logical and empirical consequences.

3.6.2 Decision Rule Objective

The rationale for sample locations, sample number, and analytical parameters is provided in the main text of the various supplemental Work Plans and Scopes of Work, and subsequent amendments or sampling programs.

1. Define parameters characterizing the population and incorporate the scale of decision making (i.e., AOI size). Samples will be collected discreetly and biased towards locations with the highest likelihood to encounter maximum contaminant levels to provide an indication of impacted zones.
2. Identify action levels (e.g., EGLE Part 201 Criteria, Risk-based Screening Levels [RBSLs]); Regional Screening Levels [RSLs]); or a reference-based standard based on a Site Conceptual Model that will be developed in consultation with USEPA.
3. If appropriate, the maximum contaminant concentration or the 95th percent Upper Confidence Limit of the valid data set for each parameter detected within an AOI will be used to conduct or update the baseline human health and ecological risk assessment for the evaluation of corrective actions.

The current EGLE generic cleanup criteria and screening levels will be used to compare analytical results in order to define whether detection limits, blank contamination criteria, and other quality control metrics are sufficient. Groundwater analytical results will be compared to EGLE drinking water generic cleanup criteria (DW), and groundwater-surface interface generic cleanup criteria (GSI). Soil analytical results will be compared to drinking water protection generic cleanup criteria (DW), and groundwater-surface interface protection generic cleanup criteria (GSI). Note, there are no screening levels or criteria that exist for the for the drinking water protection pathway for PFAS in soil.

Samples that fall outside of that criteria will be evaluated to identify the source(s) of data failure and re-collected or eliminated from consideration in the Site evaluation.

3.7 Level of Quality Control Effort

Equipment rinsate (if required), trip (if required by the type of contaminant), method blank samples, field duplicate samples, laboratory control, and MS/MSD samples will be prepared and analyzed to determine the data quality provided by the sampling and analysis activities conducted during the execution of the investigative program.

Equipment rinsate blanks will be prepared by field personnel and submitted for analysis of target parameters. Equipment rinsate blanks will provide the means to assess the quality of data resulting from the field program. Equipment rinsate blank samples will be analyzed to check for cross-contamination of equipment introduced during sampling at the Site. One equipment rinsate blank, if required by use of non-disposable or non-dedicated equipment, or for investigation events including samples to be analyzed for PFAS, will be collected for every 10 investigative samples or 1 per sampling phase. However, a minimum of one will be collected each day of sampling activities for each type of non-dedicated or non-disposable equipment.

Trip blanks are used to assess the potential for contamination during sample storage and shipment. The trip blank consists of laboratory purified water that has been purged with an inert gas by the laboratory and provided with the sample containers to be used for the sampling of VOCs and PFAS. Trip blanks will be preserved and handled in the same manner as the investigation samples. One trip blank will be included along with each shipment cooler containing project samples to be analyzed for VOCs and PFAS.

Method blank samples will be prepared by the laboratory and analyzed concurrently with all project samples to assess potential contamination introduced during the analytical process. Method blanks will be prepared and/or analyzed at a frequency required by the analytical method.

Field duplicate samples are analyzed to check for sampling and analytical reproducibility. One field duplicate will be collected for every 10 or fewer investigative samples collected during sampling activities, excluding waste samples, discharge samples, and wipe samples.

MS will provide information to assess the precision and accuracy of the analysis of the target parameters within the environmental media collected at the Site. MS will be performed in duplicate for all designated parameters. Initially, one MS/MSD will be collected for every 20 or fewer investigative samples per sample matrix (e.g., soil, groundwater). Based on the Corrective Action sampling reason, the frequency of MS/MSD samples may be reduced to every 20 investigative samples collected during the year or at a minimum, once per year. Aqueous and non-aqueous MS/MSD samples require triple the normal sample volume for all requested analysis.

4.0 Special Training/Certification Sampling Procedures

All consultant field personnel all hold current hazardous waste site operation (HAZWOPER) certification required by 29 CFR 1910.120. Consultant field personnel also undergo an extensive training program relative to all activities in which they are involved. Field personnel must first read the SOPs. Field personnel will accompany peer and senior staff and observe field tasks being performed then demonstrate they are proficient in the skill being evaluated. Once senior staff are satisfied, they are proficient in the particular field task, they are allowed to work independently. These training requirements pertain to sampling procedures and the calibration/operation of field instrumentation.

5.0 Sampling Procedures

Samples of groundwater, surface water, soil, and sediment may be obtained throughout the Corrective Action sampling activity phases. The sampling procedures will be consistent for the objectives of the project and the particular phase of the Corrective Action and as agreed to between RACER and USEPA. The field sampling SOPs provided in Appendix D describes each of the sampling tasks and objectives.

5.1 Sample Containers

Sample containers for each sampling task will be provided by the project laboratory. The containers will be cleaned by the manufacturer to meet or exceed the analyte specifications established in the USEPA, "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", April 1992, OSWER Directive #9240.0-0.5A. Certificates of analysis for each lot of sample containers used during the Corrective Action sampling activity will be maintained by the laboratory and will be available upon request.

The appropriate sample containers, preservation method, maximum holding times, and shipping information for each target parameter and sampling task are provided in Table 5.1.

5.2 Sample Labeling

Each sample will be labeled with a unique sample number that will facilitate tracking and cross-referencing of sample information. Field blank and field duplicate samples also will be numbered with a unique sample number to prevent analytical bias of field QC samples.

The sample numbering system for the project has been designed to uniquely identify each sample from each sampling program and event. The Site-specific sample number should consist of the following, at a minimum:

SL - SD - YYMMDD

where SL - Designates sample location (as identified on maps and boring logs)
SD – Sample Depth (soil samples only)
YYMMDD - Date of collection

5.3 Field QC Sample Collection

5.3.1 Equipment Rinsate Blank Sample Collection

Equipment rinsate blank samples will be collected when non-dedicated or non-disposable sampling equipment is used to collect samples. Equipment rinsate blanks consist of laboratory purified water that has been routed through decontaminated sampling equipment and collected into the appropriate containers. The containers will be filled in order of decreasing analyte volatility (i.e., VOCs first, SVOCs second, which are followed by the containers for the remaining analyses). One Equipment rinsate blank per day will be collected.

5.3.2 Field Duplicate Sample Collection

5.3.2.1 Water Samples

Field duplicate samples will be collected concurrently with the investigative sample alternating the filling of each sample container. One field duplicate per 10 samples (minimum of one field duplicate per event) will be collected.

5.3.2.2 Soil and Solid Samples

Soil and sediment field duplicates will be collected concurrently with the investigative sample using the procedures identified in Appendix D. One field duplicate per 10 samples (minimum of one field duplicate per event) will be collected.

5.3.3. MS/MSD Sample Collection

MS/MSD sample collection for aqueous and non-aqueous samples requires triple the sample volume. One MS/MSD sample per event will be collected.

6.0 Custody Procedures

Custody is one of several factors necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for admissibility: relevance and authenticity. Sample custody is addressed in three parts: field sample collection, laboratory analysis, and final evidence files. Final evidence files, including all originals of laboratory reports, are maintained under document control in a secure area.

Custody of a sample begins when it is collected by or transferred to an individual and ends when that individual relinquishes or disposes of the sample. A sample or evidence file is under your custody if:

- The item is in actual possession of a person
- The item is in the view of the person after being in actual possession of the person
- The item was in actual possession but is stored to prevent tampering
- The item is in a designated and identified secure area

6.1 Field Custody Procedures

Field personnel will be required to keep written records of field activities on applicable preprinted field forms, in a bound field notebook, or in an electronic format. The records provide the means of recording data collecting activities. Non-electronic records will be written legibly in ink and will contain pertinent field data and observations. Written entry errors or changes will be crossed out with a single line, dated, and initialed by the person making the correction. The records will be periodically reviewed by the Æ QA Officer. The team may have one record or logbook (or electronic record) for the team, which is kept as the project record. Additionally, task specific Æ forms will be used to record field observations. If this is the project standard, all samplers must record their findings in the same record location/logbook. Each title page should include field team member's name, project name, project start date, project end date, and unique page number.

The beginning of each entry in the record will contain the following information:

- Date
- Start time
- Weather
- Names of field personnel (including subcontractors)
- Level of personal protection used at the Facility
- Names of all visitors and the purpose of their visit

For each measurement and sample collected the following will be recorded:

- Detailed description of sample point
- Equipment used to collect sample or make measurement and the date and time equipment was last calibrated
- Time sample was collected
- Sample description
- Depth sample was collected
- Volume and number of containers
- Sampler identification

6.1.1 Field Procedures

The data quality can be affected by sample collection activities. If the integrity of collected samples is questionable, the data, regardless of its analytical quality, also will be questionable.

The following procedure describes the process to maintain the integrity of the samples:

1. Upon collection, samples are placed in the proper containers. In general, samples collected for organic analysis will be placed in pre-cleaned glass containers, and samples collected for inorganic analysis will be placed in pre-cleaned bottles. The sample container, preservation methods, shipping, and packaging requirements are presented in Table 5.1.
2. Samples will be assigned a unique sample number and will have a sample label affixed to the sample container. The information to be placed on the sample label will include the sample ID number, the sample type, the sampler's name, date collected, preservation technique, and analytical parameter and method to be performed. Information on the labels will be completed with a ballpoint pen or indelible marker, or pre-printed labels may be available containing most of the required information. The remaining information then would need to be added with a ballpoint pen or indelible marker.
3. Samples will be properly and appropriately preserved by field personnel in order to minimize loss of the constituent(s) of interest due to physical, chemical, or biological mechanisms. Sample bottles for aliquots that require preservation (pH adjustment) will be pre-preserved by the laboratory before sending (each bottle will have the appropriate preservative already added).
4. Appropriate volumes will be collected to ensure that the EQLs can be successfully achieved and that the required QC Sample Analyses can be completed.

6.1.2 Transfer of Custody and Shipment Procedures

1. A COC record will be completed during sample collection and will accompany each shipment identifying the contents of the shipment. The COC record will accompany the samples to the laboratory. The field personnel collecting the samples will be responsible for the custody of the samples until the samples are relinquished to the laboratory. Sample transfer will require the individuals relinquishing and receiving the samples to sign, date, and note the time of sample transfer on the COC record. As few people as possible should handle the samples.
2. Samples will be shipped or delivered in a timely fashion to the laboratory so that holding times and/or analysis times as prescribed by the methodology can be met.
3. Samples will also be transported in containers (coolers) packed with ice to maintain the temperatures prescribed in Table 5.1. Samples will be packaged for shipment and shipped to the appropriate laboratory for analysis. The samples will be packed to prevent breakage and movement during shipping. If one COC is used and there are multiple coolers, copies of the COC should be placed in all coolers. The number of coolers must be written on the COC. If one COC per cooler is completed and if coolers split up samples, copies of the original COC may be placed in all coolers related to that sample ID with page numbers (i.e., 1 of 3) on the batched COCs and coolers to alert the lab of the common sample delivery group (SDG). VOC samples will be placed in bubble wrap bags or foam bottle holders. The remaining samples in glass containers will be wrapped in bubble wrap or other lab-supplied packaging material and placed in the sample cooler. Samples in polyethylene

containers will be placed upright directly in the sample cooler. All samples will be placed in an upright position and limited to one layer of samples per each cooler. Additional bubble wrap or packaging material will be added to fill the cooler. Shipping containers will be secured with strapping tape and custody tape for shipment to the laboratory.

4. When samples are split with a regulatory agency and RACER representatives, a separate COC will be prepared for the samples and marked to indicate to whom the samples are being split. The person relinquishing the samples to the regulatory agency or the Site will require the representative's signature acknowledging sample receipt.
5. If samples are sent by a commercial carrier, a bill of lading will be used. A copy of the bill of lading will be retained as part of permanent documentation. Commercial carriers are not required to sign the custody record as long as the custody record is sealed inside the sample cooler and the custody tape remains intact.
6. Samples will be picked up by a laboratory courier or transported overnight by a courier to the laboratory. In cases where there is more than one day in a given sampling event, samples may be stored in a secure location under proper chain of custody until shipping or delivery to the lab. This cost saving effort would reduce the number of laboratory batches and, in most cases, reduce the amount of associated QC samples/data reporting from the lab. Additional ice will be added to the cooler as needed to maintain proper preservation temperatures.

6.2 Laboratory Chain of Custody Procedures

A full-time sample custodian will be assigned the responsibility of sample control. It will be the responsibility of the sample custodian to receive all incoming samples. Once received, the custodian will document that the custody tape on the coolers is unbroken, that each sample is received in good condition (e.g., unbroken, cooled, etc.), that the associated paperwork, such as COC forms, have been completed, and will sign the COC forms. In special cases, the custodian will document for appropriate sub-samples that COC with proper preservation has been accomplished. The custodian also will document that sufficient sample volume has been received to complete the analytical program. The sample custodian then will place the samples into secure, limited access storage (refrigerated storage, if required). The sample custodian will assign a unique number to each incoming sample for use in the laboratory. The unique number will then be entered into the sample-receiving log. The laboratory date of receipt also will be noted.

Consistent with the analyses requested on the COC form, analyses by the laboratory's analysts will begin in accordance with the appropriate methodologies. Samples will be removed from secure storage only after internal COC sign-out procedures have been followed.

6.3 Storage of Samples

Sample containers with volume remaining will be returned to secure and limited access storage. Upon completion of all laboratory analyses for each sample submittal and generation of the laboratory report, samples will be stored by the sample custodian. The length of time that samples are held will be at least 30 days after reports have been submitted. Disposal of remaining samples will be completed in compliance with all Federal, State, and local requirements.

Laboratory custody procedures and document control for those samples analyzed by the project laboratory will be carried out using the laboratory's SOPs.

6.4 Final Project Files Custody Procedures

The final project file will be the central repository for all documents with information relevant to sampling and analysis activities as described in this QAPP. The Æ Project Manager will be the custodian of the project file. The project files for the sampling activity, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews will be maintained in a secured, limited access area and under custody of the Æ Project Manager or their designee.

The final project file will include:

- Project plans and drawings
- Field data records
- Sample identification documents
- Soil boring/monitoring well logs
- All COC documentation
- Correspondence
- References, literature
- Laboratory data deliverables
- Data validation and assessment reports
- Progress reports, QA reports
- Final reports

Reports submitted to the regulatory agency will included appropriate site drawings, field logs (such as low flow sampling logs), sample identification documents, soil boring/monitoring well logs, COC documentation, and data validation memos.

The laboratory will be responsible for maintaining analytical logbooks, laboratory data, and sample COC documents, both hard copy and electronic. Raw laboratory data files and copies of hard copy reports will be inventoried and maintained by the laboratory for a period of 10 years. Lab and field records will be stored for 10 years in Æ's electronic filing system.

7.0 Calibration Procedures and Frequency

This section describes procedures for maintaining the accuracy for all the instruments and measurement equipment, which will be used for conducting field tests and laboratory analyses. These instruments and equipment will be calibrated prior to each use or according to a periodic schedule.

7.1 Field Instrument Calibration Procedures

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated as specified in the field SOPs.

The field instruments are likely to include dissolved oxygen meters, oxidation reduction potential (ORP) pH meters, turbidity meters, specific conductance meters, water-level meters, and photoionization detectors (PIDs). Field instruments will be used for real-time sample measurement during monitoring well sampling and organics screening for both on-Facility screening of soil samples and for health and safety air monitoring, as described in the HASP.

Satisfactory completion of the pre-operation inspection will be noted on the Field Sampling Record, along with the results of each field measurement.

7.2 Laboratory Instrument Calibration Procedures

Calibration procedures for a specific laboratory instrument will consist of initial calibration, initial calibration verification, and continuing calibration verification. The SOPs in Appendix B present the specific calibration procedures for each method of analysis. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria, and the conditions that will require calibration. In all cases, the initial calibration will be verified using an independently prepared calibration verification solution.

The use of materials of known purity and quality will be utilized for the analysis of environmental samples. The laboratory will carefully monitor the use of all laboratory materials including solutions, standards, and reagents through well-documented procedures.

All solid chemicals and acids/bases used by the laboratory will be reagent grade or better. All gases will be high purity or better. All SRMs or Performance Evaluation (PE) Materials will be obtained from approved vendors of the NIST, the USEPA Environmental Monitoring Support Laboratories (EMSL), or reliable CRADA certified commercial sources.

All materials including standards or standard solutions will be dated upon receipt, and will be identified by material name, lot number, purity or concentration, supplier, receipt/preparation date, recipient/preparer's name, expiration date, and all other pertinent information.

8.0 Analytical Procedures

Analytical procedures to be utilized for analysis of environmental samples will be based on referenced USEPA analytical protocols and the laboratory SOPs that implement these methods, with the exception of the analysis of PFAS, which does not have an approved USEPA method. For analysis of PFAS, the laboratory performs ASTM D7979 method with isotopic dilution for groundwater samples and ASTM D7968 method with isotopic dilution for soil samples. These project-specific SOPs are provided in Appendix B and D to this QAPP.

8.1 Field Analytical Procedures

Field analytical procedures include the measurement of pH/temperature, specific conductivity, dissolved oxygen, turbidity, and ORP during sampling of groundwater, and the qualitative measurement of VOC (for areas of known, suspected or unknown VOC impacts) during the collection of soil samples at the Site. Specific guidance in the measurement of these parameters is presented in the SOPs provided in Appendix D of this QAPP.

8.2 Laboratory Analytical Procedures

Laboratory preparation and analytical SOPs and the methods upon which they are based. The referenced SOPs provided in Appendix B of this document are based on the USEPA methodology requirements promulgated in:

1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846 EPA, USEPA Office of Solid Waste, 3P Edition and promulgated updates, 1986
2. "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983
3. "Standard Methods for the Examination of Water and Wastewater", APHA, AWWA, and WEF, 22th Edition, 2009 (with subsequent editions)

4. ASTM D7979-19, Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), 2019

5. ASTM D7968-17, Standard Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), 2017

The EQLs for the target analytes and compounds for the environmental media to be analyzed as part of the investigation are presented in Table 1.2.

8.2.1 List of Project Target Compounds and Laboratory Detection Limits

Complete listings of project target compounds and project EQLs for each analyte group are listed in Table 1.2. MDLs have been determined experimentally by the project laboratory using the procedure identified in 40 CFR, Part 136 Appendix B. The laboratory's most recent MDLs will be provided upon request.

8.2.2 List of Method Specific Quality Control Criteria

The laboratory SOPs include a section that presents the minimum QC requirements for the project analyses. Section 9 references the frequency of the associated QC samples for each sampling effort and matrix.

9.0 Internal Quality Control Checks

This section presents the internal QC checks that will be employed for field and laboratory measurements.

9.1 Field Quality Control

QC procedures for pH/temperature, turbidity, and conductivity of water samples and PID screening soil samples will include calibrating the instruments as described in Section 7 of this QAPP, measuring duplicate samples and checking the reproducibility of the measurements by taking multiple readings on a single sample or the measurement reference standards. The ORP meter cannot be calibrated; it can only be checked for accuracy using a known solution. The QC information for field equipment is stated in Section 3 of this QAPP. Assessment of field sampling precision and bias will be made by collecting field duplicates and equipment rinsate blanks for laboratory analysis. Collection of the samples will be in accordance with the applicable procedures in Section 5 of this QAPP.

9.1.1 Equipment Rinsate Blanks

Internal QC checks will include analysis of equipment rinsate blanks to validate successful equipment cleaning activities if the equipment is used and decontaminated between sampling locations. Whenever possible, dedicated equipment (no rinsate blank necessary) will be employed to reduce the possibility of cross-contamination of samples.

The frequency of non-disposable equipment rinsate blank sample preparation will be one for every 20 investigative samples. However, at a minimum, one will be collected each day for each type of sampling equipment on which decontamination procedures have been performed.

9.1.2 Trip Blanks

Trip blanks samples will be prepared by the project laboratory using laboratory purified water placed within pre-cleaned 40-milliliter (mL) VOC vials equipped with Teflon septa.

Trip blanks will accompany each SDG of environmental samples collected for analysis of VOCs and PFAS.

Trip blank samples will be placed in each cooler which stores and transports project samples to be analyzed for VOCs along with the project samples.

9.1.3 Field Duplicate Samples

Field duplicate samples are collected in a similar fashion to investigative samples at a minimum frequency of 1 duplicate per 10 investigative samples by matrix. Field duplicate samples are analyzed by the laboratory to evaluate matrix, sample, and analytical reproducibility.

9.2 Laboratory Procedures

The laboratory identified in Section 2 of this QAPP has QC programs to ensure the reliability and validity of the analysis performed at the laboratory. All analytical procedures are documented in writing as SOPs and each SOP includes a QC section, which addresses the minimum QC requirements for the procedure. The internal QC checks may vary slightly for each individual procedure but, in general, will include the following QC requirements:

- Calibration Standards
- Instrument Performance Checks – Organics
- Initial and Continuing Calibration Checks
- Internal Standard Performance
- Method Blank Samples
- LCSs and QC Check Samples
- MS/MSD
- Surrogates
- Inductively Coupled Plasma (ICP) Interference Check Samples (ICS)
- ICP Serial Dilution
- ICP and ICP/MS QC Analyses
- Reagent Checks
- Blind Check Samples

All data will be properly recorded. Any samples analyzed in nonconformance with QC criteria will be reanalyzed by the laboratory, if sufficient volume is available.

10.0 Data Reduction, Validation, and Reporting

All data generated through in field activities or by the laboratory operation shall be reduced and validated prior to reporting in accordance with the following procedures.

10.1 Data Reduction

10.1.1 Field Data Reduction Procedures

Field data reduction procedures will be minimal in scope compared to those implemented in the laboratory setting. Only direct read instrumentation will be employed in the field. The pH, conductivity, ORP temperature, turbidity, and PID readings collected in the field will be generated from direct read instruments following calibration per manufacturer's recommendations. Such data will be written into field logbooks, field forms or entered into a portable electronic device immediately after measurements are taken. If errors are made, results will be legibly crossed out, initialed, and dated by the field member, and corrected in a space adjacent to the original entry. Later, when the results forms required for this study are being filled out, the Æ Project Coordinator will proof the forms to determine whether any transcription errors have been made by the field crew. Copies of field notes, forms or electronic forms will be included as an attachment in the appropriate report.

10.1.2 Laboratory Data Reduction Procedures

For this project, the equations that will be employed in reducing data are found in the appropriate chapter of SW-846, Third Edition. Two of these equations, expressing analytical accuracy and precision, are presented in Section 3 of this QAPP. Such formulae make pertinent allowances for matrix type. All calculations are checked at the conclusion of each operating day. Errors are noted; and corrections are made, but the original notations are crossed out legibly. Analytical results for soil samples shall be calculated and reported on a dry weight basis.

QC data (e.g., laboratory duplicates, surrogates, MS, and MSD) will be compared to the method acceptance criteria or to laboratory acceptance criteria when no method criteria are available. Data considered to be acceptable will be entered into the laboratory computer system. Data summaries will be sent to the Laboratory QA Officer for review. If approved, data are logged into the project database format. Unacceptable data shall be appropriately qualified in the project report. Case narratives will be prepared, which will include information concerning data that fell outside acceptance limits and any other anomalous conditions encountered during sample analysis.

10.2 Data Validation

Data validation procedures shall be performed for both field and laboratory operations as described below.

10.2.1 Procedures Used to Evaluate Field Data

Procedures to evaluate field data for this project will include review of field logbooks and checking for transcription errors to project specific documents. This task will be the responsibility of the Æ QA Officer.

10.2.2 Procedures to Validate Laboratory Data

The Æ QA Officer or designee will perform analytical data validation using the following documents as guidance for the review process.

"National Functional Guidelines for Superfund Organic Methods Data Review", EPA 540-R-2017-002, January 2017, "National Functional Guidelines for Inorganic Superfund Methods Data Review", EPA 540-R-2017-001, January 2017 and "Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed Using EPA Method 537", EPA 910-R-18-001, November 2018.

The specific data qualifiers used will be as presented and defined in the Contract Laboratory Program (CLP) National Functional Guidelines. The level of validation will depend on the stage or phase of the Project. The stages of data validation and review are defined in "Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use", 2009.

A Stage 1A data validation will be performed on 50 percent of the laboratory data for all data except PFAS Characterization samples. The Stage 1A deliverables will consist, at minimum, of the following components:

Organic Analysis

- Technical holding times
- Method, trip and field blanks
- Field duplicate samples

Inorganic Analysis

- Technical holding times
- Blanks
- Field duplicate samples

The laboratory data package will include sample COC forms, analytical results, QC summaries, and supporting raw data from instrument printouts. If QC issues are suspected during the Stage 1A validation, a higher stage of validation, Stage 2A, may be performed on the data.

A Stage 2A data validation will be performed on 100 percent of the laboratory data for PFAS Characterization samples. The Stage 2A deliverables will consist of the following components:

Organic Analysis

- Technical holding times
- Method, trip and field blanks
- System monitoring compounds (surrogate spikes)
- MS/MSD results
- LCS
- Field duplicate samples

Inorganic Analysis

- Technical holding times
- Blanks
- LCS
- MS/MSD and MD results
- Field duplicate

The laboratory data package will include sample COC forms, analytical results, QC summaries, and supporting raw data from instrument printouts. If QC issues are suspected during the Stage 2A validation, a higher stage of validation, Stage 3, may be performed on the data.

The Stage 3 deliverables will consist of the following components:

Organic Analysis

- Technical holding times
- GC/MS instrument performance check
- Initial and continuing calibration
- Internal standard performance
- Method, trip and equipment rinsate blanks
- System monitoring compounds (surrogate spikes)
- MS/MSD results
- Laboratory control samples
- Field duplicate samples

Inorganic Analysis

- Technical holding times
- Initial calibration
- Initial and continuing calibration verification
- Calibration and method blanks
- ICP interference check samples
- ICP/MS internal standards
- ICP serial dilutions
- Laboratory control samples
- MS/MSD results

- Field duplicate

A Stage 1 validation will be performed on the remaining project scope, including monitoring and Post Injection sampling. The laboratory data package will include sample COC forms, analytical results, and QC summaries. The data will be reviewed for completeness.

The Data Validator will evaluate the completeness of each data package. Completeness checks will be administered on all data to determine whether deliverables specified in the QAPP are present. At a minimum, deliverables will include sample COC forms, analytical results, QC summaries, and supporting raw data from instrument printouts. The review will determine whether all required items are present and request copies of missing deliverables.

10.3 Data Reporting

Data reporting procedures shall be carried out for field and laboratory operations as indicated below.

10.3.1 Field Data Reporting

Field data reporting shall be conducted principally through the transmission of report sheets containing tabulated results of all measurements made in the field and documentation of all field calibration activities.

10.3.2 Laboratory Data Reporting

The laboratory data reporting package will be sufficient to perform a data validation in accordance with protocols described in Section 10.2.2. The task of reporting laboratory data by Æ will be initiated after the completion of data validation.

The Laboratory Project Manager will perform a final review of the QC data summary packages and case narratives to determine whether the report meets the project requirements. In addition to the record of the COC, the final laboratory data report format shall consist of the following:

1. Title Page
    - Project name and number
    - Laboratory project or lot number
    - Signature of the Laboratory QA Officer or his designee
    - Date issued
2. Table of Contents - Laboratory Report Contents
3. Case Narrative
    - Number of samples and respective matrices
    - Laboratory analysis performed
    - Any deviations from intended analytical strategy
    - Definition of data qualifiers used
    - QC procedures utilized and references to the acceptance criteria
    - Condition of samples "as received"

- Discussion of whether or not sample holding times were met
- Discussion of technical problems or other observations which may have created analytical difficulties
- Discussion of laboratory QC checks which failed to meet project criteria

4. Analytical Methods Summary - Methods of Sample Preparation and Analyses for Samples
5. Analytical Sample Summary – Cross-Reference Table of Laboratory Sample to Project Sample Identification Numbers
6. Shipping and Receiving Documents
   - Sample container documentation
   - Sample reception information and original COC record
7. Chemistry Data Package by Analysis
   - Sample Results
     - Sample quantitation reporting limit (RL), reporting MDL, and estimated values between the RL and MDL
     - Methods of sample preparation and analyses for samples
     - Raw data for sample results (dated chromatograms, parameter specific quantitation reports, mass spectra, and instrument printouts) --required upon Æ request or when stage 3 validation is required
   - QC Summary Data with Current Control Limits
     - MS/MSD recoveries, LCS, method blank results, and surrogate recoveries
     - GC/MS tuning results and internal standards (organics)-- required upon Æ request or when stage 3 validation is required
     - MS recoveries and MD RPDs, LCS, method blank results
     - Serial dilutions, reagent blank results, and interference check standards (inorganics) required upon Æ request or when stage 3 validation is required

The project laboratory will provide electronic data deliverables (EDDs). The EDDs are imported into excel spreadsheets for manipulation and presentation.

11.0 Performance and System Audits

A performance audit is an independently obtained quantitative comparison with data routinely obtained in the field or the laboratory. Performance audits include two separate, independent parts: internal and external audits.

11.1 Field Performance and System Audits

11.1.1 Internal Field Audit Responsibilities

Internal audits of field activities include the review of sampling and field measurements conducted by the Æ QA Officer. The audits will verify that all procedures are being followed. Internal field audits will be conducted once during each phase (or once per year for routine repetitive sampling) of the sampling and at the conclusion of the project. The audits will include examination of the following:

1. Field sampling records, screening results, instrument operating records
2. Sample collection
3. Handling and packaging in compliance with procedures
4. Maintenance of QA procedures
5. COC reports

Follow-up audits will be conducted to correct deficiencies and to verify that procedures are maintained throughout the investigation. A Field Audit Memo will be included as an attachment in the corresponding report which the data is presented. The field audit checklist will be included in Appendix E.

11.1.2 External Field Audit Responsibilities

External audits may be conducted by the Regulatory Agency Project Coordinator at any time during the field operations. These audits may or may not be announced and are at the discretion of the regulatory agency. The external field audits can include (but are not limited to) the following:

1. Sampling equipment decontamination procedures
2. Sample bottle preparation procedures
3. Sampling procedures
4. Examination of HASPs
5. Procedures for verification of field duplicates
6. Field screening practices

11.2 Laboratory Performance and System Audits

11.2.1 Internal Laboratory Audit Responsibilities

The laboratory system audits will be conducted by the Laboratory Project QA Officer or designee and performed on an annual basis. Laboratory performance audits will be conducted prior to field activities or on an annual basis, depending on the duration of the project.

The system audit will include an examination of laboratory documentation including: sample receiving logs, sample storage, COC procedures, sample preparation and analysis, and instrument operating records.

The performance audits will include submittal of blind performance evaluation samples along with project samples. The Laboratory Project QA Officer will evaluate the analytical results to ensure the lab is maintaining acceptable QC performance. The laboratory audit checklist is provided in Appendix F.

System audits, as opposed to performance audits, are strictly qualitative and consist of an on-Facility review of a laboratory's QA system and physical facilities for calibration and measurement.

At the conclusion of internal or external system audits, reports are provided to the laboratory's operating divisions for appropriate comment and remedial/corrective action where necessary. Written response to internal as well as external audits will be required. Records of audits and corrective actions are maintained by the Laboratory QA Officer.

11.2.2 External Laboratory Audit Responsibilities

External audits may be conducted as required, by appropriate QA personnel of the regulatory agency and may be conducted at least once prior to sampling and analysis activities.

External audits may include any of the following:
1. Review of laboratory analytical procedures
2. Laboratory on-Facility visits
3. Submission of performance evaluation samples for analysis

Failure of any of the above audit procedures may lead to laboratory disqualification, and another suitable laboratory may have to be chosen. An on-Facility review can consist of:
1. Sample receipt procedures
2. Custody, sample security, and log-in procedures
3. Review of instrument calibration logs
4. Review of QA procedures
5. Review of logbooks
6. Review of analytical SOPs
7. Personnel interviews

A review of a data package from samples recently analyzed by the laboratory can include (but not be limited to) the following:
1. Comparison of resulting data to the SOP or method
2. Verification of initial and continuing calibrations within control limits
3. Verification of surrogate recoveries and instrument timing results
4. Review of extended quantitation reports for comparisons of library spectra to instrument spectra, where applicable
5. Assurance that samples are run within holding times

12.0 Preventative Maintenance

12.1 Field Instrument Preventative Maintenance

The field equipment preventative maintenance program ensures the effective completion of the sampling effort and is designed to minimize equipment downtime. Program implementation is concentrated in three areas:

- Maintenance responsibilities
- Maintenance schedules
- Inventory of critical spare parts and equipment

The maintenance responsibilities for field equipment will be assigned to the task leaders in charge of specific field operations. Field personnel will be responsible for daily field checks and calibrations and for reporting any problems with the equipment. The maintenance schedule will follow the manufacturer's recommendations. In addition, the field personnel will be responsible for determining that critical spare parts are included with the field equipment. An adequate inventory of spare parts will be maintained. The inventory will primarily contain parts that are subject to frequent failure, have limited useful lifetimes, and/or cannot be obtained in a timely manner.

12.2 Laboratory Instrument Preventative Maintenance

Analytical instruments at the laboratory will undergo routine and/or preventative maintenance. The extent of the preventative maintenance will be a function of the complexity of the equipment.

Generally, annual preventative maintenance service will involve cleaning, adjusting, inspecting, and testing procedures designed to deduce instrument failure and/or extend useful instrument life.

Between visits, routine operator maintenance and cleaning will be performed according to manufacturer's specifications by laboratory personnel.

Maintenance records will be placed on file at the laboratory and can be made available upon request.

13.0 Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness

The following sections include the procedures and formulae utilized to assess the levels of precision, accuracy, and completeness achieved during the associated sample analyses.

13.1 Field Measurements

Field generated information such as pH and specific conductance data will be reviewed for validity. The review will be performed by the Æ QA Officer and typically will include electronic or bound logbooks/forms, data entry, and calculation checks. Field data will be assessed by the Æ QA Officer who will review the field results for compliance with the established QC criteria that are specified in Section 3 of this QAPP. The accuracy of pH and specific conductance will be assessed using daily instrument calibration, calibration check, and blank data.

13.2 Laboratory Data

Laboratory results will be assessed for compliance with required precision, accuracy, and completeness detailed in the following subsections.

13.2.1 Precision

The precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSD analyses. The RPD will be calculated for each pair of duplicate analyses (laboratory MS/MSDs and field duplicates).

13.2.1.1 Accuracy

The accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Sections 3 and 8 of the QAPP using the analytical results of method blanks, reagent/preparation blank, SRMs or QC check samples, and MS/MSD samples. The percent recovery (%R) of MS samples and SRMs will be calculated.

13.2.2 Completeness

Completeness will be assessed by comparing the number of valid (usable) results (as determined by the Æ QA Officer) to the total possible number of results using the formula presented in Section 3.4.

13.3 Statistical Evaluations

In the examination of data and determination of their precision and accuracy, standard statistical formulae will be used. Further details are provided in the following subsections.

13.3.1 Percent Recovery

The percent recovery of a parameter is calculated by dividing the amount recovered by the true amount added and multiplying by 100. The percent recoveries of spiked samples are evaluated to establish the analytical accuracy of a measurement. Percent recovery is calculated using the following formula:

$$\%\mathrm{R} = \frac{\mathrm{SSR\text{-}SR}}{\mathrm{SA}} \times 100$$

where:

SSR = Spiked Sample Result
SR = Sample Result or Background
SA = Spike Added

13.3.2 Relative Percent Difference

The RPD is calculated by dividing the absolute value of the difference between two numbers by their arithmetic mean and multiplying by 100. The RPD is used to evaluate the analytical precision of two replicate measurements (i.e., MS/MSD). RPD is calculated using the following formula:

$$\mathrm{RPD} = \frac{\mathrm{R1\text{-}R2}}{\mathrm{R1+R2}} \times 200$$

where:

R1 = value of first result
R2 = value of second result

14.0 Corrective Action

14.1 Field Corrective Action

Corrective action is intended to address problems that arise by identification, recommendation, approval, and implementation of measures that counter unacceptable procedures or deficient QC performance. The Æ QA Officer will be responsible for ensuring the quality of the sampling procedures and environmental data and as such, will be responsible for initiating corrective action when appropriate.

The corrective action procedures will be as follows:

1. Identify/define the problem.
2. Assign responsibility for investigating the problem.
3. Investigate/determine the cause of the problem.
4. Determine an appropriate corrective action to eliminate the problem.
5. Implement the corrective action.
6. Evaluate the effectiveness of the corrective action.
7. Verify that the corrective action has eliminated the problem.
8. Prepare a written record detailing the problem, corrective action utilized, and solution of the problem.
9. Submit the Corrective Action Record (CAR) to whoever initiated the corrective action and the Æ QA Officer, Æ Project Manager and RACER Project Manager.

The above procedures may be implemented through the use of the Systems Audit as described previously. Any Field Team member of the project may initiate corrective action procedures by reporting in writing the nature of the suspected problem to the Æ Project Manager or Æ QA Officer. The Æ Project Manager will begin corrective action by relating the problem to appropriate personnel.

14.2 Laboratory Corrective Action

The following paragraphs define the corrective action decision process relative to possible noncompliant events encountered during laboratory analysis of the project samples. Corrective actions will be initiated by the laboratory QA personnel and will be implemented by laboratory staff chemists under the oversight of the laboratory QA personnel. As with field corrective actions, the laboratory QA personnel will document the problem, the corrective action undertaken, and the resolution of the problem. The corrective actions will be performed prior to release of the data from the laboratory.

Documentation will be provided to the Laboratory QA Officer, Æ QA Officer, Æ Project Manager, and RACER Project Manager.

14.3 Corrective Action During Data Validation and Data Assessment

The Æ QA Officer may identify the need for corrective action during either the data validation or data assessment processes. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory (if possible).

These actions are dependent upon the ability to mobilize the field team and whether the data to be collected is necessary to meet the required QA objectives (i.e., the holding time for samples is not exceeded). When the Æ QA Officer identifies a corrective action situation, the RACER Project Manager will be responsible for approving the implementation of corrective action, including resampling, during data assessment. All corrective actions will be documented by the Æ Project Manager.

15.0 Quality Assurance Reports

Critically important to the successful implementation of the QA Plan is a reporting system that provides the means by which the program can be reviewed, problems identified, and programmatic changes made to improve the plan.

QA reports to management include:

- Audit reports, internal and external audits with responses
- Performance evaluation sample results; internal and external sources
- Daily QA/QC exception reports/corrective actions

QA/QC corrective action reports will be prepared by the Æ QA Officer when appropriate and presented to the project and/or laboratory management personnel so that performance criteria can be monitored for all analyses from each analytical department.

16.0 References

United States Environmental Protection Agency, (2001). *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations*. EPA QA/R-5, March 2001

United States Environmental Protection Agency (1991). *Preparation Aids for the Development of Category I Quality Assurance Project Plans.* USEPA/600/8-91/003, Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, Ohio, February 1991

United States Environmental Protection Agency, (1993). *Data Quality Objectives Process for Superfund Interim Final Guidance*. USEPA/540/R-93-071, Office of Solid Waste and Emergency Response (OSWER), September 1993

United States Environmental Protection Agency, (1992). *Specifications and Guidance for Contaminant-Free Sample Containers.* OSWER Directive 9240.0-05A, April 1992

United States Environmental Protection Agency. *USEPA National Functional Guidelines for Superfund Organic Methods Data Review*. USEPA 540-R-2017-002

United States Environmental Protection Agency. *USEPA National Functional Guidelines for Inorganic Superfund Methods Data Review.* USEPA 540-R-2017-001

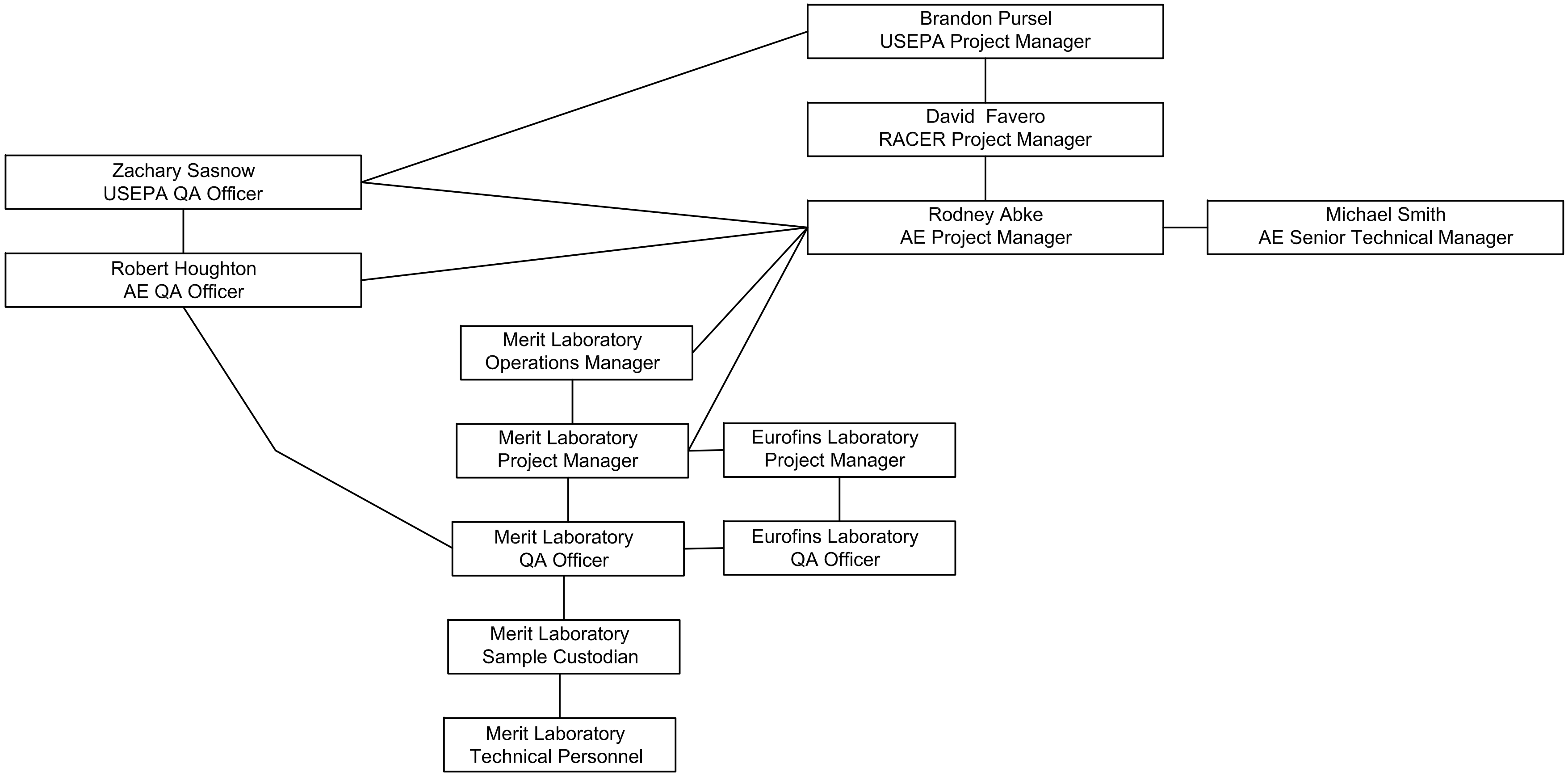
Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed Using EPA Method 537, EPA 910-R-18-001, November 2018.

United States Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Office of Solid Waste, USEPA, SW-846, November 1986, with updates

United States Environmental Protection Agency. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use Office of Solid Waste, USEPA 540-R-05-005.

FIGURES

Applied EcoSystems, Inc.
Environmental Management, Consulting & Field Services

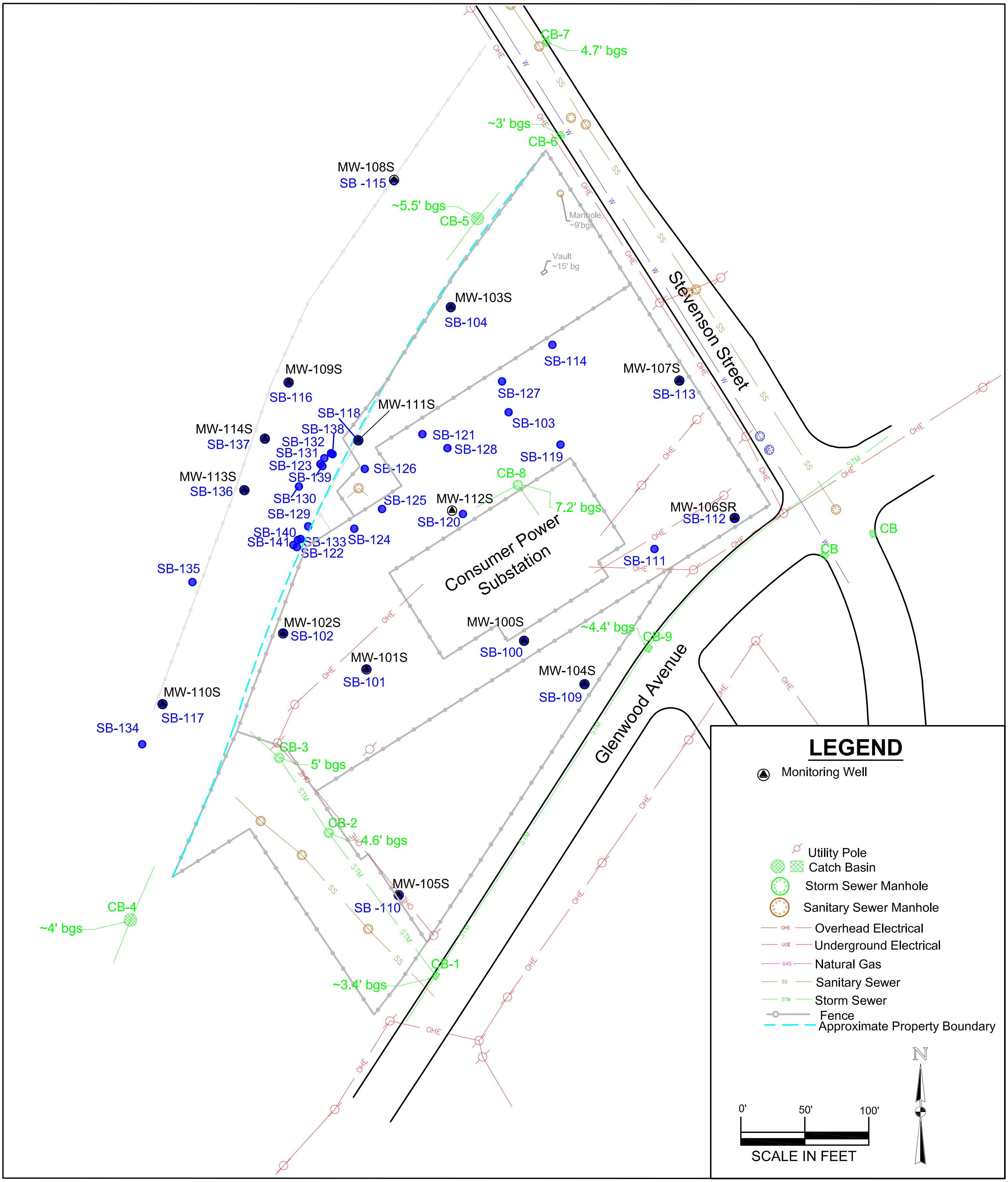


Applied *Eco*Systems, Inc.
Environmental Management, Consulting & Field Services
G-4300 South Saginaw Street, Burton, Michigan 48529
Phone: 810.715.2525; Fax: 810.715.2526

Project Organization Chart

Racer Flint West -12990
Flint West Industrial Land, Flint, Michigan

DRAWING DATE: 04/01/2021	**CHECKED BY:** MDS
PROJECT: 11-4317-102	**FIGURE:** 1



Applied *Eco*Systems, Inc.
Environmental Management, Consulting & Field Services
G-4300 South Saginaw Street, Burton, Michigan 48529
Phone: 810.715.2525; Fax: 810.715.2526

Site Map

Racer Flint West -12990
Flint West Industrial Land, Flint, Michigan

DATE: 01/07/2021	**CHECKED BY:** MDS
PROJECT: 11-4317-102	**FIGURE:** 2

TABLES

Applied EcoSystems, Inc.
Environmental Management, Consulting & Field Services

Table 1.1

Summary of Sampling and Analysis Program
RACER Flint West #12990
Glenwood Avenue and Stevenson Street, Flint Michigan

			Quality Control Samples[1]			
Sample Matrix	**Field Parameters**	**Laboratory Parameters**	**Field Blanks**	**Trip Blanks**	**Field Duplicates**	**MS/MSD**
A. Bi-annual Sampling						
Water	pH, Temperature, Dissolved Oxygen, Conductivity, Turbidity, ORP	Volatile Organic Compounds	1 per day	1 per sample shipment	1 per every 10 samples	1 per sampling event per media
		dissolved and total Metals (Ar, Cr (total), Hex-Cr, Cu, Pb, Se, Zn)	1 per day		1 per every 10 samples	1 per sampling event per media
B. HRC Injection Monitoring						
Water	pH, Dissolved Oxygen Conductivity, ORP, Turbidity	Volatile Organic Compounds	1 per day	1 per sample shipment	1 per every 10 samples	1 per sampling event per media
		dissolved and total Metals (Ar, Cr (total), Hex-Cr, Cu, Pb, Se, Zn, Fe, Mn)	1 per day		1 per every 10 samples	1 per sampling event per media
		Total Organic Carbon			1 per every 10 samples	
		Methane			1 per every 10 samples	
Soil	Photoionization Detector with a 11.7 eV lamp	Volatile Organic Compounds			1 per every 10 samples	
C. PFAS Investigation Sampling						
Water	pH, Temperature, Dissolved Oxygen, Conductivity, Turbidity, ORP	28 per- and polyfluoroalky substances (PFAS) recommended by EGLE		1 per sample shipment	1 per every 10 samples	
Soil	Photoionization Detector with a 11.7 eV lamp	28 per- and polyfluoroalky substances (PFAS) recommended by EGLE		1 per sample shipment	1 per every 10 samples	

[1] - Sample types and numbers based on EGLE recommended QA/QC sampling.

Table 1.2

Target Compound and Target Analyte Parameter List - Merit Analytical Laboratory
RACER Flint West #12990
Glenwood Avenue and Stevenson Street, Flint Michigan

							Accuracy		Precision
Media	**Method Description**	**Method Code**	**Analyte Description**	**Estimated Quantitation Limit (EQL)**	**Method Detection Limit (MDL)**	**Units**	**LCL %**	**UCL %**	**RPD %**
Water Parameters	Arsenic, Dissolved	E200.8	Arsenic, Dissolved	1	0.085	ug/l	85%	115%	20
	Arsenic, Total	E200.8	Arsenic, Total	1	0.085	ug/l	85%	115%	20
	Chromium, Dissolved	E200.8	Chromium, Dissolved	5	0.041	ug/l	85%	115%	20
	Chromium, Total	E200.8	Chromium, Total	5	0.041	ug/l	85%	115%	20
	Chromium VI, Dissolved	SM3500-Cr B	Chromium VI, Dissolved	10	6	ug/l	90%	110%	15
	Chromium VI, Total	SM3500-Cr B	Chromium VI, Total	10	6	ug/l	90%	110%	15
	Copper, Dissolved	E200.8	Copper, Dissolved	1	0.038	ug/l	85%	115%	20
	Copper, Total	E200.8	Copper, Total	1	0.038	ug/l	85%	115%	20
	Iron, Dissolved	E200.8	Iron, Dissolved	20	2.043	ug/l	85%	115%	20
	Iron, Total	E200.8	Iron, Total	20	2.043	ug/l	85%	115%	20
	Lead, Dissolved	E200.8	Lead, Dissolved	3	0.019	ug/l	85%	115%	20
	Lead, Total	E200.8	Lead, Total	3	0.019	ug/l	85%	115%	20
	Manganese, Dissolved	E200.8	Manganese, Dissolved	5	0.052	ug/l	85%	115%	20
	Manganese, Total	E200.8	Manganese, Total	5	0.052	ug/l	85%	115%	20
	Selenium, Dissolved	E200.8	Selenium, Dissolved	5	0.48	ug/l	85%	115%	20
	Selenium, Total	E200.8	Selenium, Total	5	0.48	ug/l	85%	115%	20
	Zinc, Dissolved	E200.8	Zinc, Dissolved	5	0.128	ug/l	85%	115%	20
	Zinc, Total	E200.8	Zinc, Total	5	0.128	ug/l	85%	115%	20
	VOC	SW 8260/8260C	Diethyl ether	10	0.499	ug/l	67%	121%	30
		SW 8260/8260C	Acetone	50	1.385	ug/l	30%	162%	30
		SW 8260/8260C	Methyl iodide	1	0.254	ug/l	69%	116%	30
		SW 8260/8260C	Carbon disulfide	5	0.139	ug/l	64%	137%	30
		SW 8260/8260C	tert-Methyl butyl ether (MTBE)	5	0.185	ug/l	73%	122%	30
		SW 8260/8260C	Acrylonitrile	2	0.565	ug/l	70%	129%	30
		SW 8260/8260C	2-Butanone (MEK)	25	3.972	ug/l	44%	134%	30
		SW 8260/8260C	Dichlorodifluoromethane	5	0.333	ug/l	10%	223%	30
		SW 8260/8260C	Chloromethane	5	0.165	ug/l	24%	167%	30
		SW 8260/8260C	Vinyl chloride	1	0.332	ug/l	44%	149%	30
		SW 8260/8260C	Bromomethane	5	0.276	ug/l	57%	151%	30
		SW 8260/8260C	Chloroethane	5	0.267	ug/l	53%	149%	30
		SW 8260/8260C	Trichlorofluoromethane	1	0.204	ug/l	60%	152%	30
		SW 8260/8260C	1,1-Dichloroethene	1	0.242	ug/l	70%	139%	30
		SW 8260/8260C	Methylene chloride	5	0.237	ug/l	73%	121%	30
		SW 8260/8260C	trans-1,2-Dichloroethene	1	0.221	ug/l	74%	129%	30
		SW 8260/8260C	1,1-Dichloroethane	1	0.225	ug/l	72%	126%	30
		SW 8260/8260C	cis-1,2-Dichloroethene	1	0.311	ug/l	77%	122%	30
		SW 8260/8260C	Tetrahydrofuran	90	1.267	ug/l	59%	118%	30
		SW 8260/8260C	Chloroform	1	0.2	ug/l	78%	124%	30
		SW 8260/8260C	Bromochloromethane	1	0.381	ug/l	78%	121%	30
		SW 8260/8260C	1,1,1-Trichloroethane	1	0.277	ug/l	79%	131%	30
		SW 8260/8260C	4-Methyl-2-pentanone (MIBK)	50	0.343	ug/l	72%	125%	30
		SW 8260/8260C	2-Hexanone	50	0.377	ug/l	55%	137%	30
		SW 8260/8260C	Carbon tetrachloride	1	0.259	ug/l	73%	133%	30
		SW 8260/8260C	Benzene	1	0.16	ug/l	80%	125%	30
		SW 8260/8260C	1,2-Dichloroethane	1	0.262	ug/l	76%	126%	30
		SW 8260/8260C	Trichloroethene	1	0.352	ug/l	80%	124%	30
		SW 8260/8260C	1,2-Dichloropropane	1	0.261	ug/l	79%	126%	30
		SW 8260/8260C	Bromodichloromethane	1	0.313	ug/l	80%	128%	30
		SW 8260/8260C	Dibromomethane	1	0.201	ug/l	77%	122%	30
		SW 8260/8260C	cis-1,3-Dichloropropene	1	0.198	ug/l	80%	130%	30
		SW 8260/8260C	Toluene	1	0.173	ug/l	60%	125%	30
		SW 8260/8260C	trans-1,3-Dichloropropene	1	0.166	ug/l	74%	131%	30
		SW 8260/8260C	1,1,2-Trichloroethane	1	0.285	ug/l	79%	123%	30
		SW 8260/8260C	Tetrachloroethene	1	0.213	ug/l	75%	125%	30
		SW 8260/8260C	trans-1,4-Dichloro-2-butene	1	0.199	ug/l	69%	135%	30
		SW 8260/8260C	Dibromochloromethane	5	0.127	ug/l	75%	127%	30

Table 1.2

Target Compound and Target Analyte Parameter List - Merit Analytical Laboratory
RACER Flint West #12990
Glenwood Avenue and Stevenson Street, Flint Michigan

							Accuracy		Precision
Media	**Method Description**	**Method Code**	**Analyte Description**	**Estimated Quantitation Limit (EQL)**	**Method Detection Limit (MDL)**	**Units**	**LCL %**	**UCL %**	**RPD %**
		SW 8260/8260C	1,2-Dibromoethane	1	0.187	ug/l	70%	134%	30
		SW 8260/8260C	Chlorobenzene	1	0.229	ug/l	79%	123%	30
		SW 8260/8260C	1,1,1,2-Tetrachloroethane	1	0.236	ug/l	80%	126%	30
		SW 8260/8260C	Ethylbenzene	1	0.224	ug/l	80%	129%	30
		SW 8260/8260C	Total Xylenes	3	0.591	ug/l	79%	132%	30
		SW 8260/8260C	p,m-Xylene	2	0.395	ug/l	79%	132%	30
		SW 8260/8260C	o-Xylene	1	0.196	ug/l	80%	131%	30
		SW 8260/8260C	Styrene	1	0.194	ug/l	70%	127%	30
		SW 8260/8260C	Isopropylbenzene	5	0.24	ug/l	74%	122%	30
		SW 8260/8260C	Bromoform	1	0.292	ug/l	69%	128%	30
		SW 8260/8260C	1,1,2,2-Tetrachloroethane	1	0.468	ug/l	80%	126%	30
		SW 8260/8260C	1,2,3-Trichloropropane	1	0.325	ug/l	78%	139%	30
		SW 8260/8260C	n-Propylbenzene	1	0.228	ug/l	82%	131%	30
		SW 8260/8260C	Bromobenzene	1	0.269	ug/l	79%	125%	30
		SW 8260/8260C	1,3,5-Trimethylbenzene	1	0.262	ug/l	81%	129%	30
		SW 8260/8260C	tert-Butylbenzene	1	0.179	ug/l	81%	129%	30
		SW 8260/8260C	1,2,4-Trimethylbenzene	1	0.221	ug/l	81%	131%	30
		SW 8260/8260C	sec-Butylbenzene	1	0.247	ug/l	77%	130%	30
		SW 8260/8260C	p-Isopropyltoluene	5	0.208	ug/l	80%	138%	30
		SW 8260/8260C	1,3-Dichlorobenzene	1	0.209	ug/l	77%	131%	30
		SW 8260/8260C	1,4-Dichlorobenzene	1	0.165	ug/l	21%	138%	30
		SW 8260/8260C	1,2-Dichlorobenzene	1	0.137	ug/l	10%	166%	30
		SW 8260/8260C	1,2,3-Trimethylbenzene	1	0.061	ug/l	76%	124%	30
		SW 8260/8260C	n-Butylbenzene	1	0.222	ug/l	80%	133%	30
		SW 8260/8260C	Hexachloroethane	5	0.214	ug/l	24%	138%	30
		SW 8260/8260C	1,2-Dibromo-3-chloropropane	5	0.262	ug/l	21%	189%	30
		SW 8260/8260C	1,2,4-Trichlorobenzene	5	0.18	ug/l	27%	143%	30
		SW 8260/8260C	1,2,3-Trichlorobenzene	1	0.202	ug/l	75%	131%	30
		SW 8260/8260C	Naphthalene	5	0.213	ug/l	33%	136%	30
		SW 8260/8260C	2-Methylnaphthalene	5	0.163	ug/l	26%	166%	30
	Total Organic Carbon		Total Organic Carbon	1000	170	ug/l	90%	100%	15
	Methane		Methane	SUBCONT	SUBCONT				
	ASTM Method D7979 - 19 Modified (Isotopic Dilution)	ASTMD7979-19M	Perfluorobutanoic acid (PFBA)	20	2.6	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluoropentanoic acid (PFPeA)	10	2.4	ng/l	70%	130%	30
		ASTMD7979-19M	Fluorotelomer sulfonic acid (4:2 FTS)	10	0.8	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorohexanoic acid (PFHxA)	10	0.7	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorobutane sulfonic acid (PFBS)	10	0.8	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluoroheptanoic acid (PFHpA)	10	1.1	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluoropentane sulfonic acid (PFPeS)	10	1.6	ng/l	70%	130%	30
		ASTMD7979-19M	Fluorotelomer sulfonic acid (6:2 FTS)	10	1.5	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorooctanoic acid (PFOA)	10	0.6	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorohexane sulfonic acid (PFHxS)	10	1.2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorohexane Sulfonic Acid - LN (PFHxS-LN)	10	1.2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorohexane Sulfonic Acid - BR (PFHxS-BR)	10	1.2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorononanoic acid (PFNA)	10	0.6	ng/l	70%	130%	30
		ASTMD7979-19M	Fluorotelomer sulfonic acid (8:2 FTS)	10	2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluoroheptane sulfonic acid (PFHpS)	10	2.8	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorodecanoic acid (PFDA)	10	2.6	ng/l	70%	130%	30
		ASTMD7979-19M	N-Methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA)	10	1.8	ng/l	70%	130%	30
		ASTMD7979-19M	N-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA)	10	2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorooctane sulfonic acid (PFOS)	10	2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorooctane Sulfonic Acid - LN (PFOS-LN)	10	2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluorooctane Sulfonic Acid - BR (PFOS-BR)	10	2	ng/l	70%	130%	30
		ASTMD7979-19M	Perfluoroundecanoic acid (PFUnDA)	10	0.5	ng/l	70%	130%	30

Table 1.2

Target Compound and Target Analyte Parameter List - Merit Analytical Laboratory

RACER Flint West #12990

Glenwood Avenue and Stevenson Street, Flint Michigan

								Accuracy		Precision
	Media	Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units	LCL %	UCL %	RPD %
			ASTMD7979-19M	Perfluorononane sulfonic acid (PFNS)	10	1.9	ng/l	70%	130%	30
			ASTMD7979-19M	Perfluorododecanoic acid (PFDoDA)	10	0.9	ng/l	70%	130%	30
			ASTMD7979-19M	Perfluorodecane sulfonic acid (PFDS)	10	0.9	ng/l	70%	130%	30
			ASTMD7979-19M	Perfluorotridecanoic acid (PFTrDA)	10	1	ng/l	70%	130%	30
			ASTMD7979-19M	Perfluorooctane sulfonamide (FOSA)	10	1.2	ng/l	70%	130%	30
			ASTMD7979-19M	Perfluorotetradecanoic acid (PFTeDA)	10	1.5	ng/l	70%	130%	30
			ASTMD7979-19M	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	10	2.4	ng/l	70%	130%	30
			ASTMD7979-19M	9-chlorohexadecafluoro-3-oxanone1-sulfonic acid (9Cl-PF3ONS)	10	2.2	ng/l	70%	130%	30
			ASTMD7979-19M	4,8-dioxa-3H-perfluorononanoic acid (ADONA)	10	2.8	ng/l	70%	130%	30
			ASTMD7979-19M	Hexafluoropropylene oxide dimer (HFPO-DA)	10	2.5	ng/l	70%	130%	30
	Soil Parameters	Arsenic, Total	SW6020A	Arsenic, Total	500	14	ug/kg	85%	115%	20
		Chromium, Total	SW6020A	Chromium, Total	1000	3.6	ug/kg	85%	115%	20
		Chromium VI, Total	SW7196	Chromium VI, Total	1000	60	ug/kg	90%	100%	15
		Copper, Total	SW6020A	Copper, Total	1000	2.8	ug/kg	85%	115%	20
		Iron, Total	SW6020A	Iron, Total	1000	48.6	ug/kg	85%	115%	20
		Lead, Total	SW6020A	Lead, Total	1000	3.8	ug/kg	85%	115%	20
		Manganese, Total	SW6020A	Manganese, Total	100	2	ug/kg	85%	115%	20
		Selenium, Total	SW6020A	Selenium, Total	500	49	ug/kg	85%	115%	20
		Zinc, Total	SW6020A	Zinc, Total	1000	27.6	ug/kg	85%	115%	20
		VOC	SW5035A/8260C	Diethyl ether	500	26.85	ug/kg	52%	123%	30
		SW 846 Method 8260C Revision 3 August 2006 / 5035A Revision 1 July 2002	SW5035A/8260C	Acetone	2500	276.7	ug/kg	25%	155%	30
			SW5035A/8260C	Methyl iodide	50	9.4	ug/kg	57%	111%	30
			SW5035A/8260C	Carbon disulfide	250	6.4	ug/kg	57%	123%	30
			SW5035A/8260C	tert-Methyl butyl ether (MTBE)	250	7.9	ug/kg	68%	124%	30
			SW5035A/8260C	Acrylonitrile	100	13.4	ug/kg	59%	133%	30
			SW5035A/8260C	2-Butanone (MEK)	1250	26.7	ug/kg	39%	137%	30
			SW5035A/8260C	Dichlorodifluoromethane	250	10.6	ug/kg	10%	172%	30
			SW5035A/8260C	Chloromethane	250	6.4	ug/kg	30%	153%	30
			SW5035A/8260C	Vinyl chloride	50	8.3	ug/kg	45%	139%	30
			SW5035A/8260C	Bromomethane	250	11.4	ug/kg	10%	157%	30
			SW5035A/8260C	Chloroethane	250	10.7	ug/kg	10%	169%	30
			SW5035A/8260C	Trichlorofluoromethane	50	8.4	ug/kg	26%	138%	30
			SW5035A/8260C	1,1-Dichloroethene	50	7.1	ug/kg	59%	138%	30
			SW5035A/8260C	Methylene chloride	250	10.7	ug/kg	71%	122%	30
			SW5035A/8260C	trans-1,2-Dichloroethene	50	7.7	ug/kg	73%	129%	30
			SW5035A/8260C	1,1-Dichloroethane	50	4.9	ug/kg	73%	123%	30
			SW5035A/8260C	cis-1,2-Dichloroethene	50	11.7	ug/kg	75%	121%	30
			SW5035A/8260C	Tetrahydrofuran	500	77.4	ug/kg	48%	126%	30
			SW5035A/8260C	Chloroform	50	8.8	ug/kg	75%	123%	30
			SW5035A/8260C	Bromochloromethane	50	12.2	ug/kg	72%	123%	30
			SW5035A/8260C	1,1,1-Trichloroethane	50	6.7	ug/kg	74%	129%	30
			SW5035A/8260C	4-Methyl-2-pentanone (MIBK)	2500	19	ug/kg	60%	134%	30
			SW5035A/8260C	2-Hexanone	2500	21.3	ug/kg	46%	142%	30
			SW5035A/8260C	Carbon tetrachloride	50	8.1	ug/kg	73%	136%	30
			SW5035A/8260C	Benzene	50	6.4	ug/kg	75%	129%	30
			SW5035A/8260C	1,2-Dichloroethane	50	8.5	ug/kg	73%	125%	30
			SW5035A/8260C	Trichloroethene	50	7	ug/kg	74%	128%	30
			SW5035A/8260C	1,2-Dichloropropane	50	10.9	ug/kg	78%	124%	30
			SW5035A/8260C	Bromodichloromethane	50	8	ug/kg	77%	128%	30
			SW5035A/8260C	Dibromomethane	50	16.1	ug/kg	73%	127%	30
			SW5035A/8260C	cis-1,3-Dichloropropene	50	7.1	ug/kg	79%	128%	30
			SW5035A/8260C	Toluene	50	6.4	ug/kg	75%	129%	30
			SW5035A/8260C	trans-1,3-Dichloropropene	50	8.4	ug/kg	75%	130%	30
			SW5035A/8260C	1,1,2-Trichloroethane	50	13	ug/kg	71%	126%	30
			SW5035A/8260C	Tetrachloroethene	50	8.2	ug/kg	73%	125%	30

Table 1.2

Target Compound and Target Analyte Parameter List - Merit Analytical Laboratory
RACER Flint West #12990
Glenwood Avenue and Stevenson Street, Flint Michigan

								Accuracy		Precision
	Media	**Method Description**	**Method Code**	**Analyte Description**	**Estimated Quantitation Limit (EQL)**	**Method Detection Limit (MDL)**	**Units**	**LCL %**	**UCL %**	**RPD %**
			SW5035A/8260C	trans-1,4-Dichloro-2-butene	50	15.4	ug/kg	58%	143%	30
			SW5035A/8260C	Dibromochloromethane	250	8	ug/kg	69%	133%	30
			SW5035A/8260C	1,2-Dibromoethane	50	9.5	ug/kg	71%	129%	30
			SW5035A/8260C	Chlorobenzene	50	11.7	ug/kg	74%	128%	30
			SW5035A/8260C	1,1,1,2-Tetrachloroethane	50	7.2	ug/kg	77%	133%	30
			SW5035A/8260C	Ethylbenzene	50	7.9	ug/kg	78%	130%	30
			SW5035A/8260C	Total Xylenes	150	23.2	ug/kg	80%	132%	30
			SW5035A/8260C	p,m-Xylene	100	14.7	ug/kg	80%	132%	30
			SW5035A/8260C	o-Xylene	50	8.5	ug/kg	79%	132%	30
			SW5035A/8260C	Styrene	50	6.1	ug/kg	71%	119%	30
			SW5035A/8260C	Isopropylbenzene	250	8.9	ug/kg	70%	128%	30
			SW5035A/8260C	Bromoform	50	12.9	ug/kg	55%	137%	30
			SW5035A/8260C	1,1,2,2-Tetrachloroethane	50	14.5	ug/kg	65%	135%	30
			SW5035A/8260C	1,2,3-Trichloropropane	50	12.5	ug/kg	67%	155%	30
			SW5035A/8260C	n-Propylbenzene	50	8.4	ug/kg	77%	135%	30
			SW5035A/8260C	Bromobenzene	50	12.2	ug/kg	74%	132%	30
			SW5035A/8260C	1,3,5-Trimethylbenzene	50	9	ug/kg	76%	137%	30
			SW5035A/8260C	tert-Butylbenzene	50	6.8	ug/kg	76%	135%	30
			SW5035A/8260C	1,2,4-Trimethylbenzene	50	6.6	ug/kg	77%	139%	30
			SW5035A/8260C	sec-Butylbenzene	50	9.1	ug/kg	73%	136%	30
			SW5035A/8260C	p-Isopropyltoluene	250	7.9	ug/kg	77%	141%	30
			SW5035A/8260C	1,3-Dichlorobenzene	50	9.9	ug/kg	77%	131%	30
			SW5035A/8260C	1,4-Dichlorobenzene	50	9.3	ug/kg	33%	126%	30
			SW5035A/8260C	1,2-Dichlorobenzene	50	10.9	ug/kg	74%	133%	30
			SW5035A/8260C	1,2,3-Trimethylbenzene	50	8.4	ug/kg	71%	130%	30
			SW5035A/8260C	n-Butylbenzene	50	3	ug/kg	75%	139%	30
			SW5035A/8260C	Hexachloroethane	250	13.8	ug/kg	56%	129%	30
			SW5035A/8260C	1,2-Dibromo-3-chloropropane	250	43.9	ug/kg	54%	156%	30
			SW5035A/8260C	1,2,4-Trichlorobenzene	250	14.2	ug/kg	37%	131%	30
			SW5035A/8260C	1,2,3-Trichlorobenzene	50	9.8	ug/kg	59%	158%	30
			SW5035A/8260C	Naphthalene	250	9.6	ug/kg	39%	129%	30
			SW5035A/8260C	2-Methylnaphthalene	250	10.8	ug/kg	10%	176%	30
		Poly and Per-Fluorinated Alkyl Substances	ASTM D7968	Perfluorobutanoic acid (PFBA)	100	27	ng/kg	70%	130%	30
			ASTM D7968	Perfluoropentanoic acid (PFPeA)	50	16	ng/kg	70%	130%	30
			ASTM D7968	Fluorotelomer sulfonic acid (4:2 FTS)	50	11	ng/kg	70%	130%	30
			ASTM D7968	Perfluorohexanoic acid (PFHxA)	50	10	ng/kg	70%	130%	30
			ASTM D7968	Perfluorobutane sulfonic acid (PFBS)	50	11.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluoroheptanoic acid (PFHpA)	50	14	ng/kg	70%	130%	30
			ASTM D7968	Perfluoropentane sulfonic acid (PFPeS)	50	14	ng/kg	70%	130%	30
			ASTM D7968	Fluorotelomer sulfonic acid (6:2 FTS)	50	16.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluorooctanoic acid (PFOA)	50	8.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluorohexane sulfonic acid (PFHxS)	50	7	ng/kg	70%	130%	30
			ASTM D7968	Perfluorohexane Sulfonic Acid - LN (PFHxS-LN)	50	7	ng/kg	70%	130%	30
			ASTM D7968	Perfluorohexane Sulfonic Acid - BR (PFHxS-BR)	50	7	ng/kg	70%	130%	30
			ASTM D7968	Perfluorononanoic acid (PFNA)	50	13	ng/kg	70%	130%	30
			ASTM D7968	Fluorotelomer sulfonic acid (8:2 FTS)	50	20	ng/kg	70%	130%	30
			ASTM D7968	Perfluoroheptane sulfonic acid (PFHpS)	50	15	ng/kg	70%	130%	30
			ASTM D7968	Perfluorodecanoic acid (PFDA)	50	24	ng/kg	70%	130%	30
			ASTM D7968	N-Methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA)	50	11	ng/kg	70%	130%	30
			ASTM D7968	N-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA)	50	19.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluorooctane sulfonic acid (PFOS)	50	8.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluorooctane Sulfonic Acid - LN (PFOS-LN)	50	8.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluorooctane Sulfonic Acid - BR (PFOS-BR)	50	8.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluoroundecanoic acid (PFUnDA)	50	12	ng/kg	70%	130%	30
			ASTM D7968	Perfluorononane sulfonic acid (PFNS)	50	10.5	ng/kg	70%	130%	30
			ASTM D7968	Perfluorododecanoic acid (PFDoDA)	50	13	ng/kg	70%	130%	30

Table 1.2

Target Compound and Target Analyte Parameter List - Merit Analytical Laboratory
RACER Flint West #12990
Glenwood Avenue and Stevenson Street, Flint Michigan

							Accuracy		Precision
Media	**Method Description**	**Method Code**	**Analyte Description**	**Estimated Quantitation Limit (EQL)**	**Method Detection Limit (MDL)**	**Units**	**LCL %**	**UCL %**	**RPD %**
		ASTM D7968	Perfluorodecane sulfonic acid (PFDS)	50	14	ng/kg	70%	130%	30
		ASTM D7968	Perfluorotridecanoic acid (PFTrDA)	50	11.5	ng/kg	70%	130%	30
		ASTM D7968	Perfluorooctane sulfonamide (FOSA)	50	10	ng/kg	70%	130%	30
		ASTM D7968	Perfluorotetradecanoic acid (PFTeDA)	50	9.5	ng/kg	70%	130%	30
		ASTM D7968	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	50	12	ng/kg	70%	130%	30
		ASTM D7968	9-chlorohexadecafluoro-3-oxanone1-sulfonic acid (9Cl-PF3ONS)	50	11	ng/kg	70%	130%	30
		ASTM D7968	4,8-dioxa-3H-perfluorononanoic acid (ADONA)	50	14	ng/kg	70%	130%	30
		ASTM D7968	Hexafluoropropylene oxide dimer (HFPO-DA)	50	12.5	ng/kg	70%	130%	30
	Organic Carbon	Walkley-Black	fraction of organic carbon (foc)	0.05	0.01	%	NA	NA	NA

Table 5.1

Container, Preservation, Shipping and Packaging Requirements
RACER Flint West #12990
Glenwood Avenue and Stevenson Street, Flint Michigan

Analyses	Sample Containers[1]	Preservation	Maximum Holding Time from Sample Collection[2]	Volume of Sample	Shipping	Normal Packaging
Water/Liquid						
VOCs	3x 40ml vials w/ HCL	pH < 2 and Iced, 4 ± 2° C	14 days for analysis	Fill to top of bottle, no air in vial	Overnight	Foam Liner or Bubble Wrap
PNAs	1 x 1000 ml amber glass bottle	Iced, 4 ± 2° C	7 days from sample collection to extraction; 40 days from extraction to completion of analysis	Fill to neck of bottle	Overnight	Bubble-wrap
PFAS	3x 15ml plastic vials	Iced, 4 ± 2° C	14 days for extraction 28 days after extraction for analysis	5-6 ml	Overnight	Foam Liner or Bubble Wrap
Select Metals	One 250 ml plastic bottle	HN0 $_3$ to pH< 2Iced, 4 ± 2° C	180 days for analysis (28 days - mercury)	Fill to neck of bottle	Overnight	Foam Liner or Bubble Wrap
Hexavalent Chromium	One 250 ml plastic bottle	Iced, 4 ± 2° C	24 hours	Fill to neck of bottle	Overnight	Foam Liner or Bubble Wrap
TOC	Two 40ml VOC vials	H2S04 to pH<2 Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
Methane	3x 40ml vials w/ HCL (in addition to any other VOAs collected)	pH < 2 and Iced, 4 ± 2° C	14 days for analysis	Fill to neck of bottle	Overnight	Foam Liner or Bubble Wrap
Solid /Soil						
VOCs	One VOA with 40ml methanol, 40g soil	Iced, 4 ± 2° C	14 days for analysis	40ml methanol, 40 g soil	Overnight	Foam Liner or Bubble Wrap
PNAs	One 4-ounce glass jar per analysis	Iced, 4 ± 2° C	14 days for extraction; 28 days after extraction for analysis	Fill to shoulder of jar	Overnight	Bubble-wrap
PFAS	3 15ml vials + 1 250 ml plastic	Iced, 4 ± 2° C	14 days for extraction; 28 days after extraction for analysis	2 grams per vial + fill 250ml bottle	Overnight	Bubble-wrap
TOP Assay	3 15ml vials + 1 250 ml plastic	Iced, 4 ± 2° C	14 days for extraction; 28 days after extraction for analysis	2 grams per vial + fill 250ml bottle	Overnight	Bubble-wrap
TOC/FOC	One 4-ounce glass jar	Iced, 4 ± 2° C	28 days for analysis	Fill to shoulder of jar	Overnight	Bubble-wrap

Notes:

VOCs - Volatile Organic Compounds
PNAs - Polynuclear Aromatic Compounds
PFAS - Per- and Polyfluoroalkyl Substances.
TOC - Total Organic Carbon
TOP - Total Oxidizable Precursor

1 - Multiple parameters on a single sample may be combined into one single 16 ounce glass container.
2 - These are technical holding times, i.e., are based on time elapsed from time of sample collection.

Table 5.2

Estimated Soil and Groundwater Samples to be collected in 2021
RACER Flint West #12990
Glenwood Avenue and Stevenson Street, Flint, Michigan

				Quality Control Samples			
Investigation Activity	**Sample Matrix**	**Laboratory Parameters**	**Investigative Samples**	**Equipment Blank** (1)	**Field Dup**	**Trip Blank**	**MS/MSD** (2)
PFAS Investigation							
Soil Borings	soil	PFAS	32	5	2		
Soil Borings	soil	fraction organic carbon	2				
Soil Borings/Temp Well	GW	PFAS	32	5	2	1	2
Semi-annual Sampling (2 events)							
Monitoring Wells	GW	VOCs	30	4	4	1	
Monitoring Wells	GW	Metals (dissolved)	30	4	4		
Monitoring Wells	GW	Metals (total)	30	4	4		
Monitoring Wells	GW	PFAS	22	4	4	1	1

GW = Groundwater
PFAS = per- and polyfluoroalky substances
(1) - Equipment blank will be collected in the event that disposable sampling equipment is not being used.

(2) - Matrix Spike/Matrix Spike duplicate (MS/MSD) analyses are required for samples submitted for metals analyses are to be analyzed at a frequency of one per group of twenty (20) or fewer investigative samples for the activities detailed above. The MS/MSD is a pair a of two samples--spike and spike duplicate.

APPENDIX A: ANALYTICAL LABORATORY LIST

Appendix A Analytical Laboratory List

Merit Laboratories Inc. East Lansing	
Samantha Smith	Project Manager
Barbera Ball	Laboratory Operations Manager
John Laverty	Laboratory QA Officer
Laboratory Address	2680 East Lansing Drive, East Lansing, Michigan 48823
Phone	517-332-0167

Eurofins Environment Testing America	
Susan Schafer	Project Manager
Mark Loeb	QA Manager
Laboratory Address	10448 Citation Drive, Suite 200, Brighton, Michigan 48116
Phone	810-229-2763

APPENDIX B: LABORATORY STANDARD OPERATION PROCEDURES

ÆE Applied EcoSystems, Inc.

Environmental Management, Consulting & Field Services

Title: ANALYSIS OF DISSOLVED GASES IN GROUNDWATER

[Method: Method RSK-175]

Approvals (Signature/Date):

Technology Specialist — Date: 07/23/20

Health & Safety Coordinator — Date: 07/14/20

Quality Assurance Manager — Date: 07/15/20

Technical Director — Date: 07/27/20

This SOP was previously identified as SOP NC-GC-032, Rev 11, dated 06/29/20

Copyright Information:
This documentation has been prepared by TestAmerica Laboratories, Inc. d/b/a Eurofins TestAmerica and its affiliates ("Eurofins TestAmerica"), solely for their own use and the use of their customers in evaluating their qualifications and capabilities in connection with a particular project. The user of this document agrees by its acceptance to return it to Eurofins TestAmerica upon request and not to reproduce, copy, lend, or otherwise disclose its contents, directly or indirectly, and not to use it for any purpose other than that for which it was specifically provided. The user also agrees not to give access to this document to any third parties including but not limited to consultants, unless such third parties specifically agree to these conditions.

THIS DOCUMENT CONTAINS VALUABLE CONFIDENTIAL AND PROPRIETARY INFORMATION. DISCLOSURE, USE OR REPRODUCTION OF THESE MATERIALS WITHOUT THE WRITTEN AUTHORIZATION OF EUROFINS TESTAMERICA IS STRICTLY PROHIBITED. THIS UNPUBLISHED WORK BY EUROFINS TESTAMERICA IS PROTECTED BY STATE AND FEDERAL LAW OF THE UNITED STATES. IF PUBLICATION OF THIS WORK SHOULD OCCUR THE FOLLOWING NOTICE SHALL APPLY:

©COPYRIGHT 2020 TESTAMERICA LABORATORIES, INC. d/b/a EUROFINS TESTAMERICA ALL RIGHTS RESERVED

Facility Distribution No. ___________ **Distributed To:**_______________________

The controlled copies of this SOP are the PDF copy that is posted to the laboratory's SOP Directory and, where applicable, the copy that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies distributed outside of the facility are considered uncontrolled.

1. SCOPE AND APPLICATION

1.1. This document describes a procedure for the determination of dissolved gases in water. The method is applicable to the preparation of water samples by introducing headspace, and the analysis of the resultant headspace to quantify part-per-billion (ppb) levels of dissolved gases (acetylene, ethane, ethylene, methane, propane butane, 1-butene, propene, pentane and 2-methyl propane). See Tables 1 and 2 for List 1 and List 2 compounds with their associated molecular weights.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A water sample is collected in the field in a 43-mL VOA vial with no headspace. Headspace is generated using ultra high purity (UHP) helium, fortified with a surrogate compound. The sample is loaded onto the headspace autosampler and analyzed by a Gas Chromatograph (GC) equipped with a Flame Ionization Detector (FID)

3. DEFINITIONS

3.1. Refer to the glossary in the Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. 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.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. 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 Safety Data Sheet (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.

Material	Hazards	Exposure Limit (1)	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.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.1. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn when opening vials and any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.

5.3. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with a sticker that reads "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.4. All work must be stopped in the event of a known or potential compromise to the health and safety of a Eurofins TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Sample Containers:

6.1.1. Pre-preserved 43 mL VOA vials containing reagent grade or equivalent HCl

6.1.2. 43 mL VOA Vials

6.2. Instrumentation

6.2.1. Agilent 6890 Gas Chromatograph (GC) equipped with a Flame Ionization Detector (FID) or equivalent

6.2.2. Column - FID - Agilent PLOT-Q; 30m, 0.53mm ID or equivalent

6.2.3. Autosampler - EST LGX-50 or equivalent

6.3. Syringes: 10µL - 25.0-mL gas tight syringes with 22 gauge side port needles

6.4. Relief needles: 18 gauge with side port for use in relieving pressure created during headspace formation.

6.5. Data System - Agilent Chemstation or equivalent

6.6. Shaker table or equivalent

7. REAGENTS AND STANDARDS

7.1. UHP helium is used to create headspace in initial calibration vials.

7.2. Calibration Standards: The primary standard is purchased through AirGas . The calibration standard is comprised of two cylinders--one composed of nominally 0.1% (mole basis) methane, ethane, ethylene, acetylene, propane, butane, 1-butene, propene, pentane and 2-methyl propane;; and the second composed of nominally 1% methane, ethane, ethylene, acetylene, propane, butane, 1-butene, propene, pentane and 2-methyl propane. The second source standard is a 1% mix of all of the above-listed compounds, provided by Scott Specialty Gases. See the LIMS for further details.

7.3. Surrogate Calibration Standard: The surrogate calibration standard is a purchased standard that contains 5% 1,1,1-trifluoroethane in UHP helium. See the LIMS for further details.

7.4. Surrogate fortified helium: The surrogate mixture is a purchased mixture. The standard contains UHP helium fortified with 0.325% 1,1,1-trifluoroethane. The surrogate mixture is used to create headspace in all samples and standards other than the initial calibration. See the LIMS for further details.

7.5. Reagent Water: High purity water that meets the requirements for a method blank when analyzed. Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight.

7.6. Calibration levels are achieved by using a syringe to inject different amounts of the standards into 43 mL vials of reagent water. Helium is used to create the balance of the final volume of 20 mL headspace in each vial (see Table 10.1).

7.7. LCS liquid stock standard composed of Methane, Ethane, Ethylene and Propane purchased from LGC. The liquid stock standard must be stored at 4° ± 2° C and has a holding time of 45 days.

7.7.1. The LCS working standard is made up from the LCS liquid stock standard into VOA vials according to section 11.5.2.2. Multiple vials may be made at once and stored. The LCS vials are stored at 4° ± 2° C and have a holding time of 14 days.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Samples are collected in the field in 43-mL screw cap VOA vials. The samples are preserved with 1:1 HCl to a pH of less than 2. Care should be taken that no headspace is present when capping the vials. A minimum of three vials per analysis is required. Double the volume is collected for a sample with a matrix spike/matrix spike duplicate (MS/MSD).

8.2. Samples are maintained at a temperature of 4°C ± 2°C and should be analyzed within 14 days of collection. Unpreserved samples must be analyzed within 7 days of collection.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, and MSD), which are processed with the same lots of reagents, the same processes, and by the same personnel. All sample analyses must be initiated within a 24-hour period from the initial preparation and without interruption of the process.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water, and all other reagents specific to the method and is carried through the entire analytical procedure, including preparation, and analysis, with the sample batch. The MB 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. The MB should not contain any analyte of interest at or above the reporting limit (RL).

Note: Some clients may request reporting down to the Method Detection Limit (MDL). For those clients, detections above the MDL will be flagged.

9.2.2. Corrective Action for MB

9.2.2.1. If the analyte level in the MB exceeds 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 addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an impacted MB, or the impacted analyte(s) in the sample are 10X the concentration found in the MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS) / Laboratory Control Sample Duplicate (LCSD)

9.3.1. At least one LCS must be processed with each preparation batch. The LCS is fortified to the concentration of a standard near the midpoint of the calibration curve. The LCS must be carried through the entire analytical procedure with the samples and MB. 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. (see also Section 17.2 modifications to the reference method)

9.3.2. Acceptance criteria for the LCS can be found in the laboratory information management system (LIMS).

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.3.3.2. The only exception is if the LCS/LCSD recoveries are biased high and the associated sample is non-detect (ND) at the RL for the analyte(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair is processed for each batch. An MS is a field sample to which known concentrations of target analytes have been added. An MSD is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. 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. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. Corrective action for MS/MSDs

9.4.2.1. If the analyte recovery falls outside of the acceptance range, the results should be evaluated to determine the cause of the error.

9.4.2.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability. Re-preparation and/or re-analysis may be necessary.

9.4.2.3. If matrix interference is suspected, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.4.2.4. If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data is reported and flagged with a “4” in the LIMS.

9.4.2.5. If client program requirements specify to confirm matrix interference’s, re-preparation and reanalysis of the MS/MSD may be necessary.

9.5. Surrogate

9.5.1. 1,1,1-Trifluoroethane is the surrogate for RSK analytes.

9.5.2. Corrective Action for Surrogate

9.5.2.1. If the surrogate is outside established control limits in the samples or QC, the system is out of control and corrective action must occur.

9.5.2.2. If the surrogate fails in the MB and/or LCS, corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.5.2.3. For client sample surrogate outliers, it may be necessary to re-prep and re-analyze. When there is an obvious interference causing the surrogate outlier that the analyst knows a corrective action would not resolve the issue, flag the data with a qualifier indicating matrix interference.

9.5.2.4. For instrument QC (ICV and CCV), re-prep and re-analyze the CCV and/or ICV solution. Samples bracketed by an ICV and/or CCV that fails surrogate criteria must be re-analyzed. The exception to this is noted in section 9.5.2.5.

9.5.2.5. The only exception is if the surrogate recoveries are biased high and the associated sample(s) is ND for the analyte(s) of interest, the batch is acceptable. This must be addressed in the project narrative.

9.6. Control Limits

9.6.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.6.2. Unless method specified, laboratory control limits are internally generated and updated periodically. Control limits are accessible via the LIMs

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOP CA-Q-S-006.

9.7.2. MDLs are accessible via the LIMs

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration – Establish an initial calibration curve using the concentrations noted in LIMS.

10.1.1. Preparation of Initial Calibration Standards

10.1.1.1. Fill a 43-ml VOA vial with purged reagent water and cap leaving no headspace in the vial.

10.1.1.2. Withdraw UHP helium from a cylinder using a gastight syringe. Place a relief needle into the headspace vial and inject the helium while keeping the vial inverted. The helium will displace water through the relief needle. Calibration gas can now be added to the still-inverted headspace vial.

10.1.1.3. Once pressure equilibrium has been reached (no more water is escaping), the relief needle is removed. The vials are then placed septa down on a tray. Move the vials and place them horizontally on the shaker table for approximately 5 minutes. After five minutes, the vials can be placed in the autosampler. Program the autosampler to start.

10.1.2. For each analyte, calculate the mean calibration factor (CF) from analyses of the calibration solutions.

10.1.3. Calculate the standard deviation (SD) and relative standard deviation (RSD) from each mean.

10.1.4. For average calibration fit, the percent RSD average of each List 1 analyte must be $\leq$ 20%, and the List 2 analytes and the surrogate RSD average must be $\leq$ 30%.

10.1.5. For linear calibration fit, r^2 must be > 0.995.

10.1.6. Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below.

10.1.7. If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or if needed, the same run may be repeated once only. If removing a level or replacing a level with a rerun, the whole level (all compounds) must be removed or replaced. The curve is evaluated with the level removed or replaced. This must be documented. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve re-analyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

10.1.8. One of the following conditions must be satisfied to allow removal or replacement of a level.

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For external standard methods, the average amount of analyte recovered is less than 70% or greater than 130% of the expected value.

10.1.9. The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

10.1.10. Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed, then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event, the number of levels remaining in the calibration must be at least 5 non-zero points, and the calibration range upper or lower limit for the affected compound(s) must be adjusted accordingly. This must be documented.

10.2. Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least 5 non-zero points, and the calibration range upper or lower limit for the affected compound(s) must be adjusted accordingly. This must be documented. Calibration range upper or lower limit for the affected compound(s) must be adjusted accordingly Continuing Calibration Verification (CCV)

10.2.1. Mid-Range CCV

10.2.1.1. A mid-range CCV is analyzed at the beginning of each run, after every 15 samples (including batch QC samples), and at the end of each run.

10.2.1.2. Withdraw 19 mL surrogate fortified helium from a cylinder using a gastight syringe. Place a relief needle into the headspace vial and inject the helium while keeping the vial inverted. The helium will displace water through the relief needle. Calibration gas mixture can now be added to the still-inverted headspace vial.

10.2.1.3. Add 1 mL of standard to the inverted vial. Once pressure equilibrium has been reached, the relief needle is removed. The vial can be placed on the shaker table and shaken for approximately 5 minutes, then placed on the autosampler.

10.2.1.4. The percent difference / percent drift (%D) between the CCV calibration factor (CF) and the ICAL average CF for each analyte must be ≤ 20% for List 1 compounds and ≤ 30% for List 2 compounds.

10.2.1.5. CCV Resolution: Resolution, or degree of overlap, for ethane /ethane and other close eluting analyte pairs must be at least 50%. Resolution of the compounds from the surrogate must be at least 80%.

10.2.2. Low Level and High Level CCVs

10.2.2.1. One Low Level CCV and one High Level CCV must be analyzed with the first batch of samples each week.

10.2.2.2. The CCV (low) should be spiked at a concentration equivalent to the RL for each compound.

10.2.2.3. Criteria for the CCV (low) and the CCV (high) is as follows:

CCV / Compounds	**Low**	**High**
CCV (low) List 1	60	140
CCV (low) List 2	60	140
CCV (high) List 1	80	120
CCV (high) List 2	70	130

10.3. Initial Calibration Verification - An ICV must be analyzed following the acquisition of the initial calibration.

10.4. The percent difference / percent drift (%D) between the ICV calibration factor (CF) and the ICAL average CF for each analyte must be ≤ 20% for List 1 compounds and ≤ 30% for List 2 compounds.

10.5. The ICV is prepared using 1 mL of the second source standard.

10.6. Corrective Action for ICV/CCV

10.6.1. If the ICV/CCV fails to meet criteria, re-preparation and re-analysis is required. Re-calibration may be necessary for a failing ICV. The exception to this is described below.

10.6.2. If the ICV/CCV recoveries are biased high and the associated sample(s) is ND at the RL for the analyte(s) of interest, the data are acceptable. This must be addressed in the project narrative.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Equipment, supplies, reagents and standards, and/or spiking amounts detailed in this SOP are subject to change without notice.

11.4. **Note:** Various states and/or programs may have different requirements. It is the responsibility of the analyst to reference the proper work instructions for the needed requirements.

11.5. Sample Analysis

11.5.1. Sample Analysis - Remove the samples from the refrigerator. Allow the vial to come to room temperature. This will take at least one hour. Insert an 18 gauge relief needle into the septum. Using a 25 mL gastight syringe, inject 20 mL of surrogate-fortified helium into the sample. The helium forces out an equal amount of sample through the relief needle to create a headspace volume of 20 mL. Withdraw the needle and syringe from the vial, then the vials are placed septa down on a tray. Move the vials and place them horizontally on the shaker table for approximately 5 minutes. Load the sample onto the headspace autosampler. 1mL of the sample headspace is injected directly onto the GC column where the target compounds, if present, are detected by FID. Acquire the data and process on Chrom. The recommended instrument operating conditions are outlined in Appendix 1 at the end of this document. .

11.5.2. QC sample prep.

11.5.2.1. The MB is prepared as a sample (see Section 9.2).

11.5.2.2. A LCS (and LCSD if needed) is prepared using 4mL of the LCS liquid standard (List 1) into a VOA vial that is partially filled with nitrogen purged DI water. Bring to volume with nitrogen-purged DI water and cap leaving no headspace. 20 mL of headspace is then created with surrogate-fortified helium (see Sections 9.3 and 17.2). List 1 includes Methane, Ethane, Ethylene and Propane only.

11.5.2.3. When List 2 is requested, a second LCS (and LCSD if needed) is prepared using 1 mL primary source standard after 19 mL of headspace has been created with surrogate fortified helium (see Sections 9.3 and 17.2).

11.5.2.4. A MS/MSD pair is prepared as a regular sample, but 1 mL of primary source standard is injected after 19 mL of headspace has been created with surrogate-fortified helium (see Section 9.4).

11.6. Analytical Documentation

11.6.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.6.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.6.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is stored and available for each data file.

11.6.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration Factor for GC-FID

$$\mathbf{CF = A/C}$$

Where:

CF = Calibration factor of an analyte
A = Instrument response (peak area or height)
C = Concentration of an analyte in sample

12.2. Percent Difference for Calibration Factors

$$\mathbf{\%\ D = (Avg_{CF} - CF\ /\ Avg_{CF})\ x\ 100}$$

Where:

Avg_{CF} = Average CF for an analyte from the initial calibration
CF = CF for an analyte from standard

12.3. Relative Standard Deviation

$$\mathbf{\%RSD = (SD/\ Avg_{CF})\ x\ 100}$$

Where:

Avg_{cf} = Average CF for an analyte from the initial calibration
SD = Standard Deviation of CFs for a compound

12.4. Weighted Linear

$$y = \frac{1}{SD^2} \times (ax + b)$$

Where y = Instrument response
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept
SD = Standard deviation from 12.3

12.5. Sample Concentration in water

$$\mathbf{C = (A/Avg_{CF}) \times DF}$$

Where:
C = Concentration of target analyte in sample
A = Instrument response (peak area or height)
Avg_{CF} = Average CF for an analyte from the calibration
DF = Dilution factor

12.6. Additional constants, equations, and calculations are listed in Section 17.1, Tables 1 and 2, and the following SOPs:

12.6.1. Calibration Curves and the Selection of Calibration Points, CA-Q-P-003.

12.6.2. See also section 17.2 Modifications to the reference method.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file. Each laboratory must have corresponding method detection limit (MDL) study files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of analyst demonstrations of capabilities is maintained for this method in the laboratory training files.

14. POLLUTION PREVENTION

14.1. It is Eurofins TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generate (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

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 method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. All sample vials are collected in boxes and removed from the lab to storage. The Waste Coordinator handles crushing the vials and proper disposal

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Eurofins TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. RSK SOP-175, Revision 0, August 11, 1994

16.1.2. Minimum requirements for Dissolved Gas Analysis by methods RSK-175 R2-5, RSK-194 R3-4, EPA Region 1 NATATTEN Rev 1.

16.1.3. Some criteria are derived from PA-DEP3686 R1 and ASTM D8028 when the primary references don't address an area.

16.1.4. Best Practices for Dissolved Gas Analysis by methods RSK-175 R2-5, RSK-194 R3-4, EPA Region 1 NATATTEN Rev 1. Work Instruction No. CA-T-WI-017, dated 06 Jan 2020.

16.1.5. Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. Corporate Quality Management Plan (CQMP), current version

16.1.7. Eurofins TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and Eurofins TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.8. CA-T-P-005, Rev 0, Policy for Determining RT Windows for GC/ECD Tests

16.1.9. Revision History

Historical File:		Revision 6: 04/03/14		
Revision 0: 05/13/02		Revision 7: 11/19/15		
Revision 1: 11/16/04		Revision 8: 11/08/17		
Revision 2: 02/01/07		Revision 9: 03/12/18		
Revision 3: 03/21/08		Revision 10: 10/22/18		
Revision 4: 05/06/10		Revision 11: 06/29/20		
Revision 5: 04/29/13				

**4/9/19: Changed logo and copyright information. No changes made to revision number or effective date.*

16.1. Associated SOPs, Work Instructions, and Policies, current version

16.1.1. QA Policy, QA-003

16.1.2. WVDEP State Requirement Summary, WI-NC-208

16.1.3. Glassware Washing, NC-QA-014

16.1.4. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.1.5. Detections and Quantitation Limits, CA-Q-S-006

16.1.6. Standards and Reagents, NC-QA-017

16.1.7. Manual Integrations CA-Q-S-002

16.1.8. Calibration Curves and the Selection of Calibration Points, CA-Q-P-003

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The most current reporting limits can be accessed via the LIMS.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Modifications from Reference Method

17.2.1. A surrogate, not required by the RSK SOP, has been added to the analytical process

17.2.2. Laboratory control samples are prepared directly in 43 mL VOA vials with screw caps. Headspace is generated using UHP helium fortified with surrogate compounds.

17.2.3. UHP helium fortified with surrogate compounds is injected into every field and QC sample such that a consistent 20 mL of sample is displaced to create headspace. This process normalizes the way samples are processed such that the gas measured in the headspace is reflective of the total amount of gas injected; thus eliminating the need to apply the Henry's Law constant in the result calculation.

17.3. Tables and Appendices

Table 1
List 1 Compounds

Compound	Molecular Weight (g)
Methane	16
Ethane	30
Ethene	28
Propane	44

Table 2
List 2 Compounds

Compound	Molecular Weight (g)
Acetylene	26
1 Butene	56.1
n-Butane	58.1
Pentane	72.1
2-Methyl Propane	58.1
Propene	42.1

Appendix 1

EXAMPLE CALCULATION
(based on 17 mL of water and 4 mL of headspace)

(Calculations Based on 22°C at 754 mmHg – Molar Equivalent <u>.04099)</u>

2,000 ul of 10,000 ppmv – 17 mL H_20

$$\frac{10{,}000\ \text{ul CH}_4}{\text{L He}} \times \frac{1\ \text{L CH}_4}{1{,}000{,}000\ \text{ul CH}_4} \times \frac{.04099\ \text{moles CH}_4}{1\ \text{LCH}_4} \times \frac{16\ \text{g CH}_4}{1\ \text{mole CH}_4} \times \frac{.002\ \text{L He}}{.017\ \text{LH}_2\text{0}} \times$$

$$\frac{1{,}000{,}000\ \text{ug CH}_4}{1\ \text{g CH}_4} = \frac{13.1168}{.017} = \frac{771.57\text{ug CH}_4}{\text{LH}_2\ \text{0}}$$

<u>EXPLANATION OF TERMS:</u>

$\frac{10{,}000\ \text{ul Methane}}{\text{L Helium}}$ = Puts PPMV methane into volumetric ratio per liter helium. (Helium is the gas used to generate head space in the sample vial.)

$\frac{1\ \text{L Methane}}{1{,}000{,}000\ \text{ul Methane}}$ = Simple units conversion.

$\frac{.04099\ \text{moles Methane}}{\text{L Methane}}$ = Molar equipment of methane at standard temperature and pressure per ideal gas law.

$\frac{16\ \text{g Methane}}{1\ \text{mole Methane}}$ = Molar weight of methane.

$\frac{.002\ \text{L Helium}}{.017\ \text{LH}_2\text{0}}$ = Amount of helium in calibration standard distributed over 17 ml of reagent water in sample vial.

$\frac{1{,}000{,}000\ \text{ug Methane}}{1\ \text{g Methane}}$ = Units conversion from grams to µg of methane to arrive at µg/L concentration of methane.

$\frac{13.1168}{.017}$ = Collection of terms.

771.57µg L^{-1} Methane = Final concentration of methane in calibration

Appendix 2:

Recommended Instrument Operating Conditions

Recommended GC Conditions

9 psi constant flow
Oven Program: 45 for 1 minute
16°C/min to 180°C hold 1.06 min
GC Inlet Temp: 250ºC

Recommended FID Conditions

FID Temp: 250°C
Hydrogen Flow: 40 mL/min
Air Flow: 450 mL/min
Helium Makeup: 45 mL/min

Recommended Headspace Auto Sampler Conditions

Screen Mode

Blank Water Volume (mL)	0
Syringe Prime Time (sec)	3
Syringe/Rinse Needle (mL)	20
Rinse Cycles	OFF
Sample Temperature (ºC)	Off / room temperature
Stir	ON (Med)
Sample Equil. Time (min)	10
Vial Pressurization Time (sec)	5
Loop Fill Time (sec)	5
Loop Equil. Time (sec)	5
Injection Time (sec)	0
Valve Temperature (ºC)	65
GC Line Temperature (ºC)	100
GC Cycle Time (min)	14
Rinse Water Temperature (ºC)	65

STANDARD OPERATING PROCEDURE

HEXAVALENT CHROMIUM (CR VI) ALKALINE DIGESTION; CR VI ALKALINE LEACHATE METHOD 3060A

APPROVALS:

Barbara Ball

10/02/2020

QA Officer Date

10/02/2020

Technical Director Date

Number	Description of Change	Date
001-004	Previous changes were not documented	
005	Updated to comply with DoD QSM and ISO 17025 standards.	6/10/11
006	Updated to comply with DoD QSM 5.0 standards.	03/03/16
007	Updated to comply with DoD QSM 5.1 standards.	01/11/18
008	DOD Audit Corrective Action	10/02/2020
009		
010		
011		
012		
013		
014		
015		

1.0 SCOPE AND APPLICATION

This SOP is an alkaline digestion procedure for extracting CrVI from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and similar waste materials. This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF THE METHOD

This method uses an alkaline digestion to solubilize both water-insoluble and water soluble CrVI compounds in solid waste samples.

The sample is digested using 0.28M Na CO /0.5M NaOH solution and heating at 90- 95^{0}C for 60 minutes to dissolve the CrVI and stabilize it against reduction to Cr(III).

The CrVI reaction with diphenylcarbazide is the most common and reliable method for analysis of CrVI solubilized in the alkaline digestate.

3.0 INTERFERENCES

The chromium reaction with diphenylcarbazide is usually free from interferences. Some substances might interfere when the concentration of chromium is extremely high. The references listed below will give greater depth and reasoning for these interferences.

Interfering Substance	Interference Levels and Treatments
Iron	May interfere above 1 mg/L
Mercurous & Mercuric Ions	Interferes slightly
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment
Vanadium	May interfere above 1 mg/L. Wait 10 minutes before reading
Oxidizing Agents	Analyze within 24 hours. Use standard addition methods to verify and calculate to compensate for the problem.
Reducing Agents	Analyze within 24 hours. Use standard addition methods to verify and calculate to compensate for the problem.

The pH of the digestate must be carefully adjusted during the digestion procedure. Failure to meet the pH specifications will necessitate re-digestion of the samples.

4.0 APPARATUS AND MATERIALS

Digestion vessel: borosilicate glass or quartz with a volume of 100 ml.

100 ml Graduated Cylinder or equivalent.

Volumetric Flasks: Class A glassware, 1000-mL and 100-mL, with stoppers or equivalent.

Vacuum Filtration Apparatus.

Filter membranes (0.45 µm). Preferably cellulosic or polycarbonate membranes.

When vacuum filtration is performed, operation should be performed with recognition of the filter membrane breakthrough pressure.

Heating Device - capable of maintaining the digestion solution at 90-95°C.

50 ml Centrifuge tubes with caps.

Volumetric pipettes: Class A glassware, assorted sizes, as necessary.

pH Strips.

Calibrated balance.

Temperature measurement device (with NIST traceable calibration) capable of measuring up to 100°C (e.g. thermometer, thermistor, IR sensor, etc.).

5.0 REAGENTS

Nitric acid: 5.0 M HNO_3 , analytical reagent grade or spectro grade quality. Store at 20-25°C in the dark. Do not use concentrated HNO_3 to make up 5.0 M solution if it has a yellow tinge; this is indicative of photoreduction of NO_3 to NO_2, a reducing agent for Cr.(VI).

Sodium carbonate: Na_2CO_3, anhydrous, analytical reagent grade. Store at 20-25°C in a tightly sealed container. Shelf life: Indefinite. Dry at 103 °C annually.

Sodium hydroxide: NaOH, analytical reagent grade. Store at 20-25°C in a tightly sealed container. Shelf Life: 2 years.

Magnesium Chloride: $MgCl_2$ (anhydrous), analytical reagent grade. A mass of 400mg $MgCl_2$ is approximately equivalent to 100 mg Mg. Store at 20-25°C in a tightly sealed container. Shelf Life: Indefinite. Dry at 103 °C annually.

Phosphate Buffer: K_2HPO_4: and KH_2PO_4: analytical reagent grade. 0.5M K_2 HPO_4 /0.5M KH_2 PO_4 buffer at pH 7: Dissolve 8.71 g K_2HPO_4, analytical reagent grade and 6.8 g KH_2 PO_4, analytical reagent grade into 100 ml of reagent water. Shelf Life: 2 years.

Lead Chromate: $PbCrO_4$, analytical reagent grade. The insoluble matrix spike is prepared by adding 0.15g of $PbCrO_4$ to a separate sample aliquot. Store under dry conditions at 20-25°C in a tightly sealed container. Shelf Life: Indefinite. Dry at 103 °C annually.

Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in reagent water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25^{o}C and prepare fresh monthly. The pH of the digestion solution must be checked before using. The pH must be 11.5 or greater, if not, discard.

Matrix spiking solution: 50 mg/L Cr. VI-. Store at 20-25^{o}C in a tightly sealed container for use up to six months.

Deionized Water

6.0 SAMPLE HANDLING AND PRESERVATION

Soils, sludges, sediments and industrial waste samples must be stored field-moist at 4^{o}C ± 2^{o}C until analysis. Maximum holding time for soils, sludges, sediments and industrial wastes samples for Cr. IV testing is 30 days from sample collection. In addition, the holding time for Cr VI in the alkaline digestate is 7 days after extraction from soil.

7.0 PROCEDURE

Note: Quality Control requirements for this digestion are summarized in Table 1.

Insoluble Matrix Spike (MS) and Laboratory Control Sample (LCS):

- Add 0.015 g $PbCrO_4$ to the sample aliquot or the blank (LCS) that needs to be spiked.
- Record the exact amount of spike added.
- MSD prepare the same way as the MS.

Soluble Spike Matrix Spike and LCS:

- Add 2 ml of 50 mg/L CrVI spiking solution to the sample aliquot that is to be analyzed. Record the exact amount added.
- MSD prepare the same way as the MS.

Method Blank:

Prepare a method blank as you would a sample but do not add any sample. For soil matrix: add CrVI free soil.

Adjust the temperature setting of each heating device used in the alkaline digestion by preparing and monitoring a temperature blank [a 100-ml vessel filled with 40 ml-digestion solution]. Maintain a digestion solution temperature of 90-95^{o}C as measured with a NIST-traceable thermometer or equivalent. Definition of a batch is 20 samples or less.

Place 2.0 ± 0.10 g of the field-moist sample into a clean and labeled 100 ml digestion vessel. Mix the sample thoroughly before the aliquot is removed.

Spiking: For the specific sample aliquot that is being spiked only add the spike directly to the sample aliquot at this point.

Add 40 ± 1 ml of digestion solution to each sample using a graduated cylinder, and also add approximately 400 mg of $MgCl_2$ and 0.5 ml of 1.0M phosphate buffer. Avoid boiling during digestion.

Agitate the samples often or continuously (unheated) for five minutes. Heat the samples to 90-95^{o}C, then maintain the samples at 90-95^{o}C for at least 60 minutes with stirring or with frequent vigorous agitation until the volume is below 30 ml.

Filter through a 0.45µm membrane filter rinsing the tube with three successive portions of reagent water. Transfer the rinseates to the filtration apparatus. Place filtrate in a 50ml centrifuge tube and store for analysis of Cr VI colorimetrically using Merit’s Cr VI SOP # IRL-022.

Gradually cool each solution to room temperature. Transfer the contents quantitatively to a 50ml centrifuge tube and bring the volume to 40 ml.

Note: Before discarding any samples or solutions containing Cr VI (i.e. after colorimetric analysis) add an excess of ascorbic acid to the sample (start with about 200 mg of ascorbic acid) and stir. Allow the Cr VI (yellow) to be reduced to Cr III (green) before disposing of the samples or solutions.

Note: The remaining solids and filter paper resulting from filtration of the matrix spike for possible use in assessing low CrVI matrix spike recoveries. Store the filtered solid at 4 ± 2^{o}C.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 and 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.

The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.).

Method Detection limit studies are performed annually.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

Computer software and firmware can be found on Merit's network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

Hexavalent chromium solutions or waste material that are generated must be disposed of properly. One approach is to treat all Cr VI waste materials with ascorbic acid or other reducing agent to reduce the Cr VI to Cr III.

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known 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. 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.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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 (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. Depending on project specifics, MDLs will be in the form of a MDL check standard or the MDL is subject to extraction procedures. An acceptable MDL standard check must produce a signal at least 3 times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Hach Method 8023, Hexavalent Chromium.

Standard Methods for Examination of Water and Wastewaters, Twentieth Edition; 3500-Cr B.

USEPA, SW-846, Revision 3; Method 3060A.

USEPA, SW-846, Revision 3; Method 7196A.

TABLE 1: CrVI Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Method (preparation) Blank	One per batch	<MDL or 1/10 Regulatory limit	Re-digest & Re-analyze entire batch
Laboratory Control Sample (LCS) (soluble and insoluble)	One per batch	80-120%	Re-digest & Re-analyze entire batch
Post Digestion Matrix Spike	One sample per matrix analyzed	75-125%	If check indicates interference; dilute and reanalyze sample.
Matrix Spike Duplicate or Sample Duplicate	One sample for every 10 liquid samples. One sample for every 20 soil samples.	RPD<20%	Re-homogenize, Re-digest & Re-analyze entire batch
Pre-digestion Matrix Spike (soluble) (soil)	One per batch	75-125%	Re-homogenize, Re-digest & Re-analyze entire batch
Pre-digestion Matrix Spike (insoluble) (soil)	One per batch	75-125%	Re-homogenize, Re-digest & Re-analyze entire batch

Table 2: Quality Control Items, Frequency, and Corrective Actions for DoD projects

QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration (ICAL)	Daily ICAL prior to sample analysis.	R2 ≥ 0.99	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum three standards and a reagent blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	Daily before sample analysis, after every 15 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for hexavalent chromium in all samples since the last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Method Blank (MB)	One per preparatory batch.	No analytes detected > 1/2 LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze method blank and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for hexavalent chromium in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if	Correct problem, then reprep and reanalyze the LCS and all	If reanalysis cannot be performed, data must be qualified and explained in	Results may not be reported without a valid LCS. Flagging is only

		project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	the case narrative. Apply Q-flag to all results for hexavalent chromium in all samples in the associated preparatory batch.	appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	Once per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Dilute and reanalyze sample; persistent interference indicates the need to use the method of standard addition, alternative analytical conditions, or an alternative method.	Apply J-flag to all results for hexavalent chromium if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error). Verification check ensures lack of reducing conditions or interference from matrix.
Matrix spike Duplicate (MSD) or Matrix Duplicate (MD)	Aqueous matrix: One per every 10 project samples. Solid matrix: One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Dilute and reanalyze sample; persistent interference indicates the need to use the method of standard addition, alternative analytical conditions, or an alternative method. Reprep and reanalyze all samples in the prep batch.	Apply J-flag to all results for hexavalent chromium if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. Results may not be reported without a valid pair. Flagging is only appropriate in cases where the samples cannot be reanalyzed. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Soluble and Insoluble Pre-Digestion Matrix Spikes (solid matrix samples only)	One soluble and insoluble pre-digestion MS analyzed per preparatory batch prior to analysis.	MS recoveries within 75-125%.	Correct problem and rehomogenize, redigest, and reanalyze samples. If that fails, evaluate against LCS results.	Apply J-flag to all results for hexavalent chromium if acceptance criteria are not met and explain in the case narrative.	NA
Post-digestion Matrix Spike (solid matrix samples)	One per preparatory batch.	Recovery between 85-115%.	No specific CA, unless required by the project.	Apply J-flag to all results for hexavalent chromium if	Criteria apply for samples with concentrations > 50 X LOQ prior to

				acceptance criteria are not met and explain in the case narrative.	dilution.

DoD Appendix C LCS Limits
Method 7196 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
18540-29-9	Hexavalent Chromium [Cr (VI)]	84	110

Method 7196 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
18540-29-9	Hexavalent Chromium [Cr (VI)]	90	111

Figure 1: Hexavalent Chromium Bench Sheet

Analysis: ***Chromium VI*** **Batch ID:____________** **CAL ID# _________________**

Analyst:___________ **Method #**7196A Colorimetric/3500 Cr B **Program #** 1560HACH DR/4000

Date Run:_________ **Detection Limit:** 0.01 mg/l **Wavelength:** 540nm

ID	Merit #	Dilution	(mg/l) Conc.	ABS	%S	(mg/l) Result	(mg/l) Spike	% Rec	Lot/Source	(Run) Time
	Blank	25/25								
	Blank Spike	25/.05ml of 50ppm					0.10			
	Control	25/1ml of 10ppm					0.40			
	LCS	25/0.1ml of 50ppm					0.20			

Peer Review:___________________ ChromaVer **3 Reagent Lot #**___________________________

Digestion Solution/solids Prep date:__________________________________

Beginning Hot Plate temp: _________________ End Hot Plate temp: ______________

Digestion time/date:_______________________ Balance ID: _________________

STANDARD OPERATING PROCEDURE

FRACTIONAL ORGANIC CARBON BY WALKLEY-BLACK

APPROVALS:

Barbara Ball

2/09/12

QA Officer Date

2/09/12

Technical Director Date

Number	**Description of Change**	**Date**
001-002	Previous changes were not documented	
003	Required sections added and Internal Audit findings fixed.	2/09/12
004		
005		
006		
007		
008		
009		
010		
011		
012		
013		

1.0 SCOPE AND APPLICATION

This SOP is for the determination of fractional organic carbon (FOC) also known as soil organic matter (SOM). This SOP follows the Walkley Black method also known as the dichromate oxidation method. This procedure is only applicable to soils particularly those involved in environmental remediation or with FOC of less than six percent (<6%).

2.0 SUMMARY OF METHOD

This SOP is designed to give an outline on how to determine fractional organic carbon (FOC).

3.0 INTERFERENCES

Problems associated with this procedure include excessive organic matter in the soil and difficult end point determination (dark colored solution).

4.0 APPARATUS AND MATERIALS

50 ml class A Burette

Burette stand

5 ml & 10 ml glass pipets/pipettor

250 ml pyrex flask (4)

Stir bar

Stir plate

Plastic Cups

Transfer pipets

Analytical Balance

5.0 REAGENTS

1.0 M Ferrous Sulfate Solution (Titrant) (250 ml / 69.505 g FS; 3.75 ml concentrated H2SO4) prepare fresh monthly

1 N (0.16M) Potassium Dichromate (250 ml / 12.26 g Potassium Dichromate) prepare fresh monthly

Concentrated H_2SO_4

Ferroin Indicator Solution

Deionized (DI) Water

Pure Backing Soda (neutralization)

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples are collected in unpreserved glass containers and are stored in refrigerator at 4±2°C. Holding time for FOC is 28 days.

7.0 PROCEDURE

1. **Entire procedure must be done under fume hood**.
2. Pipet 5 ml of 1 N Potassium Dichromate into a 250 ml pyrex flask. Titrate 2 blank samples (no soil) before proceeding with unknown samples in order to standardize Ferrous sulfate soultion.
   - ♦ If a difference between the 2 blanks is not within 0.2 ml of tirant used, clean the burette and retitrate.
3. Add stir bar to flask.
4. Carefully pipet 10 ml concentrated H_2SO_4 to the flask containing Potassium Dichromate, mixing gently as added.
5. Allow flask to stand three to five minutes under fume hood.
6. Add 47.5 ml DI water to a tared plastic cup and add to 250 ml flask.
7. Begin gentle stir on stir plate.
8. Add four drops of Ferroin Indicator Solution using transfer pipet and immediately titrate with Ferrous Sulfate Solution.
   - ♦ As the titration proceeds, the solution will take on a green color that will abruptly change to reddish-brown when the endpoint of the titration is reached.
   - ♦ Titrate very slowly near the endpoint.
9. Record each volumetric reading to the nearest tenth of a ml.
10. For each sample weigh out 1.0-2.0 g of sample into a pyrex flask recording the exact weight.
    - ♦ For each sample repeat Sections 1 through 9.
11. Calculations
    - ♦ $$\%FOC = \frac{(meqK2Cr2O7 - meqFeSO4) \times 0.003 \times 100 \times 1.3}{grams}$$

- $$\%FOC = \frac{\left[10 - \left(10 \times \frac{(S \times 2)}{(B \times 2)}\right)\right] \times 0.003 \times 100 \times 1.3}{grams}$$
- S = Volume of Ferrous Sulfate solution required to titrate sample, in ml
- B = Average volume of Ferrous Sulfate solution required to titrate the blanks, in ml
- Grams of oven dried sample

12. Neutralize samples for proper disposal.

8.0 QUALITY CONTROL

QC is analyzed per matrix per batch of 20 samples or less. Each QC set must include the following:

- Blank
- Duplicate Sample

The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Method blanks are performed before sample titrations as well as at the end of sample batches.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Entire procedure must be done under fume hood. Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention be paid (but not limited) to

- Concentrated sulfuric acid is toxic and damaging to skin and mucus membranes. If eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit’s Waste Management Plan and Handbook. Samples and waste are neutralized with baking soda and disposed of down the drain.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

14.0 REFERENCES

FRACTIONAL ORGANIC CARBON BY WALKLEY-BLACK

Figure 1: FOC Bench Sheet

Analysis: ***Soil Organic Matter / Fractional Organic Carbon (FOC)***

Analyst: ______________ **Method #**Walkley-Black Method **Program #**_________

Date Run:_____________ **Detection Limit** 0.05% **Wavelength**________

ID	Merit #	Dilution	**1 N** (ml) $K_2Cr_2O_7$	(ml) Conc. H_2SO_4	**0.86N** (ml) Ferrous Sulfate titrant	%S	%OM	%FOC	Time
	Blank	62.5/	5	10					
	Blank	62.5/	5	10					
			5	10					
			5	10					
			5	10					
			5	10					
			5	10					
			5	10					
			5	10					
			5	10					
			5	10					
			5	10					
			5	10					

Batch ID:___________________________________

The %FOC is calculated as follows:
%C = (meq $K_2Cr_2O_7$ – meq $FeSO_4$) x 0.003 x 100 x 1.3
%C = [10 –(10x (Sx2)/Bx2)] x 0.003 x 100 x 1.3 / grams oven dried sample = FOC(%) of sample
organic matter % = organic carbon % X 1.724

S = Volume of Ferrous Sulfate solution required to titrate sample, in ml.
B = Average Volume of Ferrous Sulfate solution required to titrate 2 blanks, in ml.

(1 N)
Potassium dichromate ID___________

(0.86 N)
Ferrous Sulfate solution ID _________

(Phenanthroline)
Ferroin Indicator lot ___________(Hach)

Balance ID: ___________

Sulfuric Acid lot ___________ (VWR)

Peer Review:______________

Merit Laboratories, Inc.

STANDARD OPERATING PROCEDURE

FOR CHROMIUM VI (HEXAVALENT) USING HACH DR/6000 SPECTROPHOTOMETER
METHOD EPA 7196A/STANDARD METHOD 3500-CR B

APPROVALS:

Barbara Ball

10/02/2020

QA Officer Date

Maya Murshak

10/02/2020

Technical Director Date

Number	Description of Change	Date
001-004	Previous changes were not documented	
005	Updated to comply with DoD QSM and ISO 17025 standards.	6/10/11
006	Updated to comply with DoD QSM 5.0 standards.	03/03/16
007	Updated to comply with DoD QSM 5.1 standards.	01/10/18
008	Instrument and Program # updated	05/12/2020
009	DOD Audit Corrective Action	10/02/2020
010		
011		
012		
013		
014		
015		

1.0 SCOPE AND APPLICATION

This SOP is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts, groundwaters, and digested soils and sludges. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present. The reporting limit for hexavalent chromium is 0.01 mg/L for aqueous samples and 1 mg/kg for solid samples.

2.0 SUMMARY OF THE METHOD

Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, is determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

The chromium reaction with diphenylcarbazide is usually free from interferences. Some substances might interfere when the concentration of chromium is extremely low. The references listed below will give more information for these interferences.

Interfering Substance	Interference Levels and Treatments
Iron	May interfere above 1 mg/L
Mercurous & Mercuric Ions	Interferes slightly
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment
Vanadium	May interfere above 1 mg/L. Wait 10 minutes before reading
Oxidizing Agents	Analyze within 24 hours. Use standard addition method to verify and calculate to compensate for the problem.
Reducing Agents	Analyze within 24 hours. Use standard addition method to verify and calculate to compensate for the problem.

4.0 APPARATUS AND MATERIALS

100 ml Graduated Cylinder or equivalent.

Volumetric Flasks: Class A glassware, 1000-mL and 100-mL, with stoppers or equivalent.

Vacuum Filtration Apparatus.

Filter membranes (0.45 µm). Preferably cellulosic or polycarbonate membranes.

When vacuum filtration is performed, operation should be performed with recognition of the filter membrane breakthrough pressure.

50 ml Centrifuge tubes with caps.

Volumetric pipettes: Class A glassware, assorted sizes, as necessary.

pH Strips.

Calibrated balance.

25 ml cuvette.

HACH 6000 Spectrophotometer.

5.0 REAGENTS

ChromaVer 3 Chromium Reagent Powder Pillows Store at 20-25 ^{o}C. Shelf Life: 3 years.

Chromium, Hexavalent, Standard Solution, 50-mg/L Cr $^{6+}$ Store at 20-25 ^{o}C. Shelf Life: 3 years.

Lead chromate Primary Standard. Store at 20-25 ^{o}C. Shelf Life: Indefinite.

Nitric Acid. Store at 20-25 ^{o}C. Shelf Life: 2 years.

Sodium Hydroxide, Pellets. Store at 20-25 ^{o}C. Shelf Life: 6 months.

Potassium Dichromate Stock Standard Solution, 250 ppm

Deionized (DI) water.

Chromium VI spiking solution: 50 mg/L Cr. VI-. Store at 20-25^{o}C in a tightly sealed container for use up to six months.

6.0 SAMPLE HANDLING AND PRESERVATION

Cr. VI is best analyzed as soon as possible from the time the sample is collected. Maximum holding time for water samples from the time of sampling is 24 hours refrigerated at 4^{o} C +/- 2^{o}C.

Soils, sludges, sediments and industrial waste samples should be stored field-moist at 4^{o}C ± 2^{o}C until analysis. Maximum holding time for soils, sludges, sediments and industrial wastes samples for Cr. IV testing is 30 days from sample collection. In addition, the holding time for Cr. VI in the alkaline digestate is 7 days after extraction from soil.

7.0 PROCEDURE

1. Standard Preparation

- I. Insoluble Matrix Spike and LCS
  - a. Add 0.015 g $PbCrO_4$ to sample aliquot or the blank (LCS) that needs to be spiked.
  - b. Record the exact amount of spike added.
- II. Soluble Spike
  - a. Add 2 ml of 50 mg/L CrVI standard to the sample aliquot that is to be spiked.
  - b. For blank spike, add 1 ml of 50 mg/l CrVI standard.
  - c. Record the exact amount added.
  - d. Matrix spike duplicate is prepared the same way as the matrix spike. Always use the sample for both MS and MSD.
- III. Method Blank
  - a. Using DI water; prepare a method blank as you would a sample.

2. Color Development and Measurement
   - I. Place 5.0-mL of soil digestate or 20-mL water or wastewater sample in a 25-ml cuvette.
   - II. Neutralize with HNO_3 (4.99 N) to a pH below 7, but not lower then pH of 6.5
   - III. Dilute to 25.0-mL with DI water.
   - IV. Select the stored program for Hexavalent Chromium (Cr^{6+}) by pressing 1560 with the numeric keys and press enter. Display will show: HACH PROGRAM:90 Chromium, Hex.. Note: the wavelength (λ), 540 nm, is automatically selected.
   - V. Add contents of one (1) Chroma Ver 3 Reagent Powder Pillow to the cuvette containing the neutralized sample and swirl.
   - VI. Press the soft key under START TIMER. An five (5) minute reaction period will begin.
   - VII. Prepare a Blank by adding the same amount of the same sample to another 25-ml cuvette and neutralize. Then fill to the 25.0-ml mark with DI water, but <u>do not add</u> Chroma Ver 3.
   - VIII. When the timer beeps, place the Blank into the cell holder and close the light shield.
   - IX. Press the soft key under ZERO. The display will show: 0.000 mg/L Cr^{6+}. The spectrophotometer is zeroed for this sample.
   - X. Place the sample with the Chroma Ver 3 into the cell holder and close the light shield. Results will be displayed in mg/L Cr^{6+}. Record result on Hexavalent Chromium bench sheet (Figure 1).
3. Preparation of Calibration Curve
   - I. Prepare five standards ranging in concentration from 0.01 mg/L through 0.80 mg/L as follows:

a. Dilute 5 mL of 50 mg/L Chromium Hexavalent Standard Solution to 50 mL in a Class A volumetric flask with DI water and mix thoroughly. This is 5.0 mg/L Cr^{6+}.

b. Pipette 0.05 mL of 5.0 mg/L Cr^{6+} standard into a 25 mL cuvette and bring to volume with DI water. This is a 0.01 mg/L standard.

II. Pipette 0.25 mL of 5.0 mg/L Cr^{6+} standard into a 25 mL cuvette and bring to volume with DI water. This is a 0.05 mg/L standard.

III. Pipette 0.1 mL of 50 mg/L Cr^{6+} standard into a 25 mL cuvette and bring to volume with DI water. This is a 0.20 mg/L standard.

IV. Pipette 0.2 mL of 50 mg/L Cr^{6+} standard into a 25 mL cuvette and bring to volume with DI water. This is a 0.40 mg/L standard.

V. Pipette 0.4 mL of 50 mg/L Cr^{6+} standard into a 25 mL cuvette and bring to volume with DI water. This is a 0.80 mg/L standard.

VI. Using the 1,5 Diphenylcarbohydrazide method and the calibration procedure in the User-Entered Programs section of the DR/6000 Spectrophotometer Instrument Manual, generate a calibration curve from the standards prepared above.

VII. Alternatively, if the five standards match the pre-programmed calibration curve you can use it.

VIII. Each set the curve used must be verified using two standards (0.10 mg/L and 0.40 mg/L) and a Laboratory Control Standard (LCS).

IX. To determine whether the new standard readings match the old curve you must determine the “goodness of fit”. Calculate the “coefficient of fit” with the following formula:

$$\text{Coefficient of Fit} = \frac{\sum_{i=1}^{n}(y_{obs} - y_{mean})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - y_i)^2}{\sum_{i=1}^{n}(y_{obs} - y_{mean})^2}$$

Where:

y_{obs} = Observed response for each concentration from each initial calibration standard.

y_{mean} = Mean observed response from initial calibration.

y_I = Calculated (or predicted) response at each concentration from the initial calibration(s).

n = Total number of calibration points (i.e., 6 for a quadratic model; 7 for a third order model)

p = Number of adjustable parameters in the polynomial equation (i.e., 3 for third order; 2 for a second order polynomial)

Under ideal conditions with "perfect" fit of the model to the data, the coefficient of Fit for the determination will equal 1.0. In order to be an acceptable non-linear calibration, the coefficient of Fit must be greater than or equal to 0.99 (greater than 0.995 for DoD projects).

4. Calculations

I. $$Sample\,Concentration = \frac{A \times D \times E}{B \times C}$$

Where: A = Concentration observed in the digest (µg/mL) minus blank concentration
B = Initial moist sample weight (g)
C = % Solids/100
D = Dilution Factor
E = Final digest volume (mL)

II. Relative Percent Difference $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

III. Spike Recovery Percent Recovery $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 and 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on an as needed basis. (Ex. new instrument, etc.)
Method Detection limit studies are performed annually.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

Computer software and firmware can be found on Merit's network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.
Specific attention be paid (but not limited) to:

- ♦ Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.
- ♦ Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Hexavalent chromium solutions or waste material that are generated should be disposed of properly. One approach is to <u>treat all CrVI waste materials with ascorbic acid</u> or other reducing agent to reduce the CrVI to Cr(III).

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known 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. 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.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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 (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Initial Calibration (ICAL): set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a “calibration curve”. Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Hach DR/6000 Spectrophotometer Instrument Manual.

Hach Method 8023, Hexavalent Chromium.

Standard Methods for Examination of Water and Wastewaters, Twentieth Edition; 3500-Cr B.

USEPA, SW-846, Revision 3; Method 3060A.

USEPA, SW-846, Revision 3; Method 7196A.

Table 1: **Quality Control Items, Frequency, and Corrective Action**

QC Items	Frequency	Acceptance Criteria	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	One per batch	<MDL or 1/10 Regulatory limit	Remove contamination and rerun. Re-digest entire batch.	
Sample Blank to remove turbidity	One for each sample	Not applicable	Filter or centrifuge and rerun	
Laboratory Control Sample (LCS) Soluble and insoluble	One per batch	80%-120%	Re-digest & Rerun full batch	Reset calibration curve
Matrix Duplicate	One per batch	RPD<20%	Re-homogenize, Re-digest & rerun entire set	
Matrix Spike	One per batch per matrix	75%-125%	Analyze by Method of Standard Additions	
Matrix Spike Duplicate	One per batch for Level 3 only.	Solid 75-125% Aqueous 80-120% RPD <20%		
Dilution & Rerun	If result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	
Standard Addition Spiked pH adjusted sample after digestion for verification of result.	One each matrix spiked with 2X concentration in sample.	85%-115%	Rerun diluted.	Rerun with another method or with Standard Additions

Table 2: **Quality Control Items, Frequency, and Corrective Actions for DoD projects**

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL)	Daily ICAL prior to sample analysis.	$R^2 \geq 0.99$	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum three standards and a reagent blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	Daily before sample analysis, after every 15 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for hexavalent chromium in all samples since the last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Method Blank (MB)	One per preparatory batch.	No analytes detected > 1/2 LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze method blank and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for hexavalent chromium in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for hexavalent chromium in all samples in the associated preparatory	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

		the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.		batch.	
Matrix Spike (MS)	Once per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Dilute and reanalyze sample; persistent interference indicates the need to use the method of standard addition, alternative analytical conditions, or an alternative method.	Apply J-flag to all results for hexavalent chromium if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error). Verification check ensures lack of reducing conditions or interference from matrix.
Matrix spike Duplicate (MSD) or Matrix Duplicate (MD)	Aqueous matrix: One per every 10 project samples. Solid matrix: One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Dilute and reanalyze sample; persistent interference indicates the need to use the method of standard addition, alternative analytical conditions, or an alternative method. Reprep and reanalyze all samples in the prep batch.	Apply J-flag to all results for hexavalent chromium if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. Results may not be reported without a valid pair. Flagging is only appropriate in cases where the samples cannot be reanalyzed. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Soluble and Insoluble Pre-Digestion Matrix Spikes (solid matrix samples only)	One soluble and insoluble pre-digestion MS analyzed per preparatory batch prior to analysis.	MS recoveries within 75-125%.	Correct problem and rehomogenize, redigest, and reanalyze samples. If that fails, evaluate against LCS results.	Apply J-flag to all results for hexavalent chromium if acceptance criteria are not met and explain in the case narrative.	NA
Post-digestion Matrix Spike (solid matrix samples)	One per preparatory batch.	Recovery between 85-115%.	No specific CA, unless required by the project.	Apply J-flag to all results for hexavalent chromium if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations > 50 X LOQ prior to dilution.

DoD Appendix C LCS Limits

Method 7196 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
18540-29-9	Hexavalent Chromium [Cr (VI)]	84	110

Method 7196 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
18540-29-9	Hexavalent Chromium [Cr (VI)]	90	111

Figure 1: Hexavalent Chromium Bench Sheet

Analysis: ***Chromium VI*** **Batch ID:__________** **CAL ID# ___________________**

Analyst:_____ **Method #**7196A Colorimetric/3500 Cr B **Program #** 90 HACH DR/6000

Date Run:_________ **Detection Limit:** 0.01 mg/l **Wavelength:** 540nm

ID	Merit #	Dilution	(mg/l) Conc.	ABS	%S	(mg/l) Result	(mg/l) Spike	% Rec	Lot/Source	(Run) Time
	Blank	25/25								
	Blank Spike	25/.05ml of 50ppm					0.10			
	Control	25/1ml of 10ppm					0.40			
	LCS	25/0.1ml of 50ppm					0.20			

Peer Review:_________________ ChromaVer **3 Reagent Lot #**______________________

Digestion Solution/solids Prep date:____________________________

Beginning Hot Plate temp: ________________ **End Hot Plate temp:** _____________

Digestion time/date:_____________________ **Balance ID:** _________________

STANDARD OPERATING PROCEDURE

PERSULFATE –WET OXIDATION METHOD FOR ANALYZING TOTAL ORGANIC CARBON (TOC)
STANDARD METHOD 5310C

APPROVALS:

Barbara Ball

7/26/12

QA Officer Date

Maya Murshedy

7/26/12

Technical Director Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	2011 Internal Audit Findings	08/03/11
007	Updating Method Reference to 5310C	07/27/12
008		
009		
010		
011		
012		
013		
014		
015		
016		

1.0 SCOPE AND APPLICATION

This SOP is for the Persulfate-Wet Oxidation Method for analyzing Total Organic Carbon. This method is applicable to drinking, surface, ground waters & treated mixed wastewater. Reporting limit 1.0 mg/L for water samples. TOC is run by Standard Method 5310C.

2.0 SUMMARY OF METHOD

This SOP is a procedure for evaluating Total Organic Carbon in liquid samples. To remove TIC (total inorganic carbon), the instrument transfers a specified sample volume to the reaction chamber with a preprogrammed volume of H_3PO_4. The acidified sample (sample must be equal to or less than a pH of 2) is sparged with a stream of inert gas as bicarbonates in the sample dissociated to CO_2. The resulting gas flow is vented for the pre-programmed sparge time (nominal time: 2 minutes). NOTE: During this process, any POC (purgeable organic carbon) in the sample is removed and goes undetected. The system determines TOC by measuring carbon dioxide released by chemical oxidation of the organic carbon in the sample. After TIC removal, sodium persulfate ($Na_2S_2O_8$), a strong oxidizer, is added. This oxidant quickly reacts with organic carbon in the sample at 100°C to form carbon dioxide. When the oxidation reaction is complete, the carbon doxide is purged from the solution and routed to the NDIR detector that is sensitive to the specific absorption for the wavelength of carbon dioxide. When the TOC in the sample has been calculated, sample results are reported as ppm or ppb TOC.

3.0 INTERFERENCES

Excessive acidification of the sample, producing a reduction in pH of the persulfate solution to 1 or less, can result in sluggish and incomplete oxidation of the organic carbon. Highly turbid samples can lead to sluggish or incomplete oxidation as well. Some tannins, lignins and humic acid (complex molecules) can be oxidized slowly because persulfate oxidation is rate-limited. Samples with high chloride content can inhibit oxidation of organic molecules. Samples with greater than 0.1% chloride can prevent oxidation completely. Take care in sampling, handling, and analysis of samples below 1 mg/L, as they can be easily contaminated for trace analysis.

4.0 APPARATUS AND MATERIALS

Wet Oxidation TOC Carbon Analyzer with autosampler

40 ml VOA vials with septum

125 ml amber glass / 2,000 stock standard

100 ml volumetric flasks

1 L volumetric flask

Calibrated analytical scale

Calibrated 0.1 - 1 ml micro-pipettor with tips

5.0 REAGENTS

Deionized (DI) water

Potassium Acid Phthalate (PAP) ($C_8H_5O_4K$) / TOC Standard: Weigh 0.425 g (dried) PAP into 100 ml volumetric flask, add 60 or 70 ml DI water, add 0.1 ml concentrated phosphoric acid, bring to volume = 2,000 ppm TOC (Store this solution in dark glass under refrigeration and replace monthly).

100 ppm Working TOC Standard: Dilute 5 ml of 2,000 ppm TOC into a 100 ml volumetric flask and bring to volume (Store this solution in dark glass under refrigeration and prepare fresh weekly).

Phosphoric Acid Solution 5%(H_3PO_4): Add 59.0 ml of 85% H_3PO_4 concentrated to reagent water for a total volume of 1 L in a 1 L volumetric flask. (Shelf life is 3 weeks un-refrigerated).

Sodium Persulfate Solution 10%: weigh 100 g $Na_2S_2O_8$ into 500 ml beaker, add 400 ml DI water, dissolve. Pour into 500 ml volumetric flask and bring to volume. Purge with gas several hours after connecting bottle with solution to instrument. (Shelf life is 3 weeks un-refrigerated).

Nitrogen tank

Control ERA / TOC

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples must be collected in glass or plastic bottles with TFE-lined cap (40 ml VOA vials are preferable) and acidified to a pH < 2 with H_2SO_4. Holding time for preserved samples are 28 days from collection when stored in refrigeration at 4 ± 2° C. Holding time for unpreserved samples are 7 days from collection when stored in refrigeration at 4 ± 2° C.

7.0 PROCEDURE

1 DAILY STARTUP

- Open valve on nitrogen tank and verify that instrument input pressure is 60 psi.
- Make sure there is enough persulfate reagent in supply bottle to last through at least a day’s operation.
- Check to see that waste container is empty.
- Make sure the acid bottle has sufficient acid.

- Make sure that container with DI water is full.

2 SYSTEM ON

- Turn on computer first (do not log in into Launchpad).
- Turn on power on autosampler.
- Turn on power on main instrument unit and and log in (default log in user name is TOC, default password is TOC).
- Log into Launchpad in computer (default user name is TOC, default password is TOC).
- From Launchpad choose PC Applications and double-click on DGS icon. Verify that the right bottom icon on Status Monitor Screen is green color, which indicates that Data Gathering Service (DGC) is operational.

3 CONFIGURE THE METHOD AND ESTABLISH PROPER CALIBRATION PARAMETERS FOR MID-LEVEL METHOD

- Press Editor –Method-New button to configure a new method.
- Enter an appropriate method name, which is the date when the new method is created.
- Under sample Introduction, set the following values:
  - Select NPOC Only from the Mode dropdown list.
  - Press OK on the dialog box.
- Set (verify) the new method parameters as follows:
  - Sample volume 2 ml
  - Acid volume 0.5 ml
  - Persulfate volume 1 ml
  - EPC (psi) 20
- Press the Calibration button to access the Calibration screen and set the new parameters for the mid-level applications:
  - Calibration Standard 1.00 ppm
  - Calibration Standard 2.00 ppm
  - Calibration Standard 5.00 ppm
  - Calibration Standard 10.0 ppm
  - Calibration Standard 50.0 ppm
  - Calibration Standard 100 ppm
- Press OK to exit the Calibration screen
- Press the Times button and verify that the correct time for TOC/TC react time is entered

for the mid-level method, (2:30 min/sec)

- ♦ Press OK and Save to save the configured method.
- ♦ The instrument can run a low-level, mid-level, and high-level methods. The mid-level method (1 – 100 ppm) is used to analyze TOC.

4 CREATING THE SEQUENCE

- ♦ Press Editor →Sequence →New button.
- ♦ Enter an appropriate sequence Name (date of the sequence), for example 041211.
- ♦ Press the Add/Insert Sample button near the bottom of the screen to access the Add /Insert dialog box.
    - ○ Under Sample Type, select Clean Up from the dropdown list.
    - ○ Verify the value for # Reps is 2.
    - ○ Verify the value for # of Samples is 1.
    - ○ Press OK to exit the Add/Insert Sample screen.
- ♦ Press the Add/Insert Sample button to access the Add/Insert dialog box.
- ♦ Under Sample Type select Cal from the dropdown list.
- ♦ In the Methods section Primary dropdown list, select the method configured in the previous “Configuring a Method” section (date the method was created) for example 041211.
- ♦ Press OK to exit the Add/Insert Samples screen.
- ♦ Press Save; a message appears stating that the “Sequence has been saved”. Press OK.
    - ○ Note: Sequence of samples, check standards, and quality control samples (QC) are created by following the same steps described in “Creating a Sequence”.

5 LOADIND AND STARTING THE SEQUENCE

- ♦ Press Monitor →Sequence →Load Active Sequence button to access the Load Active Sequence dialog box.
- ♦ Highlight the sequence created in the previous “Creating a Sequence” section (date the sequence was created, for example 041211).
- ♦ Press the Load button.
- ♦ Press Start (►) to begin the sequence.

6 REPORTING

- ♦ Start TOC Reporter by double-clicking Reporter from the Launchpad PC Applications tab.
- ♦ The TOC Reporter Login dialog box appears. The default username is “toc”. The default

password is “toc”. Select an Instrument ID – C 519731232 Wet Chemistry. Click OK.

- To include samples in report, select the checkbox next to each sample in the data tree view. Create the report by right-clicking the sequence in the tree view and choosing Generate New Report.
- Before the report can be saved, it must be previewed, by clicking Preview Report, then click Save Report.
- To print a report, open the Report Viewer by previewing the report contents. Press the print icon at the top of the Report Viewer.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed annually. Method Detection Limit (MDL) studies are performed annually. Based on current method restrictions, Limit of Detection (LOD) evaluation is not required. Results will be reported only inside working range of instrument calibration. Limit of Quantitation (LOQ) is analyzed annually.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer’s procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced. All maintenance must be entered in the maintenance logbook.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Phosphoric acid is corrosive, causes severe irritation and burns on contact, contact with most metals can cause the formation of flammable and explosive hydrogen gas, when diluting the acid must always be added slowly to water in small amounts, and never use hot water and never add water to the acid.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 10 samples or less.

Method Blank or Laboratory Reagent Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known 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. 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.

Matrix Spike (also known as Spiked Sample or Fortified Sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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.

Initial Calibration (ICAL): Set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Laboratory Duplicate: Aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): A standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Standard Methods for Examination of Water and Wastewaters, Twentieth Edition; 5310C
Aurora 1030 Wet Oxidation TOC analyzer Operators Manual, Rev. 1.5 – May 2009.
Atoc Software Version 1.4.2 Operators Manual, Rev 1.2 - August 2010

Table 1. Quality Control Items, Frequency, and Corrective Action

QC Items	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points) (ICAL)	When needed or daily when required by project	R = 0.995	Terminate analysis, recalibrate and verify before sample analysis
Initial Calibration Verification (ICV) (separate source from ICAL standards)	Immediately following ICAL and at the beginning of each batch.	± 10% from expected concentration	Reprep ICV and reanalyze Identify and document problem Recalibrate and reanalyze ICV
Continuing Calibration Verification (CCV)	After every 10 samples and at the end of the run	± 10% from expected concentration	Recalibrate and verify Reanalyze samples back to last good CCV
QC Blank	After CCVs One per Batch	< 10 x RL (reporting limit)	Terminate analysis Identify and document the problem Reanalyze all associated samples
Replicate Samples	All samples must be run in replicate. Report average value and RPD.	RPD < 20%	Rerun sample. Flag associated data.
Matrix Spike (MS)	MS to be run in replicate. One MS per batch. Report average value and RPD.	± 25% from expected value	Rerun sample. Flag associated data.
Laboratory Control Sample (LCS)	LCS to be run in replicate. One LCS per batch. Report average value and RPD.	± 20% from expected concentration	Terminate analysis Identify and document the problem Reanalyze all associated samples

STANDARD OPERATING PROCEDURE

TOTAL SOLIDS (TS) AND TOTAL VOLATILE SOLIDS (TVS) FOR SOLID SAMPLES STANDARD METHOD 2540 B (TS), EPA 160.4 (TVS)

APPROVALS:

Barbara Ball

10/02/2020

QA Officer Date

10/02/2020

Technical Director Date

Number	**Description of Change**	**Date**
001-006	Previous changes were not documented	
007	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
008	Added constant weight check information	8/3/12
009	DOD Audit Corrective Action	10/02/2020
010		
011		
012		
013		
014		
015		
016		
017		

1.0 SCOPE AND APPLICATION

This SOP determines total solids (TS) in domestic and industrial wastes. This method also determines the weight of solid material combustible at 550ºC, Total Volatile Solids (TVS). The reporting limit is 1 % for TS, 1% for TVS, and 1% for Ash.

2.0 SUMMARY OF METHOD

A representative aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C (217-221°F).

3.0 INTERFERENCES

Non-representative particulates such as leaves, sticks, large rocks, fish and lumps of fecal matter must not be included in the sample.

Floating oil and grease, if present, must be included in the sample but must be mixed well with the sample before testing.

4.0 APPARATUS AND MATERIALS

Aluminum disposable evaporating dishes.

Tongue depressors.

Electronic scale.

Dessicator.

Oven, 103 ± 2ºC.

Thermometer.

Muffle Furnace.

5.0 REAGENTS

Deionized (DI) water.

Reagent Free Sand.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Collect sample in a plastic or glass bottle without preservative. Store at 4±2°C. Analysis must begin as soon as possible. Refrigeration is recommended to minimize microbiological decomposition of solids. Holding time is 7 days.

7.0 PROCEDURE

1. Be sure to run the QC samples and items listed in Table #1.
2. Mark an aluminum weighing tin on the bottom by pressing with a ball point pen to crease symbols in to the metal in order to identify it. Record this symbol (i.e. number) on the bench sheet.
3. Weigh the evaporating dish on the electronic scale, record weight on the bench sheet.
4. With tongue depressor, scoop approximately 10 g of the sample into the dish, and record the wet sample/dish weight.
5. Place weighed wet samples in the oven at 103-105 °C (217-221 °F). Record the time and temperature at which the samples which the samples were put into the oven.
6. Allow samples to dry in the oven for at least 1 hour (overnight is best since more time may be needed to dry out the inside of the samples).
7. Remove samples from oven and weigh on electronic scale. Record the dry sample/dish weight and the date when the samples were removed from the oven.
8. If samples were not dried overnight, repeat steps 6 and 7 until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less.
9. When the sample is dried to a constant weight, calculate percent total solids as follows:

   %Total Solids (TS) =[(Final weight-dish weight)/(Initial weight-dish weight)] X 100

10. If Total volatile solids (or ash) are needed place the dried weighed sample into a muffle furnace at a temperature of 550 °C for at least 30 minutes.

11. Remove from the oven, cool in a desiccator and weigh. Record weight on the bench sheet (Figure 1).

12. Calculations

- Calculate TVS as follows:

  %Total Volatile Solids (TVS) =[(Initial (TS) weight (before furnace)-Final weight (after furnace) /(Initial (TS) weight-dish weight)] X 100

- Calculate Ash as follows:

  %Ash = [(Final weight (after furnace)- dish weight) /(Initial (TS) weight-dish weight)]*100 or, %Ash=100%-%TVS

- Relative Percent Difference: $RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

This method is evaluated by testing a laboratory control sample and duplicate samples.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment must be maintained and calibrated according to manufacturer’s procedures. When equipment is not performing as required, the instrument must not be used until it is recalibrated or replaced.

Computer software and firmware can be found on Merit’s network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing solids analyses. Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit’s Waste Management Plan and Handbook.

13.0 DEFINITIONS

Total residue: the sum of the homogenous suspended and dissolved materials in a sample.

Sample Batch: samples of the same or similar matrix; a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike: Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability to generate acceptable precision and bias, to verify the analytical system’s performance, and to document method accuracy for each matrix.

Laboratory Duplicate: Aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

EPA Method 160.4

Standard Methods for Examination of Water and Wastewater, 20th edition, Method 2540B, Total Solids Dried at 103-105°C.

Table 1: Quality Control Items, Frequency, and Corrective Action

QC Sample	**Frequency**	**Acceptable Limits**	**Corrective Action**	**Follow up Corrective Action**
Blank	1/20 samples	-3 to +3 mg/l	Re-dry and Reweigh	Reset the entire set of samples
Laboratory Control Sample-Sand + known amt. water	1/20 samples	± 10 %	Re-dry and Reweigh	Reset the entire set of samples
Sample Duplicate	1/10 Samples	± 5 % of average	Reset sample duplicates	Footnote non-homogeneity
Analytical Balance Check with “Certified” Weights	1/day	±0.1% or 0.5 mg, whichever is greater	Recalibrate Balance and Reweigh	Call for Service
Constant Weight Verification	All samples	4 % or 0.5 mg whichever is less	Dry longer and reweigh.	Dry longer and reweigh.

Figure 1: Total Solids and Total Volatile Solids Benchsheet

TS: Standard Method 2540B TVS: EPA 160.4

Date Run:___________________ Date Finished:_______________ Date Checked:_______________

Time Started:________________ Time Finished:_______________ Checked By:________________

Analyst:____________________ Temperature:________________ Batch:______________________

Time in Oven:_______________ Balance ID: _________________ Oven ID: __________________

Merit #	Dish #	Dish Wt. (g)	Wet Sample. + Dish Wt. (g)	Dry Sample + Dish Wt. (g)	Reweigh Dry Sample + Dish Wt. (g)	Ash Sample + Dish Wt. (g)	% Total Solids	% Total Volatile Solids	% Ash
Blank									
LCS									
Dup 1									
Dup 2									

% LCS Recovery:______________ Acceptance Criteria: ± 10%

% RPD (Duplicate 1):___________ Acceptance Criteria: ± 5% of average

% RPD (Duplicate 2):___________

STANDARD OPERATING PROCEDURE

MICROWAVE ASSISTED ACID DIGESTION OF SOLID SAMPLES USEPA METHOD 3051A

APPROVALS:

Barbara Ball

10/01/2020

QA Officer Date

10/01/2020

Technical Director Date

Number	**Description of Change**	**Date**
001-008	Previous changes were not documented	
009	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
010	Emergency SOP Amendment Form updates	2/9/16
011	Updated to comply with DoD QSM 5.0 standards.	03/10/16
012	Updated to comply with DoD QSM 5.1 standards.	01/15/18
013	NY NELAC Audit Finding	03/05/19
014	DOD Audit Corrective Action	10/01/2020
015		
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

This digestion procedure is used for the preparation of soils and solid samples for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced within this SOP is the EPA SW-846 Method 3051A.

This method is not a total digestion technique for most samples. The method is a very strong acid digestion that will dissolve almost all elements that could become environmentally available. By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment. Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

Metal (Symbol)	CAS#:
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
*Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
*Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
*Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
*Tin (Sn)	7440-31-5
*Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

* Not approved for DoD work

2.0 SUMMARY OF METHOD

For the digestion of samples, a representative 0.05-2.0 gram (wet weight) sample is digested with nitric acid (HNO_3) using microwave heating. The resultant digestate is diluted to a final volume of 50 ml. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis. If required, a separate sample aliquot is reserved for the determination of percent total solids.

3.0 INTERFERENCES

Addition of nitric acid to samples that contain organics could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. Sludge samples can contain diverse matrix types, each of which can present its own analytical challenge. Spiked samples and any relevant standard reference material must be processed in accordance with the quality control requirements given in Section 8.0. Samples that are highly reactive or contaminated may require dilution before analysis. If samples are diluted, then any dilutions must be accounted for in all subsequent calculations. Highly reactive samples may also require pre-digestion in a hood to minimize the danger of thermal runaway and excessively vigorous reactions.

4.0 APPARATUS AND MATERIALS

Microwave Digestion System CEM–Model MDS-81D and MARSX Model # 907600.

- The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to ensure uniform microwave heating

- The MARSX consists of a microwave drying system with an operator selectable power output of 0 – 1200 watts, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

- Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

Glass Fiber Filter paper, 0.45 µm.

Membrane Filter paper, 0.45 µm.

Analytical balances, 510 g capacity, minimum accuracy ± 0.001 g, and 250g capacity, minimum accuracy ±0.0001g.

Filter funnel, glass, or disposable polypropylene.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Disposable Polypropylene vessels, 50 ml, compatible with centrifuge.

Plastic containers to support minimum of 200 ml.

Disposable tongue depressors for sample handling.

Disposable Pasteur pipettes.

Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.

Centrifuge (IEC Centra GP8).

5.0 REAGENTS

Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM standard criteria.

Concentrated nitric acid, HNO_3, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank (LRB).

Standards added to digestion:

- Spiking Solutions:
    - <u>Multi-element standard solution</u> **WS1** (Figure 1), contains 10 µg/ml (ppm) each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Sr, Sn, Ag, Tl, Ti, V, and Zn. The spiking solution is made by diluting the WS1, 2 to 1 (5 µg/ml). The 5 µg/ml spiking solution is added to the QC samples accordingly, 1.0 ml is added to MS/MSD samples and 0.5 ml is added to the laboratory control sample (LCS), using the Eppendorf automatic pipette.
    - <u>Multi-element standard solution</u> **HM** (Figure 1) contains 100 µg/ml each of Ca, K, Mg, and Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), using the Eppendorf automatic pipette or by weighing the amounts (1.0 g or 0.50 g) on the scale.
    - Spiking solutions are prepared according to the Standard Prep Log (Figure 1). The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used are recorded in the standard prep log.

- All standards are NIST traceable.

♦ Internal Standards (after digestion):

- Lithium 6, 1000 μg/ml stock solution.
- Scandium, 1000 μg/ml stock solution.
- Yttrium, 1000 μg/ml stock solution.
- Rhodium, 1000 μg/ml stock solution.
- Rhenium, 1000 μg/ml stock solution.

NOTE: The manufacturer provides the stock solutions with a certificate of analyses and MSDS sheets.

- Internal Standard working solution (**IS-WS**): From the above stock solution, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the bottle will be 2.5 μg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ± 2° Celsius. Holding times for metals are 6 months from the date of sampling, with the exception of Mercury which is not covered in this SOP.

7.0 PROCEDURE

1. The Microwave Accelerated Reaction Systems are equipped with a temperature feedback control system. Microwaves are calibrated once a year according to the manufacturer's operation manual.

2. All digestion vessels are disposable and are used only once. This allows for better sample control and prevents cross contamination.

3. Sample Digestion.

CAUTION: - Toxic nitrogen oxide fumes may evolve; therefore all work must be performed in a properly operating ventilation system.

- Loss of sample through splattering inside the microwave system needs to be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be

inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.

- Homogenize sample by chopping and mixing sample with a tongue depressor or spatula. Remove any foreign object such as sticks, leaves, or rocks. Transfer 0.2 to 0.3 grams sample (wet weight) for a soil matrix or 0.05 to 2 grams sample (wet weight) for liquidly sludges and other various solid matrices to a digestion vessel, and record the weight on the digestion log (Figure 2), to a minimum of 0.001 g.

- For every sample batch, prepare a Laboratory Reagent Blank (LRB) and Laboratory Control Sample (LCS) by transferring 0.25 grams sand to the digestion vessel. Record the weight on the digestion log (Figure 2) to a minimum of 0.001 g. Additionally, designate a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) or Duplicate (Dp) prepared as per 7.3.1.

- For all metals, except Ca, Mg, K, and Na, add 0.50 ml of the QC spiking solution to the LCS, and 1.0 ml to the MS/MSD samples. For Ca, Mg, K and Na, add 0.5 ml of the **HM** solution to the LCS, and 1.0 ml to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the digestion log. The spike solution for MS/MSD is added before digestion.

- Add 1 ± 0.1 mL of concentrated nitric acid to each conical vessel in the fume hood. Mix the slurry, then wait 5-10 minutes for any reaction to occur.

- Loosely cap the vessel and place into the carousel.
- Samples are slowly ramped in the microwave to 95 ±5 degrees Celsius over the course of a few minutes and maintained at this temperature for 5 minutes without boiling.

- Allow samples to set for 5 minutes then repeat previous step.
- After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood. When the vessels have cooled to near room temperature, determine if the microwave vessels and caps are intact. If the sample vessel look compromised (i.e. cap is not on, sides of the vessel are wet), then the sample is considered compromised and the sample must be re-digested.

- Add 1 ml of the Internal Standard working solution to each sample and QC sample using an Eppendorf automatic pipettor. Dilute to the 50 ml mark with DI Water, into a calibrated (per lot) digestion vessel.

- A post-digestion spike is performed as necessary and prepared as follows: take a 25 ml aliquot of the sample designated for MS/MSD and add to it 0.50 ml of the QC spiking solution (for all elements except Ca, Mg, K, and Na). For Ca, Mg, K, and Na add 0.5 ml of the **HM** solution.

- If the digested sample contains particulate matter, which may clog the nebulizer, the sample may be centrifuged, allowed to settle overnight, or filtered.

  - Centrifugation: centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.

  - Settling: allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

  - Filtering: the filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 μm filter paper and transfer the liquid to a new vessel. Glass fiber filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

- Calculations

Dilution factor(DF:

$$DF = \frac{Final\ Volume\ (50)}{Sample\ amount}\ x\ \frac{100}{\%\ Total\ solids}$$

Relative Percent Difference: $RPD = \frac{(S-D)}{\left[\frac{S+D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR-SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

% Difference (%D)
Used for serial dilution test in metals.

$$\%D = \left|\frac{X_1 - X_2}{X_1}\right| \times 100\%$$

where: %D = percent difference
X_1 = Initial concentration
X_2 = Duplicate concentration

- Record pertinent information onto the digestion log (Figure 2). The following information must be included: Date, start time, end time, analyst initials, method reference, sample IDs, sample weight or volume, MS/MSD/LCS spiking concentration and lot#, acid lot #, dilution factor, final volume and any pertinent remarks.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 & 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.

The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

Computer software and firmware can be found on Merit’s network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

12.0 WASTE DISPOSAL

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Samples.

- All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory waste water.

- As a "small generator" of metals, Merit Laboratories has been approved for this type of disposal from the local government.

Acid bottles.

- Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for metals a sample batch consists of 20 samples or less.

Method Blank (Laboratory Reagent Blank) (LRB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known 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 carried through the complete sample prep and analytical procedure. 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.

Matrix Spike (MS) (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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 (MSD) (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

1985 Annual Book of ASTM Standards, Vol.11.01; “Standard Specification for Reagent Water”

Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).

Gray, A.L., Spectrochim. Acta 40B, 1525 (1985); 41B, 151 (1986).

Hinners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).

Holden, N.E., "Table of the Isotopes," in Lide, D.R., Ed., CRC Handbook of Chemistry and Physics, 74th Ed., CRC press, Boca Raton, FL, 1993.

Horlick, G., et al., Spectrochim. Acta 40B, 1555 (1985).

Houk, R.S., Anal. Chem. 58, 97A (1986).

Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).

Method 200.8, Revision 5.4, 1998.

Microwave Digestion System CEM-Model MDS-81D Instrument Manual.

Microwave Digestion System MARSX-Model #907600 Instrument Manual.

Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986).

Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).

USEPA, SW-846, Revision 2, 1996, Method 3050B

USEPA, SW-846, Revision 3, Method 3051A.

USEPA, SW-846, Revision 0, 1994. Method 6020.

USEPA, SW-846, Revision 1, 2007, Method 6020A

USEPA, SW-846, Revision 3, 2003, Method 8000C

Vaughan, M.A., and Horlick, G., Appl. Spectrosc. 40, 434 (1986).

TABLE 1 Quality Control Items, Frequency and Corrective Action

QA Items	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Laboratory Reagent Blank (Method Blank)	One per sample batch	<RL/dilution	Remove contamination and re-digest sample set
Laboratory Control Sample	One per sample batch	85%-115%	Re-digest the sample set
Matrix Spike	One per every 20 samples	75%-125%	Analyze by Method of Standard Additions (MSA)
Matrix Spike Duplicate	One per ever 20 samples	75%-125% RPD <20%	Analyze by Method of Standard Additions (MSA)
Matrix Duplicate	One per every 20 samples	RPD <20%	Re-digest the sample set and QC.
Dilution	One per sample batch	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.

TABLE 2 Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Linear Dynamic Range (LDR) or High-level Check Standard	At initial set-up and checked every 6 months with a high standard at the upper limit of the range.	Within ±10% of true value.	Dilute samples within the calibration range, or re-establish/verify the LDR.	Flagging is not appropriate.	Data cannot be reported above the calibration range without an established/passing high-level check standard.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial Calibration (ICAL) for All Analytes	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r2 ≥ 0.99.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes, within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of the true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

			necessary; then reanalyze all associated samples since the last acceptable CCV.		
Low-level Calibration Check Standard (LLCCV)	Daily.	All reported analytes within ± 20% of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid low-level calibration check standard (LLCCV). LLCCV should be less than or equal to the LOQ. If the concentration of the lowest calibration standard os less than or equal to the LOQ, the lowest standard may be re-quantified against the calibration curve as LLCCV. Otherwise, a separate standard must be analyzed as the LLCCV prior to the analysis of any samples.
Internal Standards (IS)	Every field sample, standard and QC sample.	IS intensity in the samples within 30-120% of intensity of the IS in the ICAL blank.	If recoveries are acceptable for QC samples, but not field samples, the field samples may be considered to suffer from a matrix effect. Reanalyze sample at 5- fold dilutions until criteria is met. For failed QC samples, correct problem, and rerun all associated failed field samples.	Flagging is not appropriate.	Samples suffering from matrix effect should be diluted until criteria are met, or an alternate IS should be selected.
Method Blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch	Results may not be reported without a valid method blank. Non-detects associated with positive blank infractions may be reported. Samples results > 10X the LOQ associated with negative blanks

					may be reported. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV.	The absolute values of all analytes must be < ½ LOQ or 1/10th the amount measured in any sample.	ICB: Correct problem and repeat ICV/ICB analysis. If that fails, rerun ICAL. All samples following the last acceptable Calibration Blank must be reanalyzed. CCBs may not be re-analyzed without re-analysis of the associated samples and CCV(s).	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. Non-detects associated with positive blank infractions may be reported. Sample results > 10X the LOQ associated with negative blanks may be reported. For CCB, failures due to carryover may not require an ICAL.
Interference Check Solutions (ICS) (also called Spectral Interference Checks)	After ICAL and prior to sample analysis.	ICS-A: Absolute value of concentration for all nonspiked project analytes <1/2 LOQ (unless they are a verified trace impurity from one of the spiked analytes) ICS-AB: Within ± 20% of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the failed ICS.	All analytes must be within the LDR. ICS-AB is not needed if instrument can read negative responses.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of

		analyte(s) are not listed, use in-house LCS limits if project limits are not specified.		the case narrative.	difference, i.e., matrix effect or analytical error.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Dilution Test	One per preparatory batch if MS or MSD fails.	Five-fold dilution must agree within ± 10% of the original measurement.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Only applicable for samples with concentrations > 50 X LOQ (prior to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post Digestion Spike (PDS) Addition	One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible).	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 6020 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	78	124
7440-36-0	Antimony	72	124
7440-38-2	Arsenic	82	118
7440-39-3	Barium	86	116
7440-41-7	Beryllium	80	120
7440-42-8	Boron	74	128
7440-43-9	Cadmium	84	116
7440-70-2	Calcium	86	118
7440-47-3	Chromium	83	119
7440-48-4	Cobalt	84	115
7440-50-8	Copper	84	119
7439-89-6	Iron	81	124
7439-92-1	Lead	84	118
7439-93-2	Lithium	75	120
7439-95-4	Magnesium	80	123
7439-96-5	Manganese	85	116
7439-97-6	Mercury	74	126
7439-98-7	Molybdenum	83	114
7440-02-0	Nickel	84	119
7440-09-7	Potassium	85	119
7782-49-2	Selenium	80	119
7440-22-4	Silver	83	118
7440-23-5	Sodium	79	125
7440-24-6	Strontium	75	129
7440-28-0	Thallium	83	118
7440-29-1	Thorium	81	116
7440-29-1	Tin	82	121
7440-32-6	Titanium	83	117
7440-61-1	Uranium	83	120
7440-62-2	Vanadium	82	116

7440-66-6	Zinc	82	119

Method 6020 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	84	117
7440-36-0	Antimony	85	117
7440-38-2	Arsenic	84	116
7440-39-3	Barium	86	114
7440-41-7	Beryllium	83	121
7440-42-8	Boron	73	130
7440-43-9	Cadmium	87	115
7440-70-2	Calcium	87	118
7440-47-3	Chromium	85	116
7440-48-4	Cobalt	86	115
7440-50-8	Copper	85	118
7439-89-6	Iron	87	118
7439-92-1	Lead	88	115
7439-93-2	Lithium	78	126
7439-95-4	Magnesium	83	118
7439-96-5	Manganese	87	115
7439-97-6	Mercury	70	124
7439-98-7	Molybdenum	83	115
7440-02-0	Nickel	85	117
7440-09-7	Potassium	87	115
7782-49-2	Selenium	80	120
7440-22-4	Silver	85	116
7440-23-5	Sodium	85	117
7440-24-6	Strontium	82	118
7440-28-0	Thallium	82	116
7440-29-1	Thorium	87	121
7440-29-1	Tin	86	115
7440-32-6	Titanium	83	115

7440-33-7	Tungsten	85	122
7440-61-1	Uranium	87	120
7440-62-2	Vanadium	86	115
7440-66-6	Zinc	83	119

FIGURE 1: STANDARD PREP LOG

Standard Preparation PE

Inorganic Stock Solution IV-28 (100 ppm) + CGSN1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	**Volume Working Stock Solution**	**Internal Standard 5.0 ppm**	**HNO_3**	**Final Volume**
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0002 ppm	0.20 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

ICP/MS MINERALS PREP LOG

Date	IS ID	Exp. Date	Analyst

Standards **ppm**	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	Final Volume
0.0	**0.0**		**2 mls**	**2 mls**	**100 mls**
0.50	**0.5**		**2 mls**	**2 mls**	**100 mls**
1.0	**1.0**		**2 mls**	**2 mls**	**100 mls**
2.0	**2.0**		**2 mls**	**2 mls**	**100 mls**
5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**
10.0	**10.0**		**2 mls**	**2 mls**	**100 mls**
ICV – 5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**

FIGURE 2: METALS DIGESTION LOG

Metals Digestion 3015A \ 3051A

DATE ________________ PREP BATCH MTD-____________

TIME START ___________ TIME FINISH ______________ ANALYST _____________

Pipet Calibration:

Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria	Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria
2	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value	3	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value
	2					2			
	3					3			

SAMPLE#	**BTL ID**	**SAMPLE AMOUNT GRAMS (g)**	**FINAL VOLUME (ml)**	**REMARKS**	**% TOTAL SOLIDS**	**DILUTION FACTOR**
LCS -	----	50	**50**		—	1
LRB-	----	50	**50**		—	1

NOTES: *1) Spike values (unless otherwise stated):*
LCS = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

1.1. Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution
Spiking Solution – Date Prepared:____

2) Spike values for minerals (Ca-Mg-K-Na)
LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution
Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution
High Purity Stock Solution (HM)- Lot #________________________________

3) HNO_3 *Lot #____________________* *4) Centrifuge Tube Lot #_______________________________________*

5) Balance ID:_______________ *Reviewed by _____________ On _________*

STANDARD OPERATING PROCEDURE

MICROWAVE ASSISTED ACID DIGESTION OF LIQUID SAMPLES AND EXTRACTS US EPA METHOD 3015A

APPROVALS:

Barbara Ball

10/01/2020

QA Officer Date

10/01/2020

Technical Director Date

Number	Description of Change	Date
001-007	Previous changes were not documented	
008	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
009	Emergency SOP Amendment Form updates	02/09/16
010	Updated to comply with DoD QSM 5.0 standards.	03/10/16
011	Updated to comply with DoD QSM 5.1 standards.	01/15/18
012	DOD Audit Corrective Action	10/01/2020
013		
014		
015		
016		
017		
018		

1.0 SCOPE AND APPLICATION

This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced with in this SOP is SW-846 Method 3015A.

Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

Metal (Symbol)	CAS#:
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
*Boron (B)	7440-42-8
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)7439-89-6	
Lead (Pb)	7439-92-1
*Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
*Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
*Tin (Sn)	7440-31-5
*Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

* Not approved for DoD work

2.0 SUMMARY OF METHOD

A representative 0.5 to 25 g/ml aqueous sample is digested in 1 ml of concentrated nitric acid in a polypropylene digestion vessel heated using microwave heating and brought to a final volume of 50 ml. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis.

3.0 INTERFERENCES

Addition of nitric acid to samples that contain organics, such as TCLP extracts, could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. A smaller sample size can be used but the final water volume must be adjusted to approximately 10 ml prior to the heating stage.

4.0 APPARATUS AND MATERIALS

Microwave Digestion System CEM–Model MDS – 81D and MARSX-Model # 907600:

- The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to insure uniform microwave heating.

- The MARSX consists of a microwave drying system with an operator selectable power output of 0-1200 watts in, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

- Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

Analytical balances, 510g capacity, minimum accuracy ± 0.001g and 250g capacity, minimum accuracy ±0.0001g.

Filter funnel, glass or disposable polypropylene.

Glass-fiber filter paper, 0.45 µm.

Membrane filters, 0.45 µm.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Disposable polypropylene vessels, 50 ml, compatible with centrifuge.

Plastic containers to support minimum of 200 ml.

Disposable Pasteur pipettes.

Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.

Centrifuge (IEC Centra GP8).

5.0 REAGENTS

Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM standard criteria.

Concentrated nitric acid, HNO_3, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank.

Standards added to digestion:

- Spiking Solutions
    - Spiking solutions are prepared according to the Standard Prep Log (Figure 1). The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used.
    - All standards are NIST traceable.
    - Multi-element standard solution **WS1** (Figure 1), contains 10 µg/ml (ppm) each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Sr, Sn, Ag, Tl, Ti, V, and Zn. The spiking solution is made by diluting the WS1, 2 to 1 (5 µg/ml). The 5 µg/ml spiking solution is added to the QC samples accordingly, 0.5 ml is added to MS/MSD samples and 0.5 ml is added to the laboratory control sample (LCS), using the Eppendorf automatic pipette.
    - Multi-element standard solution High Purity Mineral **(HM)** (Figure 1) contains 100 µg/ml each of Ca, K, Mg, and Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), by weighing the amounts (1.0 g, 0.50 g) on the scale.
- Internal Standards (After digestion):
    - Lithium 6, 1000 µg/ml stock solution.
    - Scandium, 1000 µg/ml stock solution.
    - Yttrium, 1000 µg/ml stock solution.
    - Rhodium, 1000 µg/ml stock solution.

- Rhenium, 1000 µg/ml stock solution.
- Internal Standard working solution (**IS-WS**): From the above stock solutions, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the bottle will be 2.5 µg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* standards, samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

NOTE: The stock solutions are NIST traceable and provided with a certificate of analyses and MSDS sheets by the manufacturer.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Water samples are collected in HNO_3 pre-preserved plastic containers and are acidified to pH of <2. (Approximately 125 ml volume). Holding times for metals are 6 months from the date of sampling, with the exception of Mercury, which is not covered by this SOP.

7.0 PROCEDURE

1. The Microwave Accelerated Reaction Systems are equipped with a temperature feedback control system. Microwaves are calibrated once a year according to the manufacturer's operation manual.

2. All digestion vessels are disposable and are used only once, which allows for better sample control and prevents cross contamination.

CAUTION: - Toxic nitrogen oxide fumes may evolve; therefore all work must be performed in a properly operating ventilation system.

- Loss of sample through splattering inside the microwave system must be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.

3. Digestion using industrial Microwave.

- ♦ A 0.5 to 25 ml/grams aliquot of a well shaken sample is transferred into the digestion vessel; sample volume is determined by sample matrix and sample history. The vessel is labeled with the sample number, which is also recorded on the digestion log (Figure 2).

- With every batch of 20 analytical samples measure a volume of reagent water equal to the sample volume as described at above into a vessel labeled LRB. This represents the Laboratory Reagent Blank (LRB), which is carried through the entire digestion procedure, the same as an analytical sample.

- With every batch of samples measure a volume of reagent water equal to the sample volume as described at above into a vessel labeled LCS. This represents the Laboratory Control Sample (LCS), which is carried through the entire digestion procedure, the same as an analytical sample.

- For every 10 samples measure, in a similar manner, an amount equal to the parent sample of the sample designated for Matrix Spike (MS) and Matrix Spike duplicate (MSD) or duplicate (Dup).

- For analysis of all metals except Ca, Mg, K and Na, add 0.5 ml of the QC Spiking Solution to the QC samples (LCS, MS/MSD). For Ca, Mg, K and Na, add 0.5 ml of the HM solution to the LCS, and 1.0 ml of the HM solution to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the digestion log (Figure 2).

- Add 1 ± 0.1 ml of concentrated nitric acid to each vessel, by using the bottle top dispensers in the fume hood.

CAUTION: *Addition of nitric acid to the non-aqueous (solvents) samples needs to be performed slowly, dropwise if possible in order to control the potential reaction. When the reaction has subsided, swirl the vessel lightly, dilute the sample to approximately 10 mL, and go to the next step.*

- Loosely cap the vessel and place into the carousel.
- Samples are slowly ramped in the microwave to 95 ± 5 degrees Celsius over the course of a few minutes and maintained at this temperature for 30 minutes.

- After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood.

- When the vessels have cooled to near room temperature, determine if the microwave vessels and caps are intact. If the sample vessel look compromised (i.e. cap is not on, sides of the vessel are wet), then the sample is considered compromised and the sample must be re-digested.

- Add 1 ml of the Internal Standard working solution, using an Eppendorf automatic pipettor, and dilute to the 50 ml mark with DI Water into a calibrated digestion vessel (per lot).

- If the digested sample contains particulate matter, which has the potential to clog the nebulizer, the sample needs to be centrifuged, allowed to settle, or filtered.
  - Settling: allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this; however this can frequently be accomplished in a few hours. If it does not, centrifuge or filter the sample.
  - Centrifugation: centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.
  - Filtering: the filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 μm filter paper and transfer the liquid to a new vessel. Glass fiber filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

4. Calculations:

Dilution factor (DF:

$$DF = \frac{Final\ Volume\ (50)}{Sample\ amount}$$

Relative Percent Difference: $RPD = \frac{(S-D)}{\left[\frac{S+D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

% Difference (%D)
Used for serial dilution test in metals.

$$\%D = \left| \frac{X_1 - X_2}{X_1} \right| \times 100\%$$

where: %D = percent difference
X_1 = Initial concentration
X_2 = Duplicate concentration

- Record pertinent information onto the digestion log (Figure 2). The following information must be included: Date, start time, end time, analyst initials, method reference, sample IDs, sample weight or volume, MS/MSD/LCS spiking concentration and lot #, acid lot #, dilution factor, final volume and any pertinent remarks.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 and 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. A dilution test is performed once per every 20 samples. The dilution test is performed by taking 10 mls of a parent sample after digestion and adding 0.8 mls acid and 0.8 mls internal standard and bringing to a final volume of 50 mls with DI water. The dilution test is used to identify matrix interference and is not applicable if the measured concentration is less than 100 times the MDL for each measured analyte.

The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

Computer software and firmware can be found on Merit’s network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- ♦ Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.
- ♦ Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.
- ♦ The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

12.0 WASTE DISPOSAL

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Samples.

- ♦ All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory wastewater.
- ♦ As a “small generator” of metals, Merit Laboratories has been approved for this type of disposal from the local government.

Acid bottles.

- ♦ Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for metals a sample batch consists of 20 samples or less.

Method Blank (Laboratory Reagent Blank) (LRB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known 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 carried through the complete sample prep and analytical procedure. 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.

Matrix Spike (MS) (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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 (MSD) (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Dilution Test: a digested sample is diluted five-fold and analyzed to determine if matrix interference is present.

14.0 REFERENCES

Annual Book of ASTM Standards, Volume 11.01, “Standard Specification for Reagent Water”, 1995.

Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).

Gray, A.L., Spectrochim. Acta 40B, 1525 (1985); 41B, 151 (1986).

Hinners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).

Holden, N.E., "Table of the Isotopes," in Lide, D.R., Ed., CRC Handbook of Chemistry and Physics, 74th Ed., CRC press, Boca Raton, FL, 1993.

Horlick, G., et al., Spectrochim. Acta 40B, 1555 (1985).

Houk, R.S., Anal. Chem. 58, 97A (1986).

Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).

Microwave Digestion System CEM-Model MDS-81D Instrument Manual.

Microwave Digestion System MARSX-Model #907600 Instrument Manual.

Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986).

Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).

USEPA, SW-846, Revision 0, 1994, Method 6020

Method 200.8, Revision 5.4, 1998.

USEPA, SW-846, Revision 1, 2007, Method 6020A

USEPA, SW-846, Revision 3, 2003, Method 8000C

USEPA, SW-846, Revision 1, 2007, Method 3015A

Vaughan, M.A., and Horlick, G., Appl. Spectrosc. 40, 434 (1986).

TABLE 1 Quality Control Items, Frequency and Corrective Action

QA Items	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Laboratory Reagent Blank (Method Blank)	One per sample batch	<RL/dilution	Remove contamination and re-digest sample set
Laboratory Control Sample	One per sample batch	85%-115%	Re-digest the sample set
Matrix Spike	One per every 10 samples	75%-125%	Analyze by Method of Standard Additions (MSA)
Matrix Spike Duplicate	One per ever 10 samples	75%-125% RPD <20%	Analyze by Method of Standard Additions (MSA)
Matrix Duplicate	One per every 10 samples	RPD <20%	Re-digest the sample set and QC.
Dilution Test	One per sample batch	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.

TABLE 2 Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Linear Dynamic Range (LDR) or High-level Check Standard	At initial set-up and checked every 6 months with a high standard at the upper limit of the range.	Within ±10% of true value.	Dilute samples within the calibration range, or re-establish/verify the LDR.	Flagging is not appropriate.	Data cannot be reported above the calibration range without an established/passing high-level check standard.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial Calibration (ICAL) for All Analytes	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r2 ≥ 0.99.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes, within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of the true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

			necessary; then reanalyze all associated samples since the last acceptable CCV.		
Low-level Calibration Check Standard (LLCCV)	Daily.	All reported analytes within ± 20% of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid low-level calibration check standard (LLCCV). LLCCV should be less than or equal to the LOQ. If the concentration of the lowest calibration standard os less than or equal to the LOQ, the lowest standard may be re-quantified against the calibration curve as LLCCV. Otherwise, a separate standard must be analyzed as the LLCCV prior to the analysis of any samples.
Internal Standards (IS)	Every field sample, standard and QC sample.	IS intensity in the samples within 30-120% of intensity of the IS in the ICAL blank.	If recoveries are acceptable for QC samples, but not field samples, the field samples may be considered to suffer from a matrix effect. Reanalyze sample at 5- fold dilutions until criteria is met. For failed QC samples, correct problem, and rerun all associated failed field samples.	Flagging is not appropriate.	Samples suffering from matrix effect should be diluted until criteria are met, or an alternate IS should be selected.
Method Blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch	Results may not be reported without a valid method blank. Non-detects associated with positive blank infractions may be reported. Samples results > 10X the LOQ associated with negative blanks

					may be reported. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV.	The absolute values of all analytes must be < ½ LOQ or 1/10th the amount measured in any sample.	ICB: Correct problem and repeat ICV/ICB analysis. If that fails, rerun ICAL. All samples following the last acceptable Calibration Blank must be reanalyzed. CCBs may not be re-analyzed without re-analysis of the associated samples and CCV(s).	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. Non-detects associated with positive blank infractions may be reported. Sample results > 10X the LOQ associated with negative blanks may be reported. For CCB, failures due to carryover may not require an ICAL.
Interference Check Solutions (ICS) (also called Spectral Interference Checks)	After ICAL and prior to sample analysis.	ICS-A: Absolute value of concentration for all nonspiked project analytes <1/2 LOQ (unless they are a verified trace impurity from one of the spiked analytes) ICS-AB: Within ± 20% of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the failed ICS.	All analytes must be within the LDR. ICS-AB is not needed if instrument can read negative responses.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of

		analyte(s) are not listed, use in-house LCS limits if project limits are not specified.		the case narrative.	difference, i.e., matrix effect or analytical error.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Dilution Test	One per preparatory batch if MS or MSD fails.	Five-fold dilution must agree within ± 10% of the original measurement.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Only applicable for samples with concentrations > 50 X LOQ (prior to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post Digestion Spike (PDS) Addition	One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible).	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 6020 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	78	124
7440-36-0	Antimony	72	124
7440-38-2	Arsenic	82	118
7440-39-3	Barium	86	116
7440-41-7	Beryllium	80	120
7440-42-8	Boron	74	128
7440-43-9	Cadmium	84	116
7440-70-2	Calcium	86	118
7440-47-3	Chromium	83	119
7440-48-4	Cobalt	84	115
7440-50-8	Copper	84	119
7439-89-6	Iron	81	124
7439-92-1	Lead	84	118
7439-93-2	Lithium	75	120
7439-95-4	Magnesium	80	123
7439-96-5	Manganese	85	116
7439-97-6	Mercury	74	126
7439-98-7	Molybdenum	83	114
7440-02-0	Nickel	84	119
7440-09-7	Potassium	85	119
7782-49-2	Selenium	80	119
7440-22-4	Silver	83	118
7440-23-5	Sodium	79	125
7440-24-6	Strontium	75	129
7440-28-0	Thallium	83	118
7440-29-1	Thorium	81	116
7440-29-1	Tin	82	121
7440-32-6	Titanium	83	117
7440-61-1	Uranium	83	120
7440-62-2	Vanadium	82	116
7440-66-6	Zinc	82	119

Method 6020 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	84	117
7440-36-0	Antimony	85	117
7440-38-2	Arsenic	84	116
7440-39-3	Barium	86	114
7440-41-7	Beryllium	83	121
7440-42-8	Boron	73	130
7440-43-9	Cadmium	87	115
7440-70-2	Calcium	87	118
7440-47-3	Chromium	85	116
7440-48-4	Cobalt	86	115
7440-50-8	Copper	85	118
7439-89-6	Iron	87	118
7439-92-1	Lead	88	115
7439-93-2	Lithium	78	126
7439-95-4	Magnesium	83	118
7439-96-5	Manganese	87	115
7439-97-6	Mercury	70	124
7439-98-7	Molybdenum	83	115
7440-02-0	Nickel	85	117
7440-09-7	Potassium	87	115
7782-49-2	Selenium	80	120
7440-22-4	Silver	85	116
7440-23-5	Sodium	85	117
7440-24-6	Strontium	82	118
7440-28-0	Thallium	82	116
7440-29-1	Thorium	87	121
7440-29-1	Tin	86	115
7440-32-6	Titanium	83	115
7440-33-7	Tungsten	85	122
7440-61-1	Uranium	87	120
7440-62-2	Vanadium	86	115
7440-66-6	Zinc	83	119

FIGURE 1: STANDARD PREP LOG

Standard Preparation PE

Inorganic Stock Solution IV-28 (100 ppm) + CGSN1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	**Volume Working Stock Solution**	**Internal Standard 5.0 ppm**	**HNO_3**	**Final Volume**
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0002 ppm	0.20 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Standard Preparation HP

Inorganic Stock Solution IV-28(100 ppm) + CGSN1-1 (1000 ppm)

V. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

VI. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

VII. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

VIII. STANDARDS

Standards	**Volume Working Stock Solution**	**Internal Standard 2.5 ppm**	**HNO_3**	**Final Volume**
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

ICP/MS MINERALS PREP LOG

Date	IS ID	Exp. Date	Analyst

Standards **ppm**	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	Final Volume
0.0	**0.0**		**2 mls**	**2 mls**	**100 mls**
0.50	**0.5**		**2 mls**	**2 mls**	**100 mls**
1.0	**1.0**		**2 mls**	**2 mls**	**100 mls**
2.0	**2.0**		**2 mls**	**2 mls**	**100 mls**
5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**
10.0	**10.0**		**2 mls**	**2 mls**	**100 mls**
ICV – 5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**

FIGURE 2: METALS DIGESTION LOG

Metals Digestion 3015A \ 3050B

DATE __________________ PREP BATCH MTD-______________

TIME START ____________ TIME FINISH _______________ ANALYST ______________

Pipet Calibration:

Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria	Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria
2	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value	3	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value
	2					2			
	3					3			

SAMPLE#	**BTL ID**	**SAMPLE AMOUNT GRAMS (g)**	**FINAL VOLUME (ml)**	**REMARKS**	**% TOTAL SOLIDS**	**DILUTION FACTOR**
LCS -	----	50	**50**		—	1
LRB-	----	50	**50**		—	1

NOTES: *1) Spike values (unless otherwise stated):*

LCS = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

1.1. Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution
Spiking Solution – Date Prepared:____

2) Spike values for minerals (Ca-Mg-K-Na)
LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution
Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution
High Purity Stock Solution (HM)- Lot #__________________________________

3) HNO$_3$ Lot #_____________________ *4) Centrifuge Tube Lot #____*

5) Balance ID:________________ *Reviewed by ______________ On __________*

STANDARD OPERATING PROCEDURE

METALS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY METHODS 6020, 6020A, 200.8

APPROVALS:

Barbara Ball

10/01/2020

QA Officer Date

10/01/2020

Technical Director Date

Number	Description of Change	Date
001	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
002	Emergency SOP Amendment Form updates	02/09/16
003	Updated to comply with DoD QSM 5.0 standards.	03/10/16
004	Updated to comply with DoD QSM 5.1 standards.	01/15/18
005	Emergency SOP Amendment Form updates	02/13/19
006	DOD Audit Corrective Action	10/01/2020
007		
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable for the determination of sub-μg/L concentrations of a large number of elements in water samples and in waste extracts or digestions. When dissolved constituents are required, samples are filtered through 0.45 μm membrane filters and acid-preserved prior to analysis. No digestion is needed prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is performed for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are needed. Acid digestion is also needed prior to analysis to dissolve elements in water samples with turbidity >1 NTU. This SOP follows the guidelines of the EPA Methods 200.8, 6020, and 6020A. The metals that are determined by using this SOP are listed in Table 1 with associated reporting limits (RL) and quantitation limits (QL) and which methods can be used for each element.

If this SOP is followed to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method as well as method detection limit (MDL) and multi-point calibration. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality. Use of this SOP is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical and physical interferences in ICP-MS.

2.0 SUMMARY OF METHOD

Prior to analysis, samples which require total ("acid-leachable") values are digested using appropriate sample digestion procedures (Document #'s MET-003 and MET-001). This SOP describes the measurement of ions produced by radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios, and quantified with a channel electron multiplier. Potential interference from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundance. Interference corrections include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

3.0 INTERFERENCES

There are three fundamentally different sources of interference in ICP-MS: spectroscopic interferences, physical interferences, and memory interferences.

- **Spectroscopic Interferences** are interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass-to-charge (m/z ratio of the analyte elements). They can be isobaric elemental and isobaric molecular interferences (polyatomic, refractory oxide, and doubly charged ions).

  - Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the analyte element. These are managed by the selection of an alternate isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobaric interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca. In this case, the use of ^{43}Ca or ^{44}Ca is recommended. The appropriate elemental interference equations are incorporated in the methods (or parameter) used for calibration and data acquisition.

  - Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that affect ICP-MS determinations have been identified. Examples include ArCl$^+$ ions on the ^{75}As signal and MoO$^+$ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundance, the most precise coefficients for an instrument is determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics.

    - Example for As is as follows: Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic is calculated (approximately) as follows (where the ^{38}Ar^{37}Cl$^+$ contribution at m/z 75 is a negligible 0.06% of the ^{40}Ar^{35}Cl$^+$ signal): Corrected arsenic signal (using natural isotopes abundance for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

      NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than ^{82}Se$^+$ (e.g., ^{81}BrH$^+$ from bromine wastes[6]).

- Example for Cd is as follows: corrected cadmium signal (using natural isotopes abundance for coefficient approximations) = (m/z 114 signal) - (0.027) (m/z 118 signal) - (1.63) (m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values are biased low by this type of equation when $^{92}ZrO^+$ *ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct (*$^{94}ZrOH^+$*) and indirect (*$^{90}ZrO^+$*) additive interferences when Zr is present.*

NOTE: Since there is a certain degree of uncertainty as to which equation is better to use, and in what cases, it is up to the analyst to determine how the interference is corrected, upon the evaluation of data. It is suggested that the <u>elemental</u> isobaric interference equations be <u>included</u> in all methods (parameters) from the beginning, but potential <u>polyatomic</u> species (masses) that could interfere be <u>only monitored</u> (except for $^{40}Ar^{35}Cl^+$ *on As). When species monitored indicate that an isobaric molecular interference is present, the equations can be adjusted to correct for such interference and data be reprocessed to produce an interference free summary report. Generally, an interference is easy to spot when multiple isotopes of an element show different results. Since the interference is additive, the use of the isotope with the lowest result is suggested for data reporting, providing that all other QC criteria are met (See Table 6a & 6b for summary of QC requirements).*

- Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Wing overlap interference can occur when a small ion peak is being measured adjacent to a large one. The potential for these interferences must be recognized, and the spectrometer resolution adjusted to minimize them. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require matrix separation, or analysis using another verified and documented isotope.

- **Physical Interferences** are associated with the physical processes, which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences can result in differences between instrument responses for the samples and calibration standards. Physical interferences can 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 effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects). To minimize some of these effects, acid composition and concentration must be matched for all standards, blanks, and samples. Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. Internal standardization is effectively used to compensate for many physical interference effects. Internal standards must ideally display similar analytical behavior to the elements being determined. Generally, an internal standard must be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, ^{185}Re, and ^{209}Bi.

- **Memory Interferences** result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition can occur is dependent on the sample and needs to be minimized through the use of a rinse blank between samples. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run must be recognized and suitable rinse times must be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition. High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If memory interference is suspected, the sample must be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.

4.0 APPARATUS AND MATERIALS

Inductively coupled plasma-mass spectrometers:

- **Perkin Elmer (PE) Elan 9000 ICP-MS:**
  - Windows XP Operating System
  - Elan 3.0 Software
  - Cetac Asx510 Autosampler
- **Hewlett-Packard (HP) 4500 ICP-MS**:
  - Windows 95 Operating system.
  - Chem Station Software.

  - Cetac ASX150 Autosampler.

- **Agilent 7500Ce ICP MS:**
  - Windows XP Operating system.
  - Chem Station Software.
  - Agilent ASX 500 Series autosampler .

Argon gas supply: liquid argon cylinders

Analytical balance, 510 g capacity, minimum accuracy ± 0.001 g.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.

Note: dispensers are calibrated quarterly according to SOP #010010.

Disposable Pasteur pipettes.

Polypropylene vessels, 50 mL.

Plastic cups to support minimum of 200 ml.

Plastic bottles.

5.0 REAGENTS & STANDARDS

Nitric Acid (HNO_3), concentrated, Trace Metal Grade. Acids used in the preparation of standards and for sample processing must be of high purity. Trace metal grade (also known as re-distilled) acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at 2% (v/v) or less in the solution to be analyzed is required for ICP-MS, in order to minimize damage to the interface.

Hydrochloric Acid (HCl), concentrated, Trace Metal Grade. Several polyatomic ion interferences result when HCl is used. However, its use is recommended to maintain stability in solutions containing high concentrations of antimony and silver. When used, corrections for the chloride polyatomic ion interference must be applied to all data.

Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

Internal Standard stock solutions:

- Lithium 6, 1000 µg/ml stock solution.

- Scandium, 1000 µg/ml stock solution.
- Yttrium, 1000 µg/ml stock solution.
- Rhodium, 1000 µg/ml stock solution.
- Rhenium, 1000 µg/ml stock solution.
- Internal Standard Working Solution (IS-WS): From the above stock solution, 2.5 ml of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight), which corresponds to 2.5 µg/ml. This represents the internal standard working solution from which 1 ml (for a 50 ml final volume) must be added to all calibration standards and blanks. This provides a 0.05 ppm of internal standard concentration in all calibration standards, similar to analytical samples.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for blank page of standard preparation log book page.

Multi-element standard stock solution from three of four different vendors:

- Inorganic Venture (IV), 100 mg/L each of Ag, Al, B, Ba, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of standards.
- High Purity Standards (HM), 100 µg/ml each of Ca, Mg, K, and Na. This solution is used for the preparation of the calibration standards and for the minerals standard.
- SPEX Industries (S), 100 µg/ml each of Al, Sb, As, Ba, Be, B, Cd, Ca Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of the initial calibration verification (ICV) standards.
- Phenova, concentration varies by lot number and element but contains all of the following Al, Sb, As, Ba, Be, B Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Zn, V, Th, and S.

  Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for Standard Prep Log and Appendix 2 for ICV prep log.

Multi-element calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 2% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. The calibration standards are kept in plastic bottles and prepared every two weeks or more frequent if needed.

They must be verified using a quality control standard (ICV). Table 2 (metals) and Table 3 (minerals) are used as guidance, when preparing standards.

Blanks: Three types of blanks are required for the analysis. The calibration blank (std-0.00) is used in establishing the calibration curve. The Laboratory Reagent Blank (LRB) also known as method blank is used to monitor possible contamination resulting from the sample preparation procedure. The rinse blank (also called optional rinse or autosampler wash) is used to flush the system between all samples and standards.

- The calibration blank (std-0.00), the initial calibration blank (ICB), and the continuing calibration blank (CCB) consists of the same concentration(s) of the same acid(s) used to prepare the calibration standards, along with the appropriate concentration of internal standard. The preparation of these blanks can be found in the standards prep-log. The calibration blank is used in the calibration process, the ICB is used to check the instrument before analyzing samples, and the CCB is used to verify the instrument in the middle and end of analytical runs.

- The Laboratory Reagent Blank (LRB) also known as method blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

- The rinse blank consists of 2% HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between all standards, quality control samples, and analytical samples. Rinse blank is prepared by adding 20 ml of concentrated HNO_3 to 1000 ml of DI water in a large plastic container.

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interference such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

- Interference check stock solution A, containing 1000 μg/ml each of Al, Ca, Fe, Mg, Na, P, K, and S, 2000 μg/ml of C, 10000 μg/ml of Cl, and 20.0 μg/ml each of Mo and Ti. The ICS-A solution is prepared by weighing 10.0 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO_3, and dilution to 100 g on the scale with reagent water.

- Interference check stock solution AB, containing 2.0 µg/ml each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn. The ICS-AB solution is prepared by weighing 1.00 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO_3, and dilution to 100 g on the scale with reagent water.

- The final concentration of the elements in ICS-A and ICS-AB is listed in Table 4. These solutions are prepared fresh every 2 weeks or as needed.

The initial calibration verification solution (ICV) is used to verify the calibration before samples are analyzed. The ICV must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard (known as a second source) is defined as a standard from a source different from those used in the standards for instrument calibration.

Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Number 5, Section 7.0). This solution is also used to verify that the instrument has reached thermal stability (See See Number 4, Section 7.0).

- Tuning solution for HP 4500 ICP-MS: 10 µg/ml each of Li, Y, Ce, and Tl is used to tune the instrument according to the manufacturer instructions.

- Tuning solution for PE Elan 9000 and Agilent 7500Ce ICP-MS: 10µg/ml each of Li 7, Be 9, Mg 25, Co 59, In 115, Tl 205, and Pb 208.

Working standards and solutions are prepared every two weeks according to recipes in the standards prep log. The logbook is available in the metals lab. Concentrations of the LCS can be found on the laboratory bench sheet.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are collected in appropriate plastic or glass containers.

- Water samples are collected in HNO_3 pre-preserved plastic containers (approximately 125 ml volume), and are acidified to pH of <2.

- Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ±2 C° upon receipt.

Holding times for metals are 6 months from the date of sampling to analysis. For TCLP samples the holding time is 6 months from sampling to TCLP extraction then 6 months from TCLP extraction to analysis.

7.0 PROCEDURE

1. Solubilization and digestion procedures are presented in the Sample Preparation Document #'s (MET-003 and/or MET-001). A sample digestion log sheet is found in Figure 3.

2. Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.

3. Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

4. Operating conditions: The analyst must follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. The thermal stability must be verified by analyzing a tuning solution described in Section 5.0.

5. For all analysis tune instrument according to following parameters.

   - The tuning must include beryllium, magnesium, cobalt, indium, and lead. Conduct mass calibration and resolution checks in the mass regions of interest.

   - The mass calibration and resolution parameters are required criteria that must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value.

   - The resolution must be verified to be within 0.6-0.9 amu full width at 5 percent peak height (not applicable for HP4500 ICP-MS due to manufacturer presets).

   Note: A peak height of 5 percent is used instead of 10 percent because 5 percent is the tighter restriction and this SOP is written to meet the requirements of methods 200.8, 6020, and 6020A.

   - Perform tune after machine is warmed up and every 12 hours following.

   Note: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

6. The instrument is calibrated daily and re-calibrated as needed. Calibrate the instrument for the analytes of interest (recommended isotopes for the elements in Table 1 are provided in Table 5a and Table 5b), using the calibration blank and at least three non-zero calibration standards according to the instrument manufacturer's procedure. A multi-point calibration curve is analyzed and evaluated. For the calibration curve to be acceptable, a correlation coefficient of greater than or equal to 0.998 must be achieved. If the required correlation coefficient is not achieved then the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. If narrowing the linear range does not improve the correlation coefficient to 0.998, then replace the calibration standards and re-calibrate the instrument. The reporting limit (RL) must be greater than or equal to the lowest calibration point or the concentration of low level initial calibration verification (LLICV), whichever is lower.

The principle of calculation for the linear curve fit and the coefficient of determination (COD) is found in SW 846 method 8000C Sections 11.5.2.1 through 11.5.2.3. ICP-MS manufacturer software is preprogrammed for this calculation.

The multi point calibration is verified with a mid level ICV standard with control limits of 90%-110% and a low-level ICV with limits of 70%-130% (80%-120% for DoD projects). Table 2 and Table 3 (Section 5.0) provide information to what calibration standards are used. (More information on limits and corrective actions can be found in Section 8 and Table 6a & 6b). Flush the system with the rinse blank (Section 5.0) between each standard solution. The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

7. All masses that affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. Preferred isotopes are referenced in Tables 5a and 5b.

8. Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the initial calibration verification solution (ICV, Section 5.0) using a second source standard. When measurements exceed ± 10% of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. During the course of an analytical run, the instrument may require re-calibration to correct for instrument drift. A re-calibration must then be followed immediately by a new analysis of an ICV, LLICV, and initial calibration blank (ICB) before any further samples are analyzed. Corrective actions for specific situations are found in Section 8 and summarized in Table 6a & 6b.

9. A low-level initial calibration verification (LLICV) must be analyzed after every calibration to verify the linearity near the lower end of the calibration curve. The LLICV is made from the same source as the calibration standards at a concentration comparable to the reporting limits of elements being reported. When the LLICV measurements exceed ± 30% (± 20% for DoD projects) of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).

10. Flush the system with the rinse blank solution (Section 5.0) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (CCV), and the continuing calibration blank (CCB) at a frequency of at least once every 10 analytical samples (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).

11. Dilute and reanalyze samples that are more concentrated than the linear range (LR) (Section 8.0) for an analyte or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (Numbers 6 through 8, Section 7.0).

12. Interference Check Solutions (ICS) are run to verify the magnitude of elemental and molecular-ion isobaric interferences. This is performed every 12 hours. This is done by analyzing interference check solutions A and AB. (Concentration of elements in solution found in Table 4, other reagent information is in Section 5.0)

Corrective Action: The ICS needs to be within 70-135% (± 20%, of true value, for DoD projects). If the ICS fails, re-evaluate the equations used for the corrections, make the necessary adjustments, recalibrate the instrument and re-analyze the samples associated with the failed ICS. See Table 6a &6b for ICS summary and Section 8.0 for more information.

Note: Precipitation from solution AB can occur with some elements, specifically silver. Rinse the instrument 5 –10 minutes before analyzing any other samples to help improve performance.

13. Calculations: the quantitative values are reported in appropriate units, such as milligrams per liter (mg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples.

- ♦ The appropriate dilution factor (DF) on water samples resulted from sample preparation (see Document # MET-003) is entered in the data system for each sample at the time of programming the sequence to be analyzed. If additional dilutions are performed, the appropriate corrections must be applied to the dilution factor, using the following equation

C *x* DF = SC
Where, C = digest concentration
DF = Dilution Factor
SC = Sample Concentration

The ICP/MS software carries out this calculation for the analyst.

♦ Generally, for solid samples, DF includes the correction necessary for the determination of a dry weight result. If this is not the case or if a dry weight result is requested at a later time, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) A new DF is calculated, based on the original wet weight of the sample (from the preparation log) and the percent total solids. The sequence is updated with the new DF, data reprocessed, and a new quantitation report is generated by the data system.

(3) Manual calculation of the dry weight concentration (DWC) by the formula:

$$DWC(mg/kg) = \frac{CxV}{WxS}$$

Where, C = Digest Concentration (mg/L).
V = Final volume in liters after sample preparation.
W = Weight in kg of wet sample.
S = (% Total Solids)/100.

♦ Calculations performed by the data system include appropriate interference corrections, internal standard normalization, and the summation of signals (for example 206, 207 and 208 m/z for lead) to compensate for any differences in the abundances of these isotopes between samples and standards.

Note: The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

♦ Hardness by Calculation

The preferred method for calculating Hardness Standard Method 2340B. Hardness is calculated from the Calcium and Magnesium results from this procedure using the following equation:

CaCo3/L = 2.497 [Ca] + 4.118[Mg]
Where:
CaCO3 is the total hardness by calculation
Ca is the total Calcium by 6020A in mg/L
Mg is the total Magnesium by 6020A in mg/L

Relative Percent Difference: $RPD = \frac{(S-D)}{\left[\frac{S+D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR-SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

% Difference (%D)
Used for serial dilution test in metals.

$$\%D = \left|\frac{X_1 - X_2}{X_1}\right| \times 100\%$$

where: %D = percent difference
X_1 = Initial concentration
X_2 = Duplicate concentration

8.0 QUALITY CONTROL

All quality control data must be maintained and be available for easy reference or inspection.

Demonstration of Performance.

- The demonstration of performance is used to demonstrate instrument performance and has two parts. The first is initial demonstration of performance this is done by performing method detection limit (MDL) studies, linear range studies, and precision and accuracy studies prior to the analysis of samples. The second is continual demonstration of performance is done by annual MDLs and linear range studies. MDL studies are performed by following SOP #060004 (Determination of Method Detection Limit). Analyst performance is demonstrated by analysis of proficiency test and blind samples multiple times per year.

- Linear calibration ranges: Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range must be established by determining the signal responses from a minimum of five different concentration standards. Care must be taken to avoid potential damage to the detector during this process. The linear calibration range, which is used for the analysis of samples, must be judged by the analyst from the resulting data. The upper LR is defined as the maximum concentration for which the measured concentration is within ±10% of the true value. Determined sample analyte concentrations that are greater than the upper LR limit must be diluted and reanalyzed. The LR must be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined. See Section 7.6 for curve specific criteria.

To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If an interference source is present, and cannot be corrected, the sample elements impacted must be flagged. The ICS is used to verify the correction equations used by the instrument. Requirements are found in Section 8.0 and Table 4 and preparation information is in Section 5.0.

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard falls outside the control limits as compared with the first calibration standard (Calibration Blank or std-0.00), the following procedure is followed. Check for instrument drift, instrument drift is characterized by internal standards outside control limits for QC samples (Section 8.0), recalibrate instrument and reanalyze samples. If matrix interference is suspected, the sample must be diluted at least fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. (Summary of control limits and corrective actions can be found in Table 6a & 6b)

- The intensity levels of the internal standards for the ICV/ICB/LLICV, CCV/CCB, LCS/LRB must also be within the specified acceptance limits (refer to Section 8.0 for limits and Section 7.0, Numbers 6-12 for procedure information). If they are not within limits, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

Check the instrument calibration by analyzing appropriate quality control solutions as follows (Summarized in Table 6a & 6b):

- Initial Calibration must include a blank and minimum of three non-zero points. A correlation coefficient of 0.998 must be achieved. Section 7.0 for calibration procedure.

- Immediately after instrument calibration check instrument calibration by analyzing the ICV described in Section 5.0. ICV limits are 90%-110%. The ICB has to be less than the lower limit of quantitation for every target element. The lower limit of the calibration must be checked by analyzing the low-level initial calibration verification (LLICV) with acceptance limits of 70%-130% (± 20% for DoD projects). Summary of limits and corrective actions are found in Table 6a & 6b, the procedure for this is found in Section 7.0, Numbers 6 through 9.

- When running samples verify calibration at a frequency of every 10 analytical samples with the CCV standard with limits of 90-110% and the continuing calibration blank (CCB) with acceptance criteria of less than the lower limit of quantitation for every target element. These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. See Table 6a &6b for summary of acceptance criteria and corrective actions, the procedure for this information for this is found in Section 7.0, Number 10.

- Corrective action for out of compliance ICV, LLICV, and CCV, is to terminate the analysis, correct the problem, and recalibrate the instrument. Control limits and corrective actions are found in Section 8.0 and summarized in Table 6a & 6b.

Laboratory Reagent blank (LRB) also known as Method blank. Method blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate analytical process. The LRB has to be below the RL divided by the dilution factor for each target analyte. If the LRB does not contain target analytes at a level that interferes with the project specific requirements, then the LRB is acceptable. Control limits and corrective actions are summarized in Table 6a & 6b.

A Laboratory Control Sample (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS must be prepared and analyzed for each sample batch at a frequency of one LCS for a least every 20 samples or every 10 samples for drinking waters. The recovery limits for the LCS are 85-115% of the true value (stated in the preparation log). If the LCS is outside of the control limits the entire sample batch must be re-digested and re-analyzed. Control limits and corrective actions are summarized in Table 6a & 6b. (In method 200.8, the LCS is referred to as the Laboratory Fortified Blank, LFB).

Analyze one matrix spike (MS) sample for every 10 analytical water samples or every 20 analytical soil samples. For majority of the elements, the aqueous samples are spiked at levels similar to the LCS (0.05 ppm in the analysis solution). For solid samples, a concentration of 0.10 mg/kg is added pre-digestion. The acceptable limits for performance are summarized in Section 8.10 and Table 6a & 6b.

- Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery must be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} x100$$

where: R = percent recovery.
C_s = spiked sample concentration.
C = sample background concentration.
S = concentration equivalent of analyte added to fortify the sample.

Analyze one matrix duplicate (Dp) sample for every 10 water samples or every 20 soil samples. In some cases, a matrix spike duplicate (MSD) is used instead of the matrix duplicate, especially if the analytes in the sample are of low concentration. A control limit of 20% RPD must not be exceeded for analyte values greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user must be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed. Control limits and corrective actions are summarized in Table 6a & 6b.

The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{\left| D_1 - D_2 \right|}{\frac{D_1 + D_2}{2}} x100$$

where: RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate).

The Quality Control requirements and limits vary slightly, based upon the method referenced in the analytical report (i.e. 6020A vs. 200.8). For both methods, the calibration is verified by the analysis of ICV/ICB and CCV/CCB. Recalibration is required when either one falls outside the limits. The performance of the method is evaluated by the analysis of the LCS/LRB pair for every batch of 20 samples, and MS/MSD/Dp for every 10 water samples and 20 soil samples. The acceptable limits for performance are summarized in Table 6a & 6b and the procedures can be found in Section 7.0, Numbers 6-12.

- Requirements for all methods:
    - When the recovery for ICV/CCV falls outside ±10% terminate the analysis and recalibrate the instrument. The samples from the last CCV that was within limits are to be re-analyzed, after recalibration of the instrument.
    - The MS is represented by a spiked sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular spike fails to meet QC criteria. An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 75 to 125 percent of

the known value. The spike addition must be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample is spiked and re-analyzed according to Figure 1. The same recovery limits apply to the spiked dilution.

- The MSD is represented by a spiked duplicate sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular duplicate spike fails to meet QC criteria. The evaluation of the MSD is similar to the evaluation of the duplicate analysis described in Section 8.0.

- When the intensity of any internal standard in the sample to falls outside 70-125% of the intensity of that internal standard in the initial calibration standard (Calibration Blank or std-0.00), follow the procedure described in Section 8.0. The intensity levels of the internal standards for the ICV/LLICV/ICB and CCV/CCB must agree within ± 20 percent of the intensity level of the initial calibration standard (Calibration Blank or std-0.00). If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

- ♦ Method 6020/6020A specific requirements:
  - Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 x MDL), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected, and the results flagged. One dilution test must be included with every batch of twenty samples.

  - Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. This is done by analyzing the interference check solutions ICS-A and ICS-AB. The recovery of the elements of interest in ICS-AB (listed in Table 4 at a concentration of 0.02 ppm) must be between 70-135% (± 20% for DoD projects) (see Section 7.0, Number 12 for procedure information and Table 6a & 6b for a summary).

  - The LLICV is used to verify the linearity of the low end of the calibration curve. The LLICV must be analyzed after every new calibration with the measurements not exceeding ± 30% (± 20% for DoD projects) of the true value. If the LLICV is outside of these limits the run must be stopped and the instrument recalibrated and the new calibration verified (see Section 7.0, Number 9 for procedure information and Table 6a & 6b for a summary).

The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method. In an EPA multi-laboratory study, laboratories applied the ICP-MS technique to both aqueous and solid samples. The results are listed at the end of methods 200.8, 6020 and 6020A.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

Computer software and firmware can be found on Merit's network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

- Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

12.0 WASTE DISPOSAL

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Samples.

- All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory wastewater.

- As a "small generator" of metals, Merit Laboratories has been approved for this type of disposal from the local government.

Acid bottles.

- Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: also referred to as a Laboratory Reagent Blank. an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

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. 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.

Matrix Spike (spiked sample or fortified sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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 second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

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 method.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. An acceptable MDL standard check must produce a signal at least three times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Calibration Standards: a series of known standard solutions used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. A minimum of 4 calibration points are used for calibration. Acceptance of the calibration requires a correlation coefficient of 0.997 or better. No samples shall be analyzed without acceptable calibration.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

Initial calibration blank (ICB): a reagent blank solution, which is analyzed immediately following the ICV. The ICB is analyzed to check for drifts in calibration or possible analyte carry-over.

Continuing Calibration Blank (CCB): a reagent blank solution, which is analyzed immediately following the CCV. The CCB is analyzed to check for drifts in calibration or possible analyte carry-over.

14.0 REFERENCES

Method 200.8, Revision 5.4, 1998.

SW-846, Method 6020A Revision 1, 2007.

SW-846, Method 8000C Revision 3, 2003.

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Table 1. List of elements analyzed.

Element	**Symbol**	**CAS#**	**Reporting Limits**		**Method Reference**			DoD Reportable	Quantitaion limit * ug/L	Laboratory performance based
			mg/L	**mg/kg**	**6020**	**200.8**	**6020A**			
Aluminum	Al	7429-90-5	0.05	0.5	X	X	X	X	0.5	
Antimony	Sb	7440-36-0	0.002	0.3	X	X	X	X	2.0	
Arsenic	As	7440-38-2	0.001	0.1	X	X	X	X	0.5	
Barium	Ba	7440-39-3	0.01	1.0	X	X	X	X	0.5	
Beryllium	Be	7440-39-3	0.001	0.50	X	X	X	X	0.5	
Boron	B	7440-42-8	0.01	1.0						X
Cadmium	Cd	7440-43-9	0.0005	0.2	X	X	X	X	0.5	
Calcium	Ca	7440-70-2	0.05	10.0	X		X	X	200	
Chromium	Cr	7440-47-3	0.005	2.0	X	X	X	X	0.5	
Cobalt	Co	7440-48-4	0.01	0.5	X	X	X	X	0.5	
Copper	Cu	7440-50-8	0.004	1.0	X	X	X	X	0.5	
Iron	Fe	7439-89-6	0.1	1.0	X		X	X	2.0	
Lead	Pb	7439-92-1	0.003	1.0	X	X	X	X	0.5	
Lithium	Li	7439-93-2	0.01	1.0						X
Magnesium	Mg	7439-95-4	1.0	4.0	X		X	X	200	
Manganese	Mn	7439-96-5	0.02	1.0	X	X	X	X	2.0	
Molybdenum	Mo	7439-98-7	0.005	0.50		X		X	2.0	
Nickel	Ni	7440-02-0	0.005	1.0	X	X	X	X	0.5	
Potassium	K	7440-09-7	1.0	5.0	X		X	X	200	
Selenium	Se	7782-49-2	0.005	0.2	X	X	X	X	0.5	
Silver	Ag	7440-22-4	0.0002	0.1	X	X	X	X	0.5	
Sodium	Na	7440-23-5	0.05	10.0	X		X	X	200	
Strontium	Sr	7440-24-6	0.005	0.50					1.0	X
Tin	Sn	7440-31-5	0.02	1.0						X
Titanium	Ti	7440-32-6	0.005	1.0					0.5	X
Thallium	Tl	7440-28-0	0.001	0.50	X	X	X	X	0.5	
Vanadium	V	7440-62-2	0.004	1.0	X	X	X	X	0.5	
Zinc	Zn	7440-66-6	0.01	1.0	X	X	X	X	2.0	

* Quantitation limit for individual samples is affected by sample dilutions

Table 2.

Standard Preparation PE

Inorganic Stock Solution IV-28 (100 ppm) + CGSN1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	**Volume Working Stock Solution**	**Internal Standard 5.0 ppm**	**HNO_3**	**Final Volume**
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0002 ppm	0.20 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Standard Preparation HP

Inorganic Stock Solution IV-28(100 ppm) + CGSN1-1 (1000 ppm)

V. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

VI. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

VII. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

VIII. STANDARDS

Standards	**Volume Working Stock Solution**	**Internal Standard 2.5 ppm**	**HNO_3**	**Final Volume**
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Table 3. Standard preparation for Ca, Mg, K, Na (minerals).

Standards ppm	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	**Final Volume**
0.0	0.0	High Purity (HM) –	2 mls	2 mls	100 mls
0.20	0.2	High Purity (HM) –	2 ml	2 ml	100 ml
0.50	0.5	High Purity (HM) -	2 ml	2 ml	100 ml
1.0	1.0	High Purity (HM) -	2 ml	2 ml	100 ml
2.0	2.0	High Purity (HM) -	2 ml	2 ml	100 ml
5.0	5.0	High Purity (HM) -	2 ml	2 ml	100 ml
10.0	10.0	High Purity (HM) -	2 ml	2 ml	100 ml
ICV- 5.0	5.0	Spex –	2 ml	2 ml	100 ml

Table 4. ICS Components and Concentration.

Solution Component	**ICS-A (ppm)**	**ICS-AB (ppm)**
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.020
Cd	0.0	0.020
Cr	0.0	0.020
Co	0.0	0.020
Cu	0.0	0.020
Mn	0.0	0.020
Ni	0.0	0.020
Ag	0.0	0.020
Zn	0.0	0.020

Table 5a. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
19	K	Sc, Rh		
23	Na	Sc, Rh		
24	Mg	Sc, Rh		
43	Ca	Sc, Rh		
44	Ca	Sc, Rh	(-0.0271)(^{88}C)	Sr^{++}

Notes:
- † Recommended for PE instrument.
- ‡ Recommended for HP instrument.
- C = Counts at specified mass.
- When the concentration of Na in the samples is high, the ionization of Sc is suppressed leading to positive bias of the results, therefore Rh must be used as the internal standard, even if more than 50 amu removed from the element of interest.

Table 5b. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
6	Li	**I.S.**	-(0.0813)(^{7}C)	
7	Li	^{6}Li, Sc		
9	Be	^{6}Li, Sc		
10	B	^{6}Li, Sc		
11	B	^{6}Li, Sc		
27	Al	^{6}Li, Sc		
45	Sc	**I.S.**		CO_2H^+
47	Ti	^{6}Li, Sc		
49	Ti	^{6}Li, Sc		
51	V	^{6}Li, Sc	-(3.127)(^{53}C)+(0.352)(^{52}C)	$^{35}ClO^+$, $^{34}SOH^+$
52†	Cr	Sc, Y, Rh		ArC^+, ArO^+, $^{35}ClHO^+$
53‡	Cr	Sc, Y, Rh		$^{37}ClHO^+$
54†	Fe	Sc, Y, Rh	-(0.0284)(^{52}C)	
55	Mn	Sc, Y, Rh		$ArNH^+$
56	Fe	Sc, Y, Rh		
57‡	Fe	Sc, Y, Rh		
58†	Ni	Sc, Y, Rh		
59	Co	Sc, Y, Rh		
60	Ni	Sc, Y, Rh		
62	Ni	Sc, Y, Rh		TiO
63†	Cu	Sc, Y, Rh		$^{31}PO_2^+$, $^{40}ArNa^+$, TiO
65‡	Cu	Sc, Y, Rh		TiO
66	Zn	Sc, Y, Rh		TiO
68	Zn	Sc, Y, Rh		
75	As	Y, Rh	-(3.132)(^{77}C)+(2.736)(^{83}C)	$^{40}Ar^{35}Cl^+$
76	$^{40}Ar^{36}Ar^+$	Y, Rh		$^{40}Ar^{37}Cl^+$
77	Se	Y, Rh		
78†	Se	Y, Rh	-(0.1869)(^{76}C)‡	$^{40}Ar^{38}Ar^+$
82‡	Se	Y, Rh		$^{81}BrH^+$
83	Kr	Y, Rh		
88	Sr	Y, Rh		
89	Y	**I.S.**		
90	Zr	Y, Rh		
95	Mo	Y, Rh		$^{79}BrO^+$
98	Mo	Y, Rh	-(0.146)(^{99}C)	$^{79}BrHO^+$
99	Ru	Y, Rh		
103	Rh	**I.S.**		
105	Pd	Rh		
106	Pd, Cd	Rh		ZrO,
107	Ag	Rh		ZrO
108	MoO	Rh		ZrO, MoO
109	Ag	Rh		ZrO, MoO
111	Cd	Rh		ZrO, MoO
112	Cd	Rh	-(0.040)(^{118}C)	ZrO, MoO
114	Cd	Rh	-(0.0269)(^{118}C)	MoO
118	Sn	Rh		
119	Sn	Rh		
120	Sn	Rh	-(0.0127)(^{125}C)	
121	Sb	Rh	-(0.124)(^{125}C)	$^{40}Ar^{81}Br^+$
123	Sb	Rh		
125	Te	Rh		
137	Ba	Rh		
138	Ba	Rh	-(8.91E-04)(^{139}C)-(2.82E-04)(^{140}C)	
139	La	Rh		
140	Ce	Rh		
185	Re	**I.S.**		
203	Tl	Re		
205	Tl	Re		
206	Pb	Re		
207	Pb	Re		
208	Pb	Re	+(1.0)(^{206}C)+(1.0)($^{2.07}$C)	

Notes:
- † Recommended for the PE instrument.
- ‡ Recommended for the HP instrument.

Table 6a. Summary of Quality Control Items, Frequency, and Corrective Action.*

QC Item	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Tuning	After warm-up Every 12 hours	Manufacturer specifications	Check operating parameters, clean cones, replace malfunctioning components if necessary. Reevaluate the tuning.
Calibration Curve	Once a day and as necessary	R ≥ 0.998 The lowest non-zero calibration point must be at or below reporting limit	Remove allowed points keeping minimum of 3 non-zero points, replace calibration standards if needed and recalibrate instrument.
ICV	After every calibration	90-110%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, and recalibrate the instrument.
ICB	After every ICV	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank and/or increase the rinse time between analyses; reanalyze ICB; if within limits, continue the run; if still outside limits, determine the source of the problem, make the necessary corrections, and start from the beginning with a new calibration.
LLICV	After initial calibration	70-130% Not required for 200.8	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, prepare a fresh calibration blank, and recalibrate the instrument.
CCV	After Every 10 sample or less	90-110%	Recalibrate the instrument. Follow method specific requirements (6020, 6020A or 200.8) as to what data prior to the CCV can be used.
CCB	After Every 10 sample or less	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank; reanalyze CCB; if within limits, continue the run; if still outside limits, eliminate the source of the contamination, clean the sample introduction system if necessary, and recalibrate the instrument. Reanalyze all samples from the last good CCB.
LCS	Every batch of 20 samples or less	85-115%	Re-digest the entire sample batch and reanalyze.
LRB (MB)	Every batch of 20 samples or less	<RL/Dilution factor	Re-digest the entire sample batch and reanalyze.
Dp	Every 10 water samples or every 20 soil samples	0-20%	If all other QC acceptable continue the run; sample result must be flagged; otherwise recalibrate instrument and reanalyze samples.
MS	Every 10 water samples or every 20 soil samples, prior to digestion	75-125%	The sample is spiked and re-analyzed according to Figure 1. .
MSD†	Every 10 water samples or every 20 soil samples, prior to digestion	0-20%	Same as for duplicate.
Dil‡	Once with every batch of 20 samples or less	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.
ICS-A‡	Every 12 hours	<RL for water samples Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
ICS-AB‡	Every 12 hours	70-135% Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
IS Samples	With every sample	70-125%	Verify matrix interference by ruling out instrument drift by unacceptable IS recoveries in standards. Dilute 4+1 and reanalyze. Repeat until inside control limits.
IS QC Samples	With every QC Sample	80-120% for ICV/ICB and CCV/CCB	For CCV/CCB's recalibrate the instrument and reanalyze the affected samples.

NOTE:

- *This is a summery table for more information see Sections 8.4 to 8.10
- RL = Reporting Limit.
- Dil = Dilution Test.
- † MSD optional instead of duplicate sample.
- ‡ When Method 6020 & 6020A referenced in the analytical report.
- IS = Internal Standard

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Linear Dynamic Range (LDR) or High-level Check Standard	At initial set-up and checked every 6 months with a high standard at the upper limit of the range.	Within ±10% of true value.	Dilute samples within the calibration range, or re-establish/verify the LDR.	Flagging is not appropriate.	Data cannot be reported above the calibration range without an established/passing high-level check standard.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial Calibration (ICAL) for All Analytes	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r2 ≥ 0.99.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes, within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of the true value.	Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, 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.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Low-level Calibration Check Standard (Low Level ICV)	Daily.	All reported analytes within ± 20% of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the LOQ.
Internal Standards (IS)	Every field sample, standard and QC sample.	IS intensity in the samples within 30-120% of intensity of the IS in the ICAL blank.	If recoveries are acceptable for QC samples, but not field samples, the field samples may be considered to suffer from a matrix effect. Reanalyze sample at 5- fold dilutions until criteria is met. For failed QC samples, correct problem, and rerun all associated failed field samples.	Flagging is not appropriate.	Samples suffering from matrix effect should be diluted until criteria are met, or an alternate IS should be selected.
Method Blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Before beginning a sample run, after every 10 field samples, and at end of the analysis sequence.	No analytes detected > LOD.	Correct problem and repeat ICAL. All samples following the last acceptable calibration blank must be reanalyzed.	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. For CCB, failures due to carryover may not require an ICAL.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Interference Check Solutions (ICS) (also called Spectral Interference Checks)	After ICAL and prior to sample analysis.	ICS-A: Absolute value of concentration for all nonspiked project analytes < LOD (unless they are a verified trace impurity from one of the spiked analytes); ICS-AB: Within ± 20% of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the failed ICS.	All analytes must be within the LDR. ICS-AB is not needed if instrument can read negative responses.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
		sample and MD).			
Dilution Test	One per preparatory batch if MS or MSD fails.	Five-fold dilution must agree within ± 10% of the original measurement.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Only applicable for samples with concentrations > 50 X LOQ (prior to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post Digestion Spike (PDS) Addition	One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible).	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 6020 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	78	124
7440-36-0	Antimony	72	124
7440-38-2	Arsenic	82	118
7440-39-3	Barium	86	116
7440-41-7	Beryllium	80	120
7440-42-8	Boron	74	128
7440-43-9	Cadmium	84	116
7440-70-2	Calcium	86	118
7440-47-3	Chromium	83	119
7440-48-4	Cobalt	84	115
7440-50-8	Copper	84	119
7439-89-6	Iron	81	124
7439-92-1	Lead	84	118
7439-93-2	Lithium	75	120
7439-95-4	Magnesium	80	123
7439-96-5	Manganese	85	116
7439-97-6	Mercury	74	126
7439-98-7	Molybdenum	83	114
7440-02-0	Nickel	84	119
7440-09-7	Potassium	85	119
7782-49-2	Selenium	80	119
7440-22-4	Silver	83	118
7440-23-5	Sodium	79	125
7440-24-6	Strontium	75	129
7440-28-0	Thallium	83	118
7440-29-1	Thorium	81	116
7440-29-1	Tin	82	121
7440-32-6	Titanium	83	117
7440-61-1	Uranium	83	120

7440-62-2	Vanadium	82	116
7440-66-6	Zinc	82	119

Method 6020 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	84	117
7440-36-0	Antimony	85	117
7440-38-2	Arsenic	84	116
7440-39-3	Barium	86	114
7440-41-7	Beryllium	83	121
7440-42-8	Boron	73	130
7440-43-9	Cadmium	87	115
7440-70-2	Calcium	87	118
7440-47-3	Chromium	85	116
7440-48-4	Cobalt	86	115
7440-50-8	Copper	85	118
7439-89-6	Iron	87	118
7439-92-1	Lead	88	115
7439-93-2	Lithium	78	126
7439-95-4	Magnesium	83	118
7439-96-5	Manganese	87	115
7439-97-6	Mercury	70	124
7439-98-7	Molybdenum	83	115
7440-02-0	Nickel	85	117
7440-09-7	Potassium	87	115
7782-49-2	Selenium	80	120
7440-22-4	Silver	85	116
7440-23-5	Sodium	85	117
7440-24-6	Strontium	82	118
7440-28-0	Thallium	82	116
7440-29-1	Thorium	87	121

7440-29-1	Tin	86	115
7440-32-6	Titanium	83	115
7440-33-7	Tungsten	85	122
7440-61-1	Uranium	87	120
7440-62-2	Vanadium	86	115
7440-66-6	Zinc	83	119

FIGURE 1.
ICP/MS STANDARDS PREP LOG

DATE	Standards	IS id	Exp. Date	Analyst

Source:____

Lot #: ____________________________

Exp. Date: __________________

FIGURE 2
ICP/MS INITIAL CALIBRATION VERIFICATION (ICV) PREP LOG

DATE	**ICV ID**	**IS id**	**EXP. DATE**	**Analyst**

Source ID	**Lot#**	**Expiration Date**
S = SPEX	______________________	_______________
H = High Purity	______________________	_______________
E = ERA	______________________	_______________

FIGURE 2: METALS DIGESTION LOG

Metals Digestion 3015A \ 3050B

DATE __________________ PREP BATCH MTD-______________

TIME START ____________ TIME FINISH _______________ ANALYST ______________

Pipet Calibration:

Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria	Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria
2	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value	3	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value
	2					2			
	3					3			

SAMPLE#	BTL ID	SAMPLE AMOUNT GRAMS (g)	FINAL VOLUME (ml)	REMARKS	% TOTAL SOLIDS	DILUTION FACTOR
LCS -	----	50	**50**		—	1
LRB-	----	50	**50**		—	1

NOTES: *1) Spike values (unless otherwise stated):*

LCS = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

14.1. Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

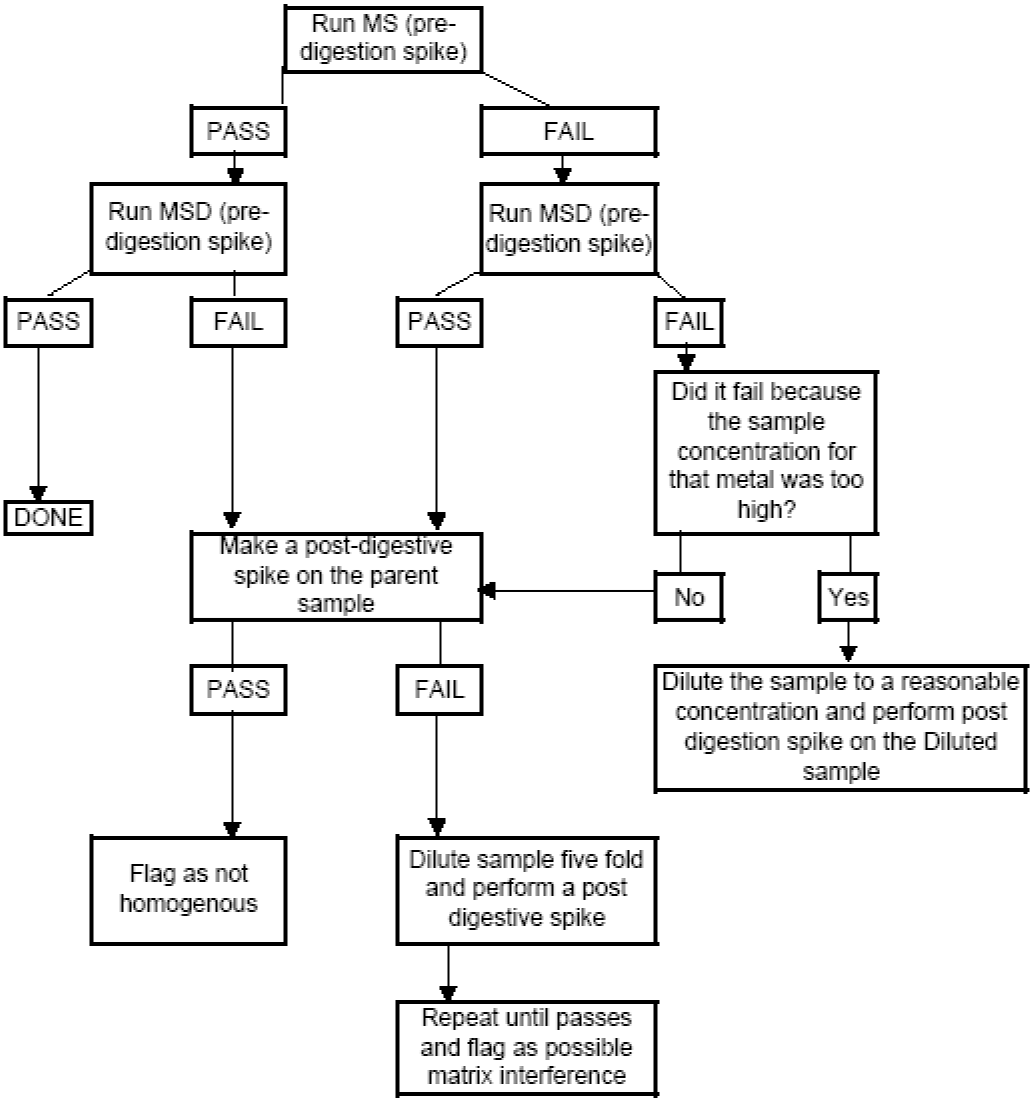
Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution
Spiking Solution – Date Prepared:____

2) Spike values for minerals (Ca-Mg-K-Na)
LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution
Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution
High Purity Stock Solution (HM)- Lot #__________________________________

3) HNO$_3$ Lot #_____________________ *4) Centrifuge Tube Lot #____*

5) Balance ID:________________ *Reviewed by ______________ On __________*

FIGURE 4 MS/MSD CORRECTIVE ACTION FLOW CHART



STANDARD OPERATING PROCEDURE

PURGE AND TRAP FOR AQUEOUS AND HIGH AND LOW CONCENTRATION SOIL SAMPLES
METHOD 5030C/5035A

APPROVALS:

Barbara Ball
09/29/2020

QA Officer Date

Maya Murshak
09/29/2020

Technical Director Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
007	Updated SOP for Method 5035A high and low level soil prep	6/14/12
008	Updated SOP for Method 5030C	9/03/13
009	Updated to comply with DoD QSM 5.0 standards.	04/01/16
010	Updated to comply with DoD QSM 5.1 standards.	01/16/18
011	DOD Audit Corrective Action	09/29/2020
012		
013		
014		
015		
016		

1.0 SCOPE AND APPLICATION

This SOP describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of low and high concentration soil and waste sample extracts prepared in Method 5035A. The method is applicable to Gas Chromotography/Mass Spectrometry (GC/MS) Method 8260B. Method 5030C can be used for 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, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process. This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF METHOD

Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample 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 adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. High Concentration Extracts from Method 5035A: An aliquot of the extract prepared in Method 5035A is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS. Low Concentration Soils: An aliquot of the soil is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and–trap GC or GC/MS. Air samples in Tedlar Bags: A volume of air is extracted from the Tedlar Bag using a gas tight syringe and is introduced to a vial of reagent water. An inert gas is bubbled through a portion of the aqueous sample at ambient temperature. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

3.0 INTERFERENCES

Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealant, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it must be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

The laboratory where volatiles analysis is performed must be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas must be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing must be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, and 500-µL.

Gas tight 5ml syringes.

Vials – 40-mL, for GC autosampler (Archon).

Magnetic stir bars.

Scale capable of displaying weight to the nearest hundredth of a gram.

Purge-and-trap device. The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber.

- The Vocarb3000 trap by Supelco is used. It is preconditioned at 270°C for 60 minutes upon installment as suggested by supplier.

Gas Chromatograph.

Mass Spectrometer.

pH paper.

5.0 REAGENTS

Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

Purge and Trap grade methanol.

Sodium Bisulfate.

See SOP ORL-007 for specifications on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous Samples

- Samples must be stored in capped bottles, with minimum headspace, at (4 ± 2)°C in an area free of solvent fumes.

- All samples must be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values. The pH of the samples is checked with pH strips after the sample has been prepared for the autosampler. If the pH is greater than 2 as determined by the pH strip the fact is noted. If the sample with pH > 2 is not analyzed within seven days of the collection date then it is noted on the report that the sample was not properly preserved. The pH is recorded on the volatile sample prep log (Figure 1).

Soil Samples

- High concentration soil samples collected and preserved in the field.
    - The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment.

    - Add 10 mL of methanol to each vial. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label.

  - (10 ± 0.5)g of sample are weighed out and added to the vial in the field.
  - Upon arrival to the lab, samples are stored at (4 ±2)°C.

- High concentration soil samples collected without a preservative.
  - When high concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.
    - The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way must be preserved in methanol within 48 hours of the sampling time. This preservation is documented in the High Level Extraction Sheet (Figure 3).
  - Weigh out (10 ±0.5)g of soil sample into a 40-mL vial and add 10-mL of Methanol.
  - Sonicate for twenty minutes.
  - Sample extracts are transferred to 4 ml vials and stored at (4 ± 2)°C.
  - Frozen samples are not acceptable for all OHIO VAP samples.
- Low concentration soil samples collected and preserved in the field.
  - The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be preserved in the field with sodium bisulfate and reagent water and analyzed by the aqueous purge-and-trap equipment described in this SOP. Note: The sampling and preservation techniques required for low concentration analysis vary widely by state and regulating agency. The end-use of the data must be considered before selecting a sampling and preservation technique and may include procedures not in this SOP.
  - Add 5 mL of reagent water and a magnetic stir bar to each vial as well as 0.2g of sodium bisulfate for every 1g of sample to be collected. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label, and Low Level Extraction Log (Figure 2).
  - (1-5 ± 0.5)g of sample are weighed out and added to the vial in the field.
  - Upon arrival to the lab, samples are stored at (4 ±2)°C.
- Low concentration soil samples collected without a preservative.

- When low concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler or an empty 40 ml vial is employed.
  - The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way must be preserved with sodium bisulfate within 48 hours of the sampling time. This preservation is documented in the Low Level Extraction Log (Figure 2).
- Weigh out (1-5 ±0.5)g of soil sample into a 40-mL vial and add 5ml of reagent water and 0.2g of sodium bisulfate for every 1g of sample. Alternatively, weigh out (1-5 ±0.5)g of soil sample into a 40-mL vial and freeze (-7°C) for up to 14 days.
- The preserved samples are stored at (4 ± 2)°C.
- Bulk sample collection using USEPA Method 5030C can be used for approved sites/QAPPs.

7.0 PROCEDURE

1. The purge-and-trap technique for aqueous samples is found in Number 2 and method for analysis of solvent extracts from the High Concentration Method in Method 5035A is found in Number 3. The gas chromatographic determinative steps are found in SOP ORL-007. The method is also applicable to the analysis of gasoline, using SOP ORL-010.

2. This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

   - Initial calibration. Calibrate system in accordance with Method 8260B.
   - If necessary or for project specific purposes, screen samples prior to purge-and-trap analysis to provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system. Screen the sample by GC/MS.
   - Sample introduction and purging.
     - Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in method SOP ORL-007 and SOP ORL-010.
     - A daily check standard containing surrogates, internal standards and 20ug/l bromoform must be analyzed prior to the analysis of the daily check standard. If levels of chloromethane or bromomethane exceed 0.5ug/l, then the trap may be too

contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced and the system recalibrated. This can be achieved in the same run as the BFB.

- GC or GC/MS calibration verification criteria must be met (SOP ORL-007 and SOP ORL-010) before analyzing samples.
- Adjust the purge gas flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.
- Use autosampler to take a 5-mL aliquot of the sample. Care must be taken to remove any bubbles from the syringe. This process of taking an aliquot destroys the validity of the liquid sample for future analysis. Re-analysis must be done with duplicate VOA.
- The autosampler adds 1.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in SOP ORL-007 and SOP ORL-010.
- Inject the aliquot into a sparge tube.
- Purge for 11.0 minutes at room temperature in the sparge tube.

- ♦ Sample desorption.
  - Non-cryogenic interface - After the recommended purge (see above), place the purge-and-trap system in the desorb mode and preheat the trap to 190 °C without a flow of carrier gas passing through the trap. Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition.
- ♦ Trap Reconditioning.
  - After desorbing the sample, recondition the trap by baking it at 210 °C for 3 minutes.

3. This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035A.

- ♦ The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007 and SOP ORL-010).

- ♦ Take 5mL's of organic-free reagent water and add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in SOP ORL-007 and SOP ORL-010.
- ♦ Measure out a 100µL aliquot of the methanol phase of the sample.
- ♦ Quickly inject the 5-mL reagent water with standard mixture and 100µL of sample into a 40-mL vial and place cap with septum on it and tighten.
- ♦ Purge for 11.0 minutes at room temperature in the 40ml vial.
- ♦ Desorb the sample and recondition the trap.

4. This section provides guidance on the analysis of Low Concentration Samples prepared by Method 5035.

- ♦ The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007 and SOP ORL-010).
- ♦ Internal standards, surrogates and matrix spikes (if applicable) must be added automatically by the autosampler or manually by puncturing the septum using a small gauge needle.
- ♦ Prior to purging the sample is preheated to 40°C for 1.5 minute while being agitated by the magnetic stir bar.
- ♦ Purge for 11.0 minutes at 40°C while being agitated by the magnetic stir bar in the 40ml vial.
- ♦ Desorb the sample and recondition the trap.

5. Tedlar Bag Air Analysis

- ♦ The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007 and SOP ORL-010).
- ♦ To a 40 ml VOA bottle add 5 ml reagent water and add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in SOP ORL-007 and SOP ORL-010.
- ♦ Take a gas tight syringe with a needle fixed to the tip. Draw in a small volume of DI water into the syringe. This will provide a bubbling effect to show air is being drawn in from the bag.

- ♦ Insert the needle of the syringe through the septa of the Tedlar Bag and with draw 5 cc into the syringe.
- ♦ Bubble into 40 ml VOA bottle with 5 ml of DI water and surrogates and internal standards then cap promptly.
- ♦ Purge for 11.0 minutes at room temperature in the 40ml vial.
- ♦ Desorb the sample and recondition the trap.

6. Sample analysis. The samples prepared by this method will be analyzed according to SOP ORL-007 and SOP ORL-010.

8.0 QUALITY CONTROL

Refer to method SOP ORL-007 and SOP ORL-010 for specific quality control procedures. Quality control items employed and evaluated are provided in Table 1 and Table 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

Computer software and firmware can be found on Merit’s network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing Volatile analyses. Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- ♦ Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

- ♦ Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit’s Waste Management Plan and Handbook.

13.0 DEFINITIONS

An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run. Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

Method Blank (MB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known 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. 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.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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 (also known as Spiked Sample or Fortified Sample Duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

14.0 REFERENCES

Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

USEPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

USEPA, SW-846, 1996, REVISION 0; METHOD 5000.

USEPA, SW-846, 1996, REVISION 2; METHOD 5030B.

USEPA, SW-846, 2003, REVISION 3; METHOD 5030C.

USEPA, SW-846, 2002, REVISION 1; METHOD 5035A.

USEPA, SW-846, 1996, REVISION 2; METHOD 8000B.

USEPA, SW-846, 1996, REVISION 2; METHOD 8260B.
USEPA, SW-846, 2006, REVISION 3; METHOD 8260C.

Table 1 Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
BFB	12-hour	Method-based	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	Method-based	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Lab-based	A failed LCS must be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS must be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	n/a	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) must result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard	All samples	Method-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate
Surrogate Standard	All samples	Lab-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample must be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Tune Check	Prior to ICAL and prior To each 12-hour period of sample analysis	Specific ion abundance criteria of BFB or DFTPP from method.	Retune instrument and verify.	Flagging criteria is not appropriate.	No samples shall be analyzed without a valid tune.
Performance Check (Method 8270 only)	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation ≤ 20% for DDT. Benzidine and pentachlorophenol shall be present at their normal responses and shall not exceed a tailing factor of 2.	Correct problem, then repeat performance checks.	Flagging is not appropriate.	No sample shall be analyzed until performance check is within criteria. The DDT breakdown and Benzidine/Pentachlorophenol tailing factors are considered overall system checks to evaluate injector port inertness and column performance and are required regardless of the reported analyte list.
Initial calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	Each analyte must meet one of the three options below: Option 1. RSD for each analyte ≤ 15%;. Option 2: linear least squares regression $r^2 \geq 0.99$; Option 3:non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging criteria is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. No samples shall be analyzed until ICAL has passed. If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements must also be met.
Retention time window position establishment and surrogate	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and surrogate.
Evaluation of relative retention times (RRT)	With each sample.	RRT of each reported analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	After maintenance is performed which may affect retention times, RRTs may be updated based on the daily CCV. RRTs shall be compared with the most recently updated RRTs.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within ± 20% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within ± 20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	NA
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	MSD: Must contain all surrogates and all analytes to be reported. The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed..	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present,	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative..		

DoD Appendix C LCS Limits
Method 8260 Solid Matrix

CAS ID	Analyte	Lower Control Limit (LCL)	Upper Control Limit (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	125
71-55-6	1,1,1-Trichloroethane	73	130
79-34-5	1,1,2,2-Tetrachloroethane	70	124
79-00-5	1,1,2-Trichloroethane	78	121
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	66	136
75-34-3	1,1-Dichloroethane	76	125
75-35-4	1,1-Dichloroethene	70	131
563-58-6	1,1-Dichloropropene	76	125
87-61-6	1,2,3-Trichlorobenzene	66	130
96-18-4	1,2,3-Trichloropropane	73	125
526-73-8	1,2,3-Trimethlybenzene	82	118
120-82-1	1,2,4-Trichlorobenzene	67	129
95-63-6	1,2,4-Trimethylbenzene	75	123
96-12-8	1,2-Dibromo-3-chloropropane	61	132
106-93-4	1,2-Dibromoethane	78	122
95-50-1	1,2-Dichlorobenzene	78	121
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	71	136
540-59-0	1,2-Dichloroethene	78	122
78-87-5	1,2-Dichloropropane	76	123
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	64	132
108-70-3	1,3,5-Trichlorobenzene	71	128
108-67-8	1,3,5-Trimethylbenzene	73	124
541-73-1	1,3-Dichlorobenzene	77	121
142-28-9	1,3-Dichloropropane	77	121
542-75-6	1,3-Dichloropropene	77	126
106-46-7	1,4-Dichlorobenzene	75	120
105-05-5	1,4-Diethylbenzene	79	114
123-91-1	1,4-Dioxane	55	138
544-10-5	1-Chlorohexane	71	130
594-20-7	2,2-Dichloropropane	67	133
78-93-3	2-Butanone (MEK)	51	148

126-99-8	2-Chloro-1,3-butadiene	65	133
110-75-8	2-Chloroethyl vinyl ether	43	149
95-49-8	Chlorotoluene	75	122
591-78-6	2-Hexanone	53	145
79-46-9	2-Nitropropane	47	150
67-63-0	2-Propanol [Isopropyl alcohol]	60	140
460-00-4	4-Bromofluorobenzene	79	119
106-43-4	4-Chlorotoluene	72	124
108-10-1	4-Methyl-2-pentanone [MIBK]	65	135
67-64-1	Acetone	36	164
75-05-8	Acetonitrile	54	143
107-02-8	Acrolein [Propenal]	47	155
107-13-1	Acrylonitrile	65	134
107-05-1	Allyl chloride	68	135
71-43-2	Benzene	77	121
100-44-7	Benzyl chloride	64	120
108-86-1	Bromobenzene	78	121
74-97-5	Bromochloromethane	78	125
75-27-4	Bromodichloromethane	75	127
75-25-2	Bromoform	67	132
74-83-9	Bromomethane	53	143
75-15-0	Carbon disulfide	63	132
56-23-5	Carbon tetrachloride	70	135
108-90-7	Chlorobenzene	79	120
124-48-1	Chlorodibromomethane	74	126
75-00-3	Chloroethane	59	139
67-66-3	Chloroform	78	123
74-87-3	Chloromethane	50	136
156-59-2	cis-1,2-Dichloroethene	77	123
10061-01-5	cis-1,3-Dichloropropene	74	126
1476-11-5	cis-1,4-Dichloro-2-butene	69	143
110-82-7	Cyclohexane	67	131
108-94-1	Cyclohexanone	30	156
1868-53-7	Dibromofluoromethane	78	119
74-95-3	Dibromomethane	78	125
75-71-8	Dichlorodifluoromethane [Freon-12]	29	149

75-43-4	Dichlorofluoromethane	47	155
60-29-7	Diethyl ether	71	129
108-20-3	Diisopropyl ether	69	127
64-17-5	Ethanol	45	159
141-78-6	Ethyl acetate	52	139
97-63-2	Ethyl methacrylate	69	129
637-92-3	Ethyl tert-butyl ether	72	126
100-41-4	Ethylbenzene	76	122
462-06-6	Fluorobenzene	81	114
142-82-5	Heptane	49	138
87-68-3	Hexachlorobutadiene	61	135
67-72-1	Hexachloroethane	72	133
110-54-3	Hexane	45	142
74-88-4	Iodomethane	71	131
78-83-1	Isobutyl alcohol	60	135
108-21-4	Isopropyl acetate [Acetic acid]	58	131
98-82-8	Isopropylbenzene	68	134
179601-23-1	m/p-Xylene [3/4-Xylene]	77	124
126-98-7	Methacrylonitrile	66	132
79-20-9	Methyl acetate	53	144
80-62-6	Methyl methacrylate	63	134
1634-04-4	Methyl tert-butyl ether [MTBE]	73	125
108-87-2	Methylcyclohexane	66	133
75-09-2	Methylene chloride	70	128
123-86-4	n-Butyl acetate	62	128
71-36-3	n-Butyl alcohol	55	131
104-51-8	n-Butylbenzene	70	128
103-65-1	n-Propylbenzene	73	125
91-20-3	Naphthalene	62	129
95-47-6	o-Xylene	77	123
99-87-6	p-Isopropyltoluene [p-Cymene]	73	127
76-01-7	Pentachloroethane	69	135
107-12-0	Propionitrile [Ethyl cyanide]	68	134
135-98-8	sec-Butylbenzene	73	126
100-42-5	Styrene	76	124
994-05-8	tert-Amyl methyl ether [TAME]	73	126

75-65-0	tert-Butyl alcohol	68	133
98-06-6	tert-Butylbenzene	73	125
127-18-4	Tertachloroethene	73	128
109-99-9	Tetrahydrofuran	61	135
108-88-3	Toluene	77	121
2037-26-5	Toluene-d8	85	116
156-60-5	trans-1,2-Dichloroethene	74	125
10061-02-6	trans-1,3-Dichloropropene	71	130
110-57-6	trans-1,4-Dichloro-2-butene	62	136
79-01-6	Trichloroethene	77	123
75-69-4	Trichlorofluoromethane [Freon-11]	62	140
108-05-4	Vinyl acetate	50	151
75-01-4	Vinyl chloride	56	135
1330-20-7	Xylene [total]	78	124

DoD Appendix C LCS Limits
Method 8260 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	124
71-55-6	1,1,1-Trichloroethane	74	131
79-34-5	1,1,2,2-Tetrachloroethane	71	121
79-00-5	1,1,2-Trichloroethane	80	119
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	70	136
75-34-3	1,1-Dichloroethane	77	125
75-35-4	1,1-Dichloroethene	71	131
563-58-6	1,1-Dichloropropene	79	125
87-61-6	1,2,3-Trichlorobenzene	69	129
96-18-4	1,2,3-Trichloropropane	73	122
526-73-8	1,2,3-Trimethlybenzene	82	120
120-82-1	1,2,4-Trichlorobenzene	69	130
95-63-6	1,2,4-Trimethylbenzene	76	124
96-12-8	1,2-Dibromo-3-chloropropane	62	128
106-93-4	1,2-Dibromoethane	77	121
95-50-1	1,2-Dichlorobenzene	80	119
107-06-2	1,2-Dichloroethane	73	128

17060-07-0	1,2-Dichloroethane-d4	81	118
540-59-0	1,2-Dichloroethene	79	121
78-87-5	1,2-Dichloropropane	78	122
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	70	136
108-70-3	1,3,5-Trichlorobenzene	75	130
108-67-8	1,3,5-Trimethylbenzene	75	124
106-99-0	1,3-Butadiene	43	158
541-73-1	1,3-Dichlorobenzene	80	119
142-28-9	1,3-Dichloropropane	80	119
542-75-6	1,3-Dichloropropene	77	123
106-46-7	1,4-Dichlorobenzene	79	118
105-05-5	1,4-Diethylbenzene	79	118
123-91-1	1,4-Dioxane	59	139
544-10-5	1-Chlorohexane	76	124
540-84-1	2,2,4-Trimethylpentane [Isooctane]	58	132
594-20-7	2,2-Dichloropropane	60	139
75-85-4	2-Butanol	66	120
78-93-3	2-Butanone (MEK)	56	143
126-99-8	2-Chloro-1,3-butadiene	65	135
110-75-8	2-Chloroethyl vinyl ether	51	139
95-49-8	Chlorotoluene	79	122
591-78-6	2-Hexanone	57	139
91-57-6	2-Methylnaphthalene	17	142
79-46-9	2-Nitropropane	49	136
67-63-0	2-Propanol [Isopropyl alcohol]	56	142
624-95-3	3,3-Dimethyl-1-butanol	49	133
460-00-4	4-Bromofluorobenzene	85	114
106-43-4	4-Chlorotoluene	78	122
108-10-1	4-Methyl-2-pentanone [MIBK]	67	130
67-64-1	Acetone	39	160
75-05-8	Acetonitrile	50	142
107-02-8	Acrolein [Propenal]	39	155
107-13-1	Acrylonitrile	63	135
107-05-1	Allyl chloride	68	130
71-43-2	Benzene	79	120
100-44-7	Benzyl chloride	42	138

108-86-1	Bromobenzene	80	120
74-97-5	Bromochloromethane	78	123
75-27-4	Bromodichloromethane	79	125
75-25-2	Bromoform	66	130
74-83-9	Bromomethane	53	141
75-15-0	Carbon disulfide	64	133
56-23-5	Carbon tetrachloride	72	136
108-90-7	Chlorobenzene	82	118
124-48-1	Chlorodibromomethane	74	126
75-45-6	Chlorodifluoromethane	40	129
75-00-3	Chloroethane	60	138
67-66-3	Chloroform	79	124
74-87-3	Chloromethane	50	139
156-59-2	cis-1,2-Dichloroethene	78	123
10061-01-5	cis-1,3-Dichloropropene	75	124
1476-11-5	cis-1,4-Dichloro-2-butene	57	146
110-82-7	Cyclohexane	71	130
1868-53-7	Dibromofluoromethane	80	119
74-95-3	Dibromomethane	79	123
75-71-8	Dichlorodifluoromethane [Freon-12]	32	152
75-43-4	Dichlorofluoromethane	72	131
60-29-7	Diethyl ether	68	129
108-20-3	Diisopropyl ether	67	128
64-17-5	Ethanol	48	151
141-78-6	Ethyl acetate	55	138
97-63-2	Ethyl methacrylate	72	126
637-92-3	Ethyl tert-butyl ether	70	127
100-41-4	Ethylbenzene	79	121
462-06-6	Fluorobenzene	80	116
142-82-5	Heptane	49	140
87-68-3	Hexachlorobutadiene	66	134
67-72-1	Hexachloroethane	72	134
110-54-3	Hexane	48	143
74-88-4	Iodomethane	69	131
78-83-1	Isobutyl alcohol	63	133
108-21-4	Isopropyl acetate [Acetic acid]	63	133

98-82-8	Isopropylbenzene	72	131
179601-23-1	m/p-Xylene [3/4-Xylene]	80	121
126-98-7	Methacrylonitrile	63	133
79-20-9	Methyl acetate	56	136
80-62-6	Methyl methacrylate	67	128
1634-04-4	Methyl tert-butyl ether [MTBE]	71	124
108-87-2	Methylcyclohexane	72	132
75-09-2	Methylene chloride	74	124
123-86-4	n-Butyl acetate	69	125
71-36-3	n-Butyl alcohol	59	131
104-51-8	n-Butylbenzene	75	128
109-60-4	n-Propyl acetate	76	126
103-65-1	n-Propylbenzene	76	126
91-20-3	Naphthalene	61	128
95-47-6	o-Xylene	78	122
99-87-6	p-Isopropyltoluene [p-Cymene]	77	127
76-01-7	Pentachloroethane	69	133
109-66-0	Pentane	16	134
107-12-0	Propionitrile [Ethyl cyanide]	64	136
135-98-8	sec-Butylbenzene	77	126
100-42-5	Styrene	78	123
994-05-8	tert-Amyl methyl ether [TAME]	68	128
75-65-0	tert-Butyl alcohol	68	129
762-75-4	tert-Butyl formate	65	132
98-06-6	tert-Butylbenzene	78	124
127-18-4	Tertachloroethene	74	129
109-99-9	Tetrahydrofuran	57	133
108-88-3	Toluene	80	121
2037-26-5	Toluene-d8	89	112
156-60-5	trans-1,2-Dichloroethene	75	124
10061-02-6	trans-1,3-Dichloropropene	73	127
110-57-6	trans-1,4-Dichloro-2-butene	43	140
79-01-6	Trichloroethene	79	123
75-69-4	Trichlorofluoromethane [Freon-11]	65	141
108-05-4	Vinyl acetate	54	146
75-01-4	Vinyl chloride	58	137

1330-20-7	Xylene [total]	79	121

Figure 1: Volatiles Sample Preparation

VOLATILES
Sample Prep

Date: ___________
Analyst: ___________
Batch QC ID#: ___________

#	**Merit #**	**Matrix**	**Surrogate ID**	**Vol. (ul)**	**Spike ID**	**Vol. (ul)**	**Time Start / End**	**PH**	**Notes**
	BFB								
	SPCC								
	LCS								
	LCSD								
	BLK								
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									

Reviewed by: __________________

Date: __________________

FIGURE 2. METHOD 5035A (LOW LEVEL) EXTRACTION SHEET

Method 5035A (Low Level)
Extraction Sheet

Analyst: ____________
Date: ____________
Batch QC ID #______

Merit Number	Tare wt (g)	Vial wt (g)	Sample wt.(g)	Time Start / End	Decontaminated	Decontamination Date	Notes

Reviewed By: ____________
Date: ____________

Figure 3. Method 5035A (High Level) Extraction Sheet

Method 5035A (High Level)
Extraction Sheet

Analyst: ____________
Date: ______________
Batch QC ID#________

Merit Number	Tare wt (g)	Vial wt (g)	Sample wt.(g)	Methanol (mL)	Sonicate (min)	Time Start / End	Notes

Reviewed By: ____________
Methanol Lot: ________________
Date: ____________

5035A High Level
Prepared by Merit Laboratories, Inc

STANDARD OPERATING PROCEDURE

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
METHOD SW-846 8260C/ EPA 624.1

APPROVALS:

Barbara Ball

09/29/2020

QA Officer
Date

09/29/2020

Technical Director
Date

Number	Description of Change	Date
001-011	Previous revisions not documented	
0012	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
013	Updated to method 8260C	9/4/13
014	Updated to comply with DoD QSM 5.0 standards.	04/01/16
015	Updated to comply with DoD QSM 5.1 standards.	01/17/18
016	NY NELAC Audit Finding	03/13/19
017	DOD Audit Corrective Action	09/29/2020
018		
019		

1.0 SCOPE AND APPLICATION

This SOP is used to determine volatile organic compounds (VOC) in a variety of matrices, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. See Table 1 for a list of compounds (along with their characteristic ions) that have been evaluated.

There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by SW-846 Methods 5030C (aqueous samples) and 5035A (solid, waste, and oil samples), are the most commonly used technique for volatile organic analytes. SW-846 Method 5000 provides general information on the selection of other introduction methods.

The practical quantitation limit (PQL) for an individual compound is instrument dependent and also dependent on the choice of the sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 50 µg/kg (wet weight) for solid samples and 1 µg/L for ground water. When lower reportable detection limits (RDLs) are required, the mass spectrometer (MS) can be set to selective ion monitoring (SIM) to achieve limits approximately 20 times lower then obtainable using the full scan method. Regardless of the sample matrix, PQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

Method Detection Limits (MDL) and Practical Quantitation Limits (PQL) are available in Merit's LIMs system.

This SOP is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF THE METHOD

VOC are introduced into the gas chromatograph by the purge-and-trap method or by other methods. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer interfaced to the gas chromatograph.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five point (or more) calibration curve.

The method includes specific calibration and quality control steps that supersede the general requirements provided in SW-846 Method 8000.

3.0 INTERFERENCES

Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds will be concentrated in the trap during the purge operation.

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to allow the system to be cleaned as well as to demonstrate the ultimate absence of cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

4.0 APPARATUS AND MATERIALS

Gas chromatograph/mass spectrometer system

- Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
- 20 m × 0.18 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 1-µm film thickness, or equivalent.
- Mass spectrometer capable of scanning from 35 to 200 amu every 2 sec 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 4-bromofluorobenzene (BFB) which meets the criteria in Table 4.
- GC/MS interface - The capillary column is interfaced through a direct connection to the GC/MS system.

- ♦ Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

Purge-and-trap device.

Microsyringes - 2 to 500-µL.

Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

Glass bottles - 40-mL, with PTFE-lined screw-caps.

pH paper.

5.0 REAGENTS

Reagent grade inorganic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.

Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

Stock standard solutions.

- ♦ Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.
- ♦ Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a high-concentration stock solution).
- ♦ Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.
- ♦ Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicate a problem.

Internal standard solutions - The internal standards used are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 (see Table 2). Internal standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 µg/L (i.e. 10µL per 5000µL purge volume). For SIM (selective ion monitoring) analysis, internal standards are the same, but with concentrations at 0.1 ppb (µg/L).

Calibration standards - A minimum of five calibration standards are prepared at different concentrations. The lowest calibration standard corresponds to a sample concentration at or below the standard reporting limit. The remaining standards should represent the working range of the GC/MS system. Each standard should contain each analyte for quantitation by this method. For DoD projects, each standard shall contain all target compounds.

Surrogate standards - The surrogates used are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Surrogate standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 µg/L, or less. For SIM (selective ion monitoring) analysis, surrogate standards are the same, but with concentrations at 0.1 ppb (µg/L).

Matrix spike (MS), matrix spike duplicate (MSD) and laboratory control standards (LCS) - Matrix spiking solutions are prepared using the same standards as those used for the calibration.For DoD projects, matrix spiking solutions shall contain all target compounds.

- Matrix spiking mixes for individual analytes are created at 100 mg/L and spiked into samples at 50 µg/L (*i.e.* 2.50µL per 5000µL purge volume).
- For SIM (selective ion monitoring) analysis, compounds of interest are spiked at concentrations of 0.1 ppb (µg/L).

Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

6.0 SAMPLE HANDLING AND PRESERVATION

Unanalyzed samples are refrigerated at 4 ± 2 degrees Celsius in sealed vials or containers.

Aqueous samples are preserved to a pH <2with HCl and/or $Na_2S_2O_3$ (unless unpreserved requested) and collected in a 40 ml. Preserved samples must be analyzed within 14 days from sample collection; unpreserved samples must be analyzed within 7 days from sample collection.

Soil samples collected Encore^{TM} Samplers must be preserved within 48 hours and analyzed within 14 days. Soil samples collected in glass jars shall be kept refrigerated and analyzed within 14 days from sample collection. For additional information on sample collection, handling and preservation for soil samples see SOP #ORL-005.

7.0 PROCEDURE

Sample introduction.

- Direct injection - This method of introduction is used only rarely, generally when the compounds of interest exhibit poor purging efficiency. Quantitation in this case, if required, is generally subject to external standard calibration procedures (*cf*. Method 8000).
- Purge-and-trap - This is generally used for sample introduction for both soil and water samples. All samples, standards, spikes, and blanks are introduced into the GC/MS system in an identical manner (see Merit SOP# ORL-005).

GC/MS operating conditions - see Table 3 for routine operating conditions for VOC analysis.

- For SIM, the MS is put into the SIM mode. Based on compounds of interest, the time windows are set within the run (i.e. for internal standards, surrogate standards, compounds). For each time window, corresponding to a compound, including internal and surrogate standards, a minimum of 3 ions are chosen for qualitative analysis. One ion (primary ion), generally the most abundant ion is used for quantitative analysis.

Initial calibration.

- Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for 4-bromofluorobenzene. Analysis does not begin until these criteria are met.
    - In the absence of any other manipulations, evaluate the mass spectrum of the peak apex or the scan immediately preceding or following from the total ion chromatogram for the BFB peak. This is the default approach used.
    - If the above evaluation is adversely affected by ion peak asymmetry, average the three highest intensity scans of the peak or average the mass spectrum ranging from the 10% initial peak intensity to the tailing 10% peak intensity level from the total ion chromatogram for the BFB peak.
    - If the above evaluation is adversely affected by background contamination, perform a background subtraction with a spectrum within 20 scans of the BFB peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.
    - The BFB mass intensity criteria in Table 4 are used as tuning acceptance criteria.

  - All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must use the identical mass spectrometer instrument conditions, Exception: for SIM, tune is run using full scan acquisition and subsequent samples are acquired using SIM.

- Purge and analyze each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary. The purge volume must be the same for all standards and sample extracts. Table 5 details the dilutions necessary to create a set of calibration standards. Figure 1 shows a chromatogram of a midpoint calibration standard.

- Calculate response factors (*RF*s) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.

- System performance check compounds (SPCCs).
  - A system performance check must be performed to ensure that minimum *RF*s are met before the calibration curve is used. For volatiles, the SPCCs are: chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene, and 1,1,2,2-tetrachloroethane (Table 2). No response factor criteria are applied to SIM analysis.
  - The minimum acceptable average *RF* for these compounds is 0.1 (for chloromethane, 1,1-dichloroethane, and bromoform) and 0.3 (for chlorobenzene and 1,1,2,2-tetrachloroethane). These SPCCs typically have low *RF*s and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.
  - It is also recommended that a minimum response factor for the most common target analytes as noted in Table 2b, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration level is important in demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed, some compounds will fail to meet this criteria. In particular, poor performers such as ketones and 1,2-dibromo-3-chloropropane are likely to fail this criteria but have been demonstrated to perform adequately overall.

  - If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination in the purge-and-trap system, excessively high or low purge flow rates, and active sites in the column or chromatographic system. Replacing the calibration standards, clipping and/or replacing the column will likely solve this problem.

- Calibration check compounds (CCCs).
  - The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is in addition to the successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.
  - Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 20% for each target analyte. However, the RSD for each individual CCC compound (1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride; see Table 2) must be less than or equal to 30%.If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.
- Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. This is accomplished by setting the retention time extraction windows in the Chemstation software.
- Linearity of target analytes - If the %RSD of any target analytes is 20% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.
  - Refer to SW-846 Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. The coefficient of determination for any regression fit should be ≥0.99. In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters.

- When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc*.
- The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and the quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve. The recalculated concentration of the low calibration point should be within 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives. For analytes which do not meet the minimum quantitation calibration re-fitting criteria reporting those analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.
- The initial calibration curve should be verified immediately after performing the standard analyses using a second source standard at a concentration near the midpoint of the calibration range. The acceptance limits are 70-130% or project specific. Analytes that fail this criteria are considered estimated values.
- The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e.* average RF or regression coefficients), and the appropriate calibration quality metric (*i.e.* %RSD or COD).

♦ GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

♦ Prior to the analysis of samples or calibration standards, purge the BFB standard into the GC/MS system. The resultant mass spectrum for BFB must meet the criteria given in Table 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the BFB.

♦ The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC/MS (50 µg/L; this represents 2.50 µL of the 100 mg/L calibration standard solution in a 5mL purge volume). A concentration of 0.1µg/L is analyzed for SIM procedures. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the SPCC and CCC compounds. In addition the internal standards should be within 10s of those in the midpoint calibration standard and the responses should be 50-200% of those in the midpoint calibration standard.

- A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants. A method blank/wash sample is also run after calibration check/spike samples and prior to analytical samples in order to eliminate carryover contamination from the purge-and-trap system.
- System performance check compounds (SPCCs).
    - A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet the minimum response factors given above. This is the same check that is applied during the initial calibration (see §7.3.4.2).
    - Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 2b . This is the same check that is applied during the initial calibration and exceptions are noted above.
    - If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.
- Calibration check compounds (CCCs).
    - After the system performance check is met, the CCCs listed in Table 2 are used to check the validity of the initial calibration. Percent drift is used to evaluate the CCC response and it must be ≤20%.
    - All target compounds of interest must be evaluated using a 20% variability criterion. If the percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation

limit. For situations when a failed compound is present, the concentration is an estimated value.Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = \left|C - C_{spike}\right| / C_{spike}$.

- ○ Problems similar to those listed under initial calibration could affect the calibration verification. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

GC/MS analysis of samples.

- ♦ Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.
- ♦ Use a 5 mL syringe to take a 5 mL aliquot from the sample vial. Be sure to eliminate any air bubbles from within the syringe. Table 5 has a list of commonly used dilutions as well as the required amount of sample, water, and internal standard for each dilution.
- ♦ Add 10 μL of 25 mg/L internal/surrogate standard mixture to each sample. For SIM analysis, internal and surrogate standards are spiked at 0.1μg/L.
- ♦ If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.
- ♦ The Extracted Ion Current Profile (EICP) area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Table 6a and 6b). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.

Qualitative analysis.

- The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Figures 1a and 1b. Compounds are identified when the following criteria are met.
    - Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound specific retention time.
    - The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.
    - The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)
    - Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
    - Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
    - Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.
    - In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of

continued uncertainty, the analyst should preferentially make a conservative judgment and accept an identified hit, allowing the potential for a false positive.

- 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. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:
  - Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
  - The relative intensities of the major ions should agree within ± 20%.
  - Molecular ions present in the reference spectrum should be present in the sample spectrum.
  - Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
  - 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 coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Quantitative analysis.

- Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.
- The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s / A_i = k_0 + k_1 [C_s / C_i] + k_2 [C_s / C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th}-order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv \langle RF \rangle$, while k_0, $k_2 \equiv 0$.
- The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the tentatively identified compound (TIC) areas for the nearest internal standard and target compound. The resulting concentration should be reported

indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

- Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-xylene).

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 6a and 6b. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. Control limits for surrogates and matrix spikes are listed in Table 7. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Laboratory specific performance data is provided for Merit’s LIMs system. Each sample batch contains a method blank, laboratory control sample and matrix spike samples. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

Computer software and firmware can be found on Merit’s network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention shall be paid (but not limited) to:

a. Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.
b. Hydrochloric acid is corrosive. Extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

4-Bromofluorobenzene (BFB), is used to verify that the GC/MS is properly tuned and ready for calibration and sample analyses. BFB is directly injected at 25-50 ng and precedes all other analyses. A twelve hour analysis time window is used before another BFB injection is required.

An Initial Calibration Verification standard (ICV) is analyzed before the analysis of samples as a check on the calibration curve. The ICV shall be of a second source, meaning a separate vendor and/or lot # shall be used to prepare this standard. A second source is needed to validate the integrity and concentration of the standards used for calibration.

An Initial Calibration Blank (ICB) is also analyzed before samples to confirm that the deionized water (DI H2O) used for standards, blanks, and dilutions are free from contamination. An ICB for soil samples also includes organic free sand and/or methanol used for standard and QC preparation, as well as sample dilutions and volume adjustments; the control sand and methanol must also be documented as free from contamination.

A Calibration Check Verification standard (CCV) is analyzed at the beginning of each sequence (following the BFB injection) shift and every 12 hour shift thereafter. A CCV is made up from the same standards used for calibration and is used to ensure that the calibration and retention times are stable.

An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run.

Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

Internal standards (ISTD) are added to each sample, blank, spike, and check standard. The ISTDs used are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. The ISTD is used for internal calibration as a reference peak and to check purging efficiency.

Surrogate standards (SSTD) are also added to each sample, blank, spike, and check standard. The SSTDs used are Toluene-d_4, 4-Bromofluorobenzene, 1,2-Dichloroethane-d_4, and Dibromofluoromethane. The SSTD is used as matrix interference and as a method control check.

Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

A Continuing Calibration Blank (CCB) is analyzed every 12 hour shift after the MB has been analyzed and before sample reanalyzes to ensure the system is still free from contamination.

Instrument blanks are analyzed whenever instrument contamination is a suspected possibility. The purpose of an IB is to prevent carry over from a standard, spike, or contaminated sample into another sample or blank. The acceptance criteria for an IB is the same as for a MB or CCB (for example: if an IB contains detections above acceptance criteria and a MB and/or sample following the IB exhibit the same contamination above acceptance criteria, then the instrument shall be considered contaminated). The samples and/or MBs shall be reanalyzed after the instrument is confirmed free from contamination.

Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with all target compounds and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

Matrix Spike (MS): An aliquot of sample spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

14.0 REFERENCES

Bellar, T., *Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

U.S. EPA 40 CFR Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule*, October 26, 1984.

EPA SW-846, *Test Methods for Evaluation Solid Waste*, 3rd Edition, Update I dated 7/92, Update II dated 9/94, Update IIA dated 8/93, Update IIB dated 1/95, Update III dated 12/96, Update IV dated 1/08.

International Standards Organization (ISO), 2005. *General Requirements for the Competence of Testing and Calibration Laboratories.* ISO 17025.

National Environmental Laboratory Accreditation Conference (NELAC), 2003. *Standards, Chapters 1–6*, EPA/600/R-04/003.

EPA Method 624.1, December 2016

Table 1. Summary of Retention Times† and Characteristic Ions for Volatile Organics

#	**Compound**	**t_R** (*min*)	**$t_R/t_{R,I}$** (-)	**t_R-$t_{R,I}$** (*min*)	**1^0** *m/z*	**2^0** *m/z*	**3^0*m/z***	**4^0** *m/z*
1)	PENTAFLUOROBENZENE	3.58	1.000	0.00	168	99	37	
2)	1,2-DICHLOROETHANE-D4	3.8	1.061	0.22	65	102	104	
3)	1,1,2-Trichloro-1,2,2-trifluoroethane	1.9	0.531	-1.68	101	151	103	
4)	Diethyl ether (*)	1.7	0.475	-1.88	74	59	45	
5)	Acetone (*)	1.89	0.528	-1.69	58	43	44	
6)	Methyl iodide (iodomethane)	1.97	0.550	-1.61	142	141	127	
7)	Carbon disulfide (*)	2.01	0.561	-1.57	76	78	44	
8)	Methyl Acetate	2.09	0.584	-1.49	43	74	59	
9)	tert-Methyl butyl ether (MTBE)	2.37	0.662	-1.21	73	57	41	43
10	Acrylonitrile (*)	2.39	0.668	-1.19	52	53	54	
11	2-Butanone (MEK) (*)	3.23	0.902	-0.35	43	72	57	
12	Dichlorodifluoromethane	1.17	0.327	-2.41	85	87	50	
13	Chloromethane (SPCC)	1.25	0.349	-2.33	50	52	49	
14	Vinyl Chloride (CCC)	1.32	0.369	-2.26	62	64	61	
15	Bromomethane	1.44	0.402	-2.14	94	96	81	
16	Chloroethane	1.46	0.408	-2.12	64	66	49	51
17	Acrolein	1.82	0.508	-1.76	56	55	53	
18	Trichlorofluoromethane	1.66	0.464	-1.92	101	103	66	105
19	1,1-Dichloroethene (CCC/MS)	1.86	0.520	-1.72	61	96	63	98
20	Methylene Chloride	2.19	0.612	-1.39	84	49	86	51
21	trans-1,2-Dichloroethene	2.38	0.665	-1.20	61	96	63	98
22	1,1-Dichloroethane (SPCC)	2.73	0.763	-0.85	63	65	83	
23	cis-1,2-Dichloroethene	3.21	0.897	-0.37	96	61	98	
24	Tetrahydrofuran	3.42	0.955	-0.16	42	41	71	
25	Chloroform (CCC)	3.46	0.966	-0.12	83	85	47	
26	Bromochloromethane	3.4	0.950	-0.18	130	49	93	128
27	1,1,1-Trichloroethane	3.57	0.997	-0.01	97	99	61	
28	1,1-Dichloropropene	3.67	1.025	0.09	75	77	110	
29	Cyclohexane	3.63	1.014	0.05	56	84	41	

#	**Compound**	**t_R**	**$t_R/t_{R,I}$**	**t_R-$t_{R,I}$**	**1^0**	**2^0**	**3^0*m/z***	**4^0**
		(*min*)	**(-)**	**(*min*)**	***m/z***	***m/z***		***m/z***
30	1,4-DIFLUOROBENZENE	4.07	1.000	0.00	114	88	57	
31	TOLUENE-D8	4.95	1.216	0.88	98	100	70	
32	4-Methyl-2-pentanone (MIBK)	4.9	1.204	0.83	58	85	100	43
33	2-Hexanone (*)	5.37	1.319	1.30	58	43	85	100
34	2-chloroethylvinyl ether	4.73	1.162	0.66	63	106	65	
35	Carbon Tetrachloride	3.67	0.902	-0.40	117	119	121	
36	Benzene (MS)	3.82	0.939	-0.25	78	77	51	
37	1,2-Dichloroethane	3.85	0.946	-0.22	62	98	100	64
38	Trichloroethene (MS)	4.23	1.039	0.16	95	132	130	134
39	1,2-Dichloropropane (CCC)	4.38	1.076	0.31	63	76	62	
40	Bromodichloromethane	4.56	1.120	0.49	83	85	127	129
41	Methyl Cyclohexane	4.33	1.064	0.26	55	83	41	98
42	Dibromomethane	4.47	1.098	0.40	174	93	172	79
43	cis-1,3-Dichloropropene	4.82	1.184	0.75	75	77	110	
44	Toluene (CCC/MS)	4.99	1.226	0.92	91	92	65	
45	trans-1,3-Dichloropropene	5.13	1.260	1.06	75	110	77	
46	1,1,2-Trichloroethane	5.24	1.287	1.17	83	97	99	85
47	Tetrachloroethene	5.29	1.300	1.22	166	129	164	
48	CHLOROBENZENE-D5	5.76	1.000	0.00	82	117	119	
49	4BROMOFLUOROBENZENE	6.38	1.108	0.62	174	95	176	
50	trans-1,4-Dichloro-2-butene	6.49	1.127	0.73	53	89	124	75
51	Dibromochloromethane	5.46	0.948	-0.30	129	127	79	
52	1,2-Dibromoethane	5.52	0.958	-0.24	107	109	81	
53	Chlorobenzene (SPCC/MS)	5.77	1.002	0.01	112	77	114	
54	1,1,1,2-Tetrachloroethane	5.82	1.010	0.06	131	133	117	119
55	Ethylbenzene (CCC)	5.82	1.010	0.06	91	106	77	
56	p,m-Xylene	5.88	1.021	0.12	106	91	77	
57	o-Xylene	6.09	1.057	0.33	91	106	77	
58	Styrene	6.1	1.059	0.34	104	78	103	
59	Isopropylbenzene	6.28	1.090	0.52	105	120	77	
60	Bromoform (SPCC)	6.23	1.082	0.47	173	171	175	
61	1,1,2,2-Tetrachloroethane	6.47	1.123	0.71	83	85	131	133

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	t_R-$t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
62	1,2,3-Trichloropropane	6.49	1.127	0.73	110	75	97	61
63	n-Propylbenzene	6.5	1.128	0.74	91	120	105	
64	Bromobenzene	6.46	1.122	0.70	156	77	158	
65	1,3,5-Trimethylbenzene	6.59	1.144	0.83	120	105	77	
66	tert-Butylbenzene	6.76	1.174	1.00	91	119	134	
67	1,2,4-Trimethylbenzene	6.79	1.179	1.03	120	105	77	
68	1,4-DICHLOROBENZENE-D4	6.99	1.000	0.00	152	150	115	
69	sec-Butylbenzene	6.87	0.983	-0.12	105	134	91	
70	p-Isopropyltoluene	6.95	0.994	-0.04	119	91	134	
71	1,3-Dichlorobenzene	6.95	0.994	-0.04	146	148	111	
72	1,4-Dichlorobenzene	7	1.001	0.01	146	148	111	
73	1,2-Dichlorobenzene	7.2	1.030	0.21	146	148	111	
74	1,2,3-Trimethylbenzene	7.01	1.003	0.02	105	120	77	
75	n-Butylbenzene	7.16	1.024	0.17	91	92	134	
76	Hexachloroethane	7.32	1.047	0.33	201	117	166	
77	1,2-Dibromo-3-Chloropropan	7.61	1.089	0.62	157	155	75	159
78	1,2,4-Trichlorobenzene	8.02	1.147	1.03	182	180	145	109
79	Hexachlorobutadiene	8.09	1.157	1.10	225	227	223	190
80	1,2,3-Trichlorobenzene	8.27	1.183	1.28	180	182	145	109
81	Naphthalene	8.15	1.166	1.16	128	102	127	129
82	2-Methylnaphthalene	8.72	1.247	1.73	142	141	115	

†: Absolute retention times (t_R) listed are from calibration FT060808.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e*. new, clipped, *etc*.), but the differential retention times (t_R - $t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

Table 2. Summary of Applicable Performance Compounds - Volatile Organics Analysis

#[†]	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	PENTAFLUOROBENZENE			✓		
2	1,2-DICHLOROETHANE-D4				✓	
11	Chloromethane (SPCC)		✓			
12	Vinyl Chloride (CCC)	✓				
16	1,1-Dichloroethene (CCC/MS)	✓				✓
19	1,1-Dichloroethane (SPCC)		✓			
21	Chloroform (CCC)	✓				
25	1,4-DIFLUOROBENZENE			✓		
26	TOLUENE-D8				✓	
30	Benzene (MS)					✓
32	Trichloroethene (MS)					✓
33	1,2-Dichloropropane (CCC)	✓				
37	Toluene (CCC/MS)	✓				✓
42	CHLOROBENZENE-D5			✓		
43	4-BROMOFLUOROBENZENE-				✓	
47	Chlorobenzene (SPCC/MS)		✓			✓
49	Ethylbenzene (CCC)	✓				
54	Bromoform (SPCC)		✓			
55	1,1,2,2-Tetrachloroethane (SPCC)		✓			
62	1,4-DICHLOROBENZENE-D4			✓		

[†]: Compound identification numbers listed are from calibration FR010910.M.

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

<u>Key</u>

CCC: Calibration Check Compound
SPCC: System Performance Check Compound
ISD: Internal Standard Compound
SSD: Surrogate Standard Compound
MS: Matrix Spiking Compound

Table 2b. Recommended Minimum Relative Response Factor Criteria For Initial And Continuing Calibration Verification.

Volatile Compounds	Minimum Response Factor (RF)[a]
Dichlorodifluoromethane	0.100
Chloromethane	0.100
Vinyl chloride	0.100
Bromomethane	0.100
Chloroethane	0.100
Trichlorofluoromethane	0.100
1,1-Dichloroethene	0.100
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100
Acetone	0.100
Carbon disulfide	0.100
Methyl Acetate	0.100
Methylene chloride	0.100
trans-1,2-Dichloroethene	0.100
cis-1,2-Dichloroethene	0.100
Methyl tert-Butyl Ether	0.100
1,1-Dichloroethane	0.200
2-Butanone	0.100
Chloroform	0.200
1,1,1-Trichloroethane	0.100
Cyclohexane	0.100
Carbon tetrachloride	0.100
Benzene	0.500
1,2-Dichloroethane	0.100
Trichloroethene	0.200
Methylcyclohexane	0.100
1,2-Dichloropropane	0.100
Bromodichloromethane	0.200
cis-1,3-Dichloropropene	0.200
trans-1,3-Dichloropropene	0.100
4-Methyl-2-pentanone	0.100
Toluene	0.400
1,1,2-Trichloroethane	0.100
Tetrachloroethene	0.200
2-Hexanone	0.100
Dibromochloromethane	0.100
1,2-Dibromoethane	0.100
Chlorobenzene	0.500

Volatile Compounds	Minimum Response Factor (RF)[a]
Ethylbenzene	0.100
meta-/para-Xylene	0.100
ortho-Xylene	0.300
Styrene	0.300
Bromoform	0.100
Isopropylbenzene	0.100
1,1,2,2-Tetrachloroethane	0.300
1,3-Dichlorobenzene	0.600
1,4-Dichlorobenzene	0.500
1,2-Dichlorobenzene	0.400
1,2-Dibromo-3-chloropropane	0.050
1,2,4-Trichlorobenzene	0.200

[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.

Table 3. GC/MS Operating Conditions - Volatile Organics Analysis

Operating Parameter	**Volatiles Analysis**
Chromatographic Column	DB 624, $L = 20\ m$, $ID = 0.18\ mm$
Carrier Gas	Helium (He)
Temperature Program	$T_0 = 30^{o}C$, hold 2.0 *min* $dT/dt_1 = 32^{o}C/min$ $T_1 = 195^{o}C$ $dT/dt_2 = 30^{o}C/min$ $T_2 = 235^{o}C$
Injector Temperature	$250^{o}C$
Detector Temperature	$280^{o}C$
Purge Volume	5 *mL*
Mass Scanning Range	35 *m/z* - 250 *m/z*
Mass Scanning Rate	2.0 *Hz*

Note: the above is subject to change based on GC and/or sample conditions.

Table 4. BFB Tune Evaluation Criteria

Target *m/z*	**Relative *m/z***	**LCL (%)**	**UCL (%)**
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5.0	9.0
173	174	0	2.0
174	95	50	120
175	174	4.0	9.0
176	174	93	101
177	176	5.0	9.0

Abundance criteria are for a quadrupole mass spectrometer. Alternative tuning criteria from other published EPA reference methods may be used, provided method performance is not adversely affected. Alternative tuning criteria specified by an instrument manufacturer may also be used for another type of mass spectrometer, or for an alternative carrier gas, provided method performance is not adversely affected.

Table 5. Commonly Used Dilutions for Sample Preparation

Dilution	Sample Volume (μL)	H_2O Volume (μL)	ISD/SSD Volume (μL)	Total Volume (μL)
1:1	5000	0	10.0	5010
2:1	2500	2500	10.0	5010
5:1	1000	4000	10.0	5010
10:1	500	4500	10.0	5010
20:1	250	4750	10.0	5010
50:1	100	4900	10.0	5010
100:1	50	4950	10.0	5010
200:1	25	4975	10.0	5010
500:1	10	5000	10.0	5020
1000:1	5.0	5000	10.0	5015
2500:1	2.0	5000	10.0	5012

General "*n*:1" dilution: (5000/*n*) μL of Sample
(5000 - 5000/*n*) μL H_2O
10 μL Internal/Surrogate Standard (ISD/SSD) at 25 mg/L

Table 6a. Quality Control Items, Frequency, and Corrective Action

QC Item	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
BFB	12-hour	Table 5	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	SPCC- section 7.34 CCC- section 7.3.5	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Table 7	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	<RL	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) should result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard	All samples	Section 7.5.5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged

QC Item	**Frequency**	**Acceptance Criteria**	**Corrective Action**
			appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate
Surrogate Standard	All samples	Table 7	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 6b. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within ± 20% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within ± 20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed	If corrective action fails in field samples, data must be qualified and explained in the case	NA

QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
		+100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	while system was malfunctioning is mandatory.	narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
				associated preparatory batch.	
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	MSD: Must contain all surrogates and all analytes to be reported. The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed..	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative..		
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within ± 20% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within ± 20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.

QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
			necessary; then reanalyze all associated samples since the last acceptable CCV.		
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	NA
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

DoD Appendix C LCS Limits
Method 8260 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	125
71-55-6	1,1,1-Trichloroethane	73	130
79-34-5	1,1,2,2-Tetrachloroethane	70	124
79-00-5	1,1,2-Trichloroethane	78	121
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	66	136
75-34-3	1,1-Dichloroethane	76	125
75-35-4	1,1-Dichloroethene	70	131
563-58-6	1,1-Dichloropropene	76	125
87-61-6	1,2,3-Trichlorobenzene	66	130
96-18-4	1,2,3-Trichloropropane	73	125
526-73-8	1,2,3-Trimethlybenzene	82	118
120-82-1	1,2,4-Trichlorobenzene	67	129
95-63-6	1,2,4-Trimethylbenzene	75	123
96-12-8	1,2-Dibromo-3-chloropropane	61	132
106-93-4	1,2-Dibromoethane	78	122
95-50-1	1,2-Dichlorobenzene	78	121
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	71	136
540-59-0	1,2-Dichloroethene	78	122
78-87-5	1,2-Dichloropropane	76	123
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	64	132
108-70-3	1,3,5-Trichlorobenzene	71	128
108-67-8	1,3,5-Trimethylbenzene	73	124
541-73-1	1,3-Dichlorobenzene	77	121
142-28-9	1,3-Dichloropropane	77	121
542-75-6	1,3-Dichloropropene	77	126
106-46-7	1,4-Dichlorobenzene	75	120
105-05-5	1,4-Diethylbenzene	79	114

123-91-1	1,4-Dioxane	55	138
544-10-5	1-Chlorohexane	71	130
594-20-7	2,2-Dichloropropane	67	133
78-93-3	2-Butanone (MEK)	51	148
126-99-8	2-Chloro-1,3-butadiene	65	133
110-75-8	2-Chloroethyl vinyl ether	43	149
95-49-8	Chlorotoluene	75	122
591-78-6	2-Hexanone	53	145
79-46-9	2-Nitropropane	47	150
67-63-0	2-Propanol [Isopropyl alcohol]	60	140
460-00-4	4-Bromofluorobenzene	79	119
106-43-4	4-Chlorotoluene	72	124
108-10-1	4-Methyl-2-pentanone [MIBK]	65	135
67-64-1	Acetone	36	164
75-05-8	Acetonitrile	54	143
107-02-8	Acrolein [Propenal]	47	155
107-13-1	Acrylonitrile	65	134
107-05-1	Allyl chloride	68	135
71-43-2	Benzene	77	121
100-44-7	Benzyl chloride	64	120
108-86-1	Bromobenzene	78	121
74-97-5	Bromochloromethane	78	125
75-27-4	Bromodichloromethane	75	127
75-25-2	Bromoform	67	132
74-83-9	Bromomethane	53	143
75-15-0	Carbon disulfide	63	132
56-23-5	Carbon tetrachloride	70	135
108-90-7	Chlorobenzene	79	120
124-48-1	Chlorodibromomethane	74	126
75-00-3	Chloroethane	59	139
67-66-3	Chloroform	78	123
74-87-3	Chloromethane	50	136
156-59-2	cis-1,2-Dichloroethene	77	123

10061-01-5	cis-1,3-Dichloropropene	74	126
1476-11-5	cis-1,4-Dichloro-2-butene	69	143
110-82-7	Cyclohexane	67	131
108-94-1	Cyclohexanone	30	156
1868-53-7	Dibromofluoromethane	78	119
74-95-3	Dibromomethane	78	125
75-71-8	Dichlorodifluoromethane [Freon-12]	29	149
75-43-4	Dichlorofluoromethane	47	155
60-29-7	Diethyl ether	71	129
108-20-3	Diisopropyl ether	69	127
64-17-5	Ethanol	45	159
141-78-6	Ethyl acetate	52	139
97-63-2	Ethyl methacrylate	69	129
637-92-3	Ethyl tert-butyl ether	72	126
100-41-4	Ethylbenzene	76	122
462-06-6	Fluorobenzene	81	114
142-82-5	Heptane	49	138
87-68-3	Hexachlorobutadiene	61	135
67-72-1	Hexachloroethane	72	133
110-54-3	Hexane	45	142
74-88-4	Iodomethane	71	131
78-83-1	Isobutyl alcohol	60	135
108-21-4	Isopropyl acetate [Acetic acid]	58	131
98-82-8	Isopropylbenzene	68	134
179601-23-1	m/p-Xylene [3/4-Xylene]	77	124
126-98-7	Methacrylonitrile	66	132
79-20-9	Methyl acetate	53	144
80-62-6	Methyl methacrylate	63	134
1634-04-4	Methyl tert-butyl ether [MTBE]	73	125
108-87-2	Methylcyclohexane	66	133
75-09-2	Methylene chloride	70	128
123-86-4	n-Butyl acetate	62	128
71-36-3	n-Butyl alcohol	55	131

104-51-8	n-Butylbenzene	70	128
103-65-1	n-Propylbenzene	73	125
91-20-3	Naphthalene	62	129
95-47-6	o-Xylene	77	123
99-87-6	p-Isopropyltoluene [p-Cymene]	73	127
76-01-7	Pentachloroethane	69	135
107-12-0	Propionitrile [Ethyl cyanide]	68	134
135-98-8	sec-Butylbenzene	73	126
100-42-5	Styrene	76	124
994-05-8	tert-Amyl methyl ether [TAME]	73	126
75-65-0	tert-Butyl alcohol	68	133
98-06-6	tert-Butylbenzene	73	125
127-18-4	Tertachloroethene	73	128
109-99-9	Tetrahydrofuran	61	135
108-88-3	Toluene	77	121
2037-26-5	Toluene-d8	85	116
156-60-5	trans-1,2-Dichloroethene	74	125
10061-02-6	trans-1,3-Dichloropropene	71	130
110-57-6	trans-1,4-Dichloro-2-butene	62	136
79-01-6	Trichloroethene	77	123
75-69-4	Trichlorofluoromethane [Freon-11]	62	140
108-05-4	Vinyl acetate	50	151
75-01-4	Vinyl chloride	56	135
1330-20-7	Xylene [total]	78	124

DoD Appendix C LCS Limits
Method 8260 Water Matrix

CAS ID	Analyte	Lower Control Limit (LCL)	Upper Control Limit (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	124
71-55-6	1,1,1-Trichloroethane	74	131
79-34-5	1,1,2,2-Tetrachloroethane	71	121
79-00-5	1,1,2-Trichloroethane	80	119
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane	70	136

	[Freon-113]		
75-34-3	1,1-Dichloroethane	77	125
75-35-4	1,1-Dichloroethene	71	131
563-58-6	1,1-Dichloropropene	79	125
87-61-6	1,2,3-Trichlorobenzene	69	129
96-18-4	1,2,3-Trichloropropane	73	122
526-73-8	1,2,3-Trimethlybenzene	82	120
120-82-1	1,2,4-Trichlorobenzene	69	130
95-63-6	1,2,4-Trimethylbenzene	76	124
96-12-8	1,2-Dibromo-3-chloropropane	62	128
106-93-4	1,2-Dibromoethane	77	121
95-50-1	1,2-Dichlorobenzene	80	119
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	81	118
540-59-0	1,2-Dichloroethene	79	121
78-87-5	1,2-Dichloropropane	78	122
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	70	136
108-70-3	1,3,5-Trichlorobenzene	75	130
108-67-8	1,3,5-Trimethylbenzene	75	124
106-99-0	1,3-Butadiene	43	158
541-73-1	1,3-Dichlorobenzene	80	119
142-28-9	1,3-Dichloropropane	80	119
542-75-6	1,3-Dichloropropene	77	123
106-46-7	1,4-Dichlorobenzene	79	118
105-05-5	1,4-Diethylbenzene	79	118
123-91-1	1,4-Dioxane	59	139
544-10-5	1-Chlorohexane	76	124
540-84-1	2,2,4-Trimethylpentane [Isooctane]	58	132
594-20-7	2,2-Dichloropropane	60	139
75-85-4	2-Butanol	66	120
78-93-3	2-Butanone (MEK)	56	143
126-99-8	2-Chloro-1,3-butadiene	65	135

110-75-8	2-Chloroethyl vinyl ether	51	139
95-49-8	Chlorotoluene	79	122
591-78-6	2-Hexanone	57	139
91-57-6	2-Methylnaphthalene	17	142
79-46-9	2-Nitropropane	49	136
67-63-0	2-Propanol [Isopropyl alcohol]	56	142
624-95-3	3,3-Dimethyl-1-butanol	49	133
460-00-4	4-Bromofluorobenzene	85	114
106-43-4	4-Chlorotoluene	78	122
108-10-1	4-Methyl-2-pentanone [MIBK]	67	130
67-64-1	Acetone	39	160
75-05-8	Acetonitrile	50	142
107-02-8	Acrolein [Propenal]	39	155
107-13-1	Acrylonitrile	63	135
107-05-1	Allyl chloride	68	130
71-43-2	Benzene	79	120
100-44-7	Benzyl chloride	42	138
108-86-1	Bromobenzene	80	120
74-97-5	Bromochloromethane	78	123
75-27-4	Bromodichloromethane	79	125
75-25-2	Bromoform	66	130
74-83-9	Bromomethane	53	141
75-15-0	Carbon disulfide	64	133
56-23-5	Carbon tetrachloride	72	136
108-90-7	Chlorobenzene	82	118
124-48-1	Chlorodibromomethane	74	126
75-45-6	Chlorodifluoromethane	40	129
75-00-3	Chloroethane	60	138
67-66-3	Chloroform	79	124
74-87-3	Chloromethane	50	139
156-59-2	cis-1,2-Dichloroethene	78	123
10061-01-5	cis-1,3-Dichloropropene	75	124
1476-11-5	cis-1,4-Dichloro-2-butene	57	146

110-82-7	Cyclohexane	71	130
1868-53-7	Dibromofluoromethane	80	119
74-95-3	Dibromomethane	79	123
75-71-8	Dichlorodifluoromethane [Freon-12]	32	152
75-43-4	Dichlorofluoromethane	72	131
60-29-7	Diethyl ether	68	129
108-20-3	Diisopropyl ether	67	128
64-17-5	Ethanol	48	151
141-78-6	Ethyl acetate	55	138
97-63-2	Ethyl methacrylate	72	126
637-92-3	Ethyl tert-butyl ether	70	127
100-41-4	Ethylbenzene	79	121
462-06-6	Fluorobenzene	80	116
142-82-5	Heptane	49	140
87-68-3	Hexachlorobutadiene	66	134
67-72-1	Hexachloroethane	72	134
110-54-3	Hexane	48	143
74-88-4	Iodomethane	69	131
78-83-1	Isobutyl alcohol	63	133
108-21-4	Isopropyl acetate [Acetic acid]	63	133
98-82-8	Isopropylbenzene	72	131
179601-23-1	m/p-Xylene [3/4-Xylene]	80	121
126-98-7	Methacrylonitrile	63	133
79-20-9	Methyl acetate	56	136
80-62-6	Methyl methacrylate	67	128
1634-04-4	Methyl tert-butyl ether [MTBE]	71	124
108-87-2	Methylcyclohexane	72	132
75-09-2	Methylene chloride	74	124
123-86-4	n-Butyl acetate	69	125
71-36-3	n-Butyl alcohol	59	131
104-51-8	n-Butylbenzene	75	128
109-60-4	n-Propyl acetate	76	126
103-65-1	n-Propylbenzene	76	126

91-20-3	Naphthalene	61	128
95-47-6	o-Xylene	78	122
99-87-6	p-Isopropyltoluene [p-Cymene]	77	127
76-01-7	Pentachloroethane	69	133
109-66-0	Pentane	16	134
107-12-0	Propionitrile [Ethyl cyanide]	64	136
135-98-8	sec-Butylbenzene	77	126
100-42-5	Styrene	78	123
994-05-8	tert-Amyl methyl ether [TAME]	68	128
75-65-0	tert-Butyl alcohol	68	129
762-75-4	tert-Butyl formate	65	132
98-06-6	tert-Butylbenzene	78	124
127-18-4	Tertachloroethene	74	129
109-99-9	Tetrahydrofuran	57	133
108-88-3	Toluene	80	121
2037-26-5	Toluene-d8	89	112
156-60-5	trans-1,2-Dichloroethene	75	124
10061-02-6	trans-1,3-Dichloropropene	73	127
110-57-6	trans-1,4-Dichloro-2-butene	43	140
79-01-6	Trichloroethene	79	123
75-69-4	Trichlorofluoromethane [Freon-11]	65	141
108-05-4	Vinyl acetate	54	146
75-01-4	Vinyl chloride	58	137
1330-20-7	Xylene [total]	79	121

Table 7. Summary of Control Limits: Surrogate and Matrix Spiking Compounds Percent Recovery†

#‡	COMPOUND	Water Matrix		Solid Matrix	
		LCL (%)	UCL (%)	LCL (%)	UCL (%)
2	1.2-DICHLOROETHANE-D4	66.4	124.8	70.0	136.3
26	TOLUENE-D8	82.5	118.4	84.0	138.0
43	4BROMOFLUOROBENZENE	78.4	119.6	59.0	122.8
16	1.1-Dichloroethene (CCC/MS)	59.9	145.0	59.0	172.0
30	Benzene (MS)	73.7	127.0	66.0	142.0
32	Trichloroethene (MS)	71.0	121.2	62.0	137.0
37	Toluene (CCC/MS)	71.4	127.6	59.0	139.0
47	Chlorobenzene (SPCC/MS)	75.0	130.0	60.0	133.0
n/a	Gasoline Range Organics	70.0	130.0	70.0	130.0

†: Results based on recovery data from 2001.

‡: Compound identification numbers listed are from calibration FR010910.M.

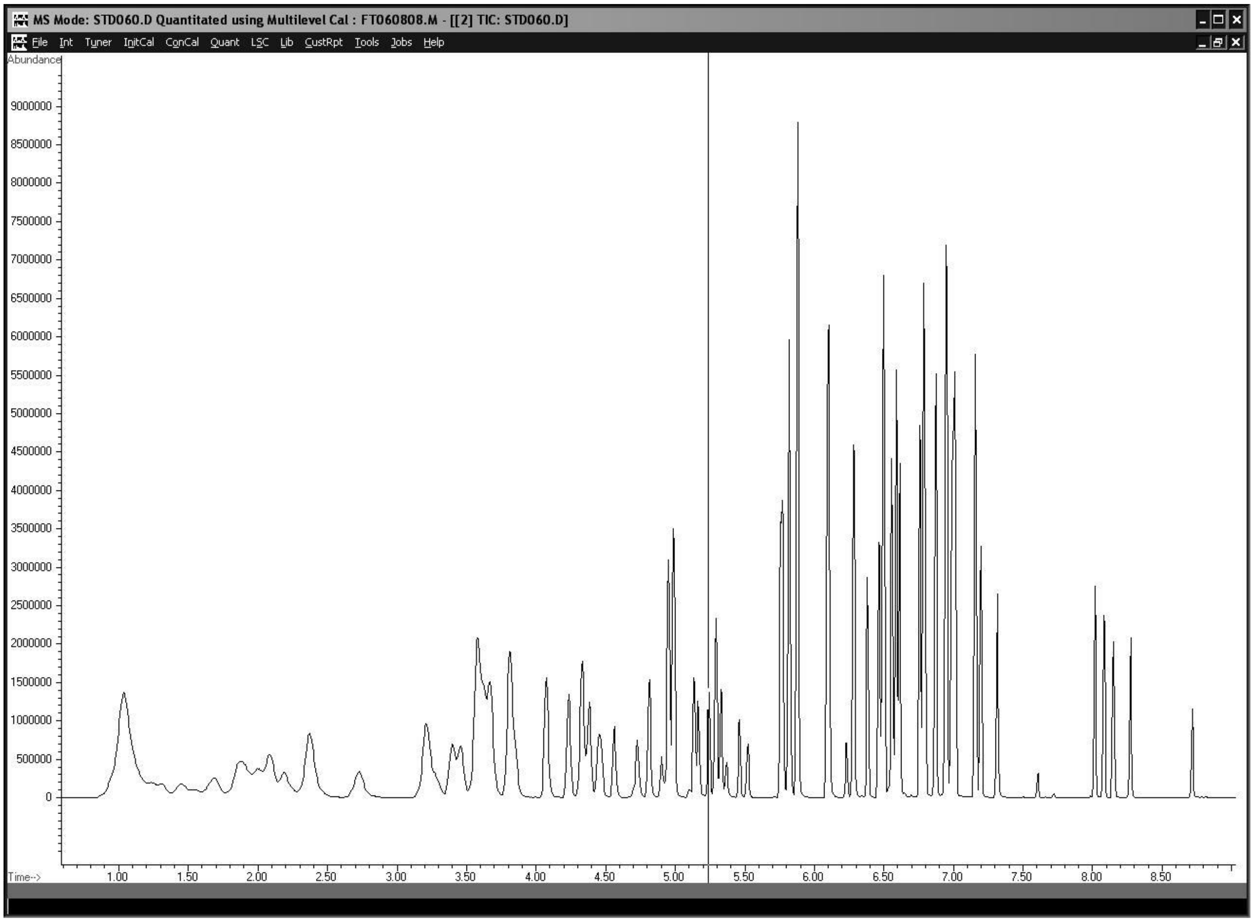
: For DoD projects, all target compounds must be included in the spikes. LCS acceptance criteria specified in the DoD QSM or in-house LCS control limits shall be used.

LCS Limits
EPA 624.1 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
71-55-6	1,1,1-Trichloroethane	70	130
79-34-5	1,1,2,2-Tetrachloroethane	60	140
79-00-5	1,1,2-Trichloroethane	70	130
75-34-3	1,1-Dichloroethane	70	130
75-35-4	1,1-Dichloroethene	50	150
95-50-1	1,2-Dichlorobenzene	65	135
107-06-2	1,2-Dichloroethane	70	130
78-87-5	1,2-Dichloropropane	35	165
541-73-1	1,3-Dichlorobenzene	70	130
106-46-7	1,4-Dichlorobenzene	65	135
110-75-8	2-Chloroethyl vinyl ether	0	225
107-02-8	Acrolein [Propenal]	60	140
107-13-1	Acrylonitrile	60	140
71-43-2	Benzene	65	135
75-27-4	Bromodichloromethane	65	135

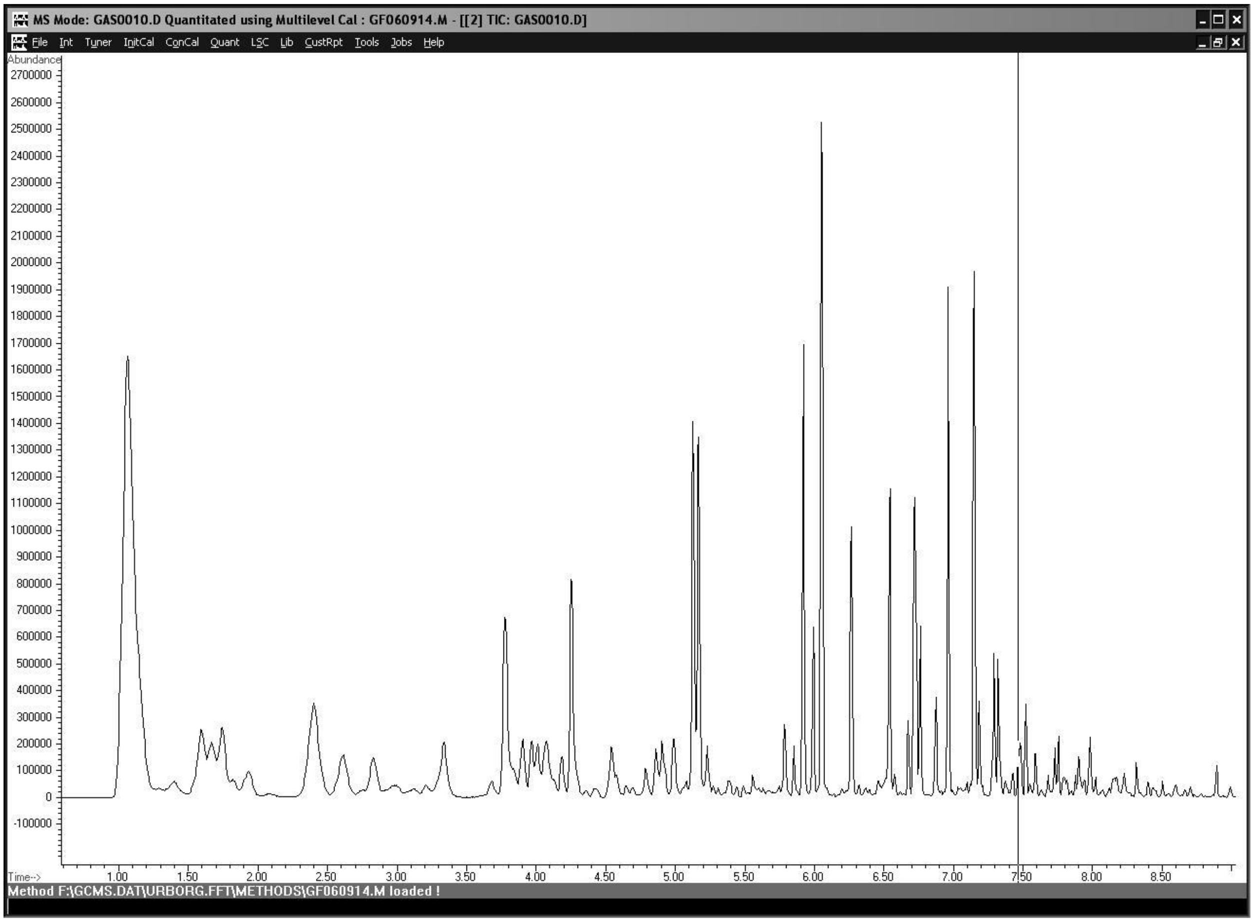
75-25-2	Bromoform	70	130
74-83-9	Bromomethane	15	185
56-23-5	Carbon tetrachloride	70	130
108-90-7	Chlorobenzene	65	135
124-48-1	Chlorodibromomethane	70	135
75-00-3	Chloroethane	40	160
67-66-3	Chloroform	70	135
74-87-3	Chloromethane	0	205
10061-01-5	cis-1,3-Dichloropropene	25	175
100-41-4	Ethylbenzene	60	140
75-09-2	Methylene chloride	60	140
127-18-4	Tetrachloroethene	70	130
108-88-3	Toluene	70	130
156-60-5	trans-1,2-Dichloroethene	70	130
10061-02-6	trans-1,3-Dichloropropene	50	150
79-01-6	Trichloroethene	65	135
75-69-4	Trichlorofluoromethane [Freon-11]	50	150
75-01-4	Vinyl chloride	5	195

Figure 1. Example Total Ion Chromatogram for a Midpoint VOA Calibration Standard[†]


MS Mode: STD060.D Quantitated using Multilevel Cal : FT060808.M - [[2] TIC: STD060.D]

[†]: Data file Std060.D (60 μg/L). GC/MS acquisition parameters are given by Table 4.

Figure 2. Example Total Ion Chromatogram for a Gasoline Range Organics Calibration Standard[†]



MS Mode: GAS0010.D Quantitated using Multilevel Cal : GF060914.M - [[2] TIC: GAS0010.D]

Method F:\GCMS.DAT\URBORG.FFT\METHODS\GF060914.M loaded !

[†]:GAS_010.D from calibration GF060914.M (1.0 mg/L). GC/MS acquisition parameters are given by Table 4.

STANDARD OPERATING PROCEDURE

POLYFLUORINATED COMPOUNDS (PFCS) LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY (LC/MS/MS) ASTM METHOD D7979 & ASTM METHOD D7968

APPROVALS:

Barbara Ball

02/06/2020

QA Officer Date

02/06/2020

Technical Director Date

Number	Description of Change	Date
001	Emergency Amendment Forms (additional compounds and soil prep)	02/06/2020
002		
003		
004		
005		
006		
007		
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

This SOP covers a method for analysis of selected polyfluorinated compounds (PFCs) in water and soil matrices by liquid chromatography/tandem mass spectrometry analysis. The samples are prepared in 50% methanol (sludge and soil samples are adjusted to pH of approximately 9-10 with ammonium hydroxide), optionally filtered, and then acidified with acetic acid (pH ~ 3-4) and analyzed by liquid chromatography/tandem mass spectrometry.

2.0 SUMMARY OF METHOD

A sample (5 mL for water and 2g for soil) is spiked with mass labelled analytes to be used as internals for the purpose of quantitation (all samples) and target PFC compounds (laboratory control and matrix spike samples), water samples are tumbled for 20 minutes after adding 5 mL of methanol. Acetic acid (10 µL) is added to all the samples to adjust to pH ~ 3-4 and the sample is analyzed by LC/MS/MS. For sludge samples, the pH is adjusted to ~ 9-10 (adding ~ 20 µl of ammonium hydroxide) before extraction and ~ 50 uL of acetic acid is needed for acidification. Soil samples are tumbled for 60 minutes after adding 5 mL of MeOH, 5 mL of DI water, and 20 µL pf Ammonium Hydroxide. 50 µL of Acetic acid is added to bring the pH to ~3-4 and the samples are centrifuged. Sample may be filtered before analysis using Acrodisc GxF/0.2µm GHP membrane syringe driven filter unit.

The target compounds are identified by comparing the dynamic multiple reaction monitoring (dMRM) transitions in the sample to the DMRM transitions in the standards (Appendix Table 5). Certain PFC analytes only have a primary DMRM transition that is used for identification and quantitation. The retention time (RT) for the analytes of interest must also agree with the RT of the calibration verification standard by ±5%. The target compounds are quantitated using the DMRM transitions of the target compounds utilizing isotopically diluted mass labelled isotopes used as internal standards for the purpose of quantitation. The response of the mass labelled internals should be 50-150% of the average of the initial calibration.

3.0 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, LC vials/caps, disposable pipettes, and other apparatus that lead to discrete artifacts or elevated baseline in the selected ion current profiles.

Matrix interferences may be caused by contaminants from the sample, sampling devices, or storage containers. The extent of matrix interferences will vary considerably from sample source to sample source, depending upon variations of the sample matrix.

All reagents and solvents should be of pesticide-residue purity or higher to minimize interference problems, preferably LC/MS grade.

Contaminants have been found in reagents, glassware, tubing, polytetrafluoroethylene (PTFE) LC vial caps, glass disposable pipettes, filters, degassers, and other apparatus that release polyfluorinated compounds. All of these materials are routinely demonstrated to be free from interferences by analyzing laboratory reagent and method blanks under the same conditions as the samples. All the supplies should be checked to determine the release of target analytes of interest. If found, measures should be taken to remove the contamination or data should be qualified.

The Liquid Chromatography system used should have components replaced, when possible, with materials known to not contain fluorinated target analytes of interest. In particular, PTFE lines should be replaced with PEEK™ tubing where possible and especially post-delay column.
Polyethylene LC autosampler vial caps or target analyte-free vial caps should be used.
Polyethylene disposable pipettes or target analyte-free pipettes should be used.
All disposable pipettes should be checked for release of target analytes of interest.
Degassers are important to continuous LC operation and are most commonly made of fluorinated polymers. To enable use, a delay column is placed after the degasser and before the sample injection valve.

4.0 APPARATUS AND MATERIALS

Liquid Chromatograph (LC) System – Agilent 1290 infinity II with flow-through needle design.
Analytical Column - An analytical column, Zorbax Eclipse Plus C18 rapid resolution HD 3.0x50mm 1.8-micron
Isolator Column – Zorbax Eclipse Plus C18 rapid resolution 4.6x50mm 3.5-micron
Mass Spectrometer (MS) System – Agilent 6470 and 6495 triple quadrupole mass spectrometer. A mass spectrometer capable of DMRM analysis with fast enough cycle time to obtain at least 10 scans over a peak is needed with adequate sensitivity.
Data System – Masshunter software must be interfaced to the LC/MS/MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.
Analytical balance accurate to ±0.1% of sample mass.
Vials Agilent 1ml polypropylene autosampler vials or Agilent 2ml amber autosampler vials
Agilent Polyethylene autosampler vial caps
Syringe – 10-25 mL filter-adaptable polypropylene or polyethylene disposable syringe rinsed with methanol.

15 mL polypropylene tubes

4ml narrow mouth polypropylene containers

Gases - ultrapure nitrogen and nitrogen

Class A volumetric glassware
Microsyringes – Hamilton microsyringes of various sizes
Glass syringe- 5ml Glass syringe.
Acrodisc GxF/0.2µm GHP membrane syringe-driven filter unit. The Acrodisc filters in combination with the disposable syringes are washed with 20 mL methanol prior to use.
Polyethylene disposable pipettes

5.0 REAGENTS

NOTE: Standard mixes are available from Wellington Labs and Absolute and contain each analyte at a given concentration, either at 1 or 2 µg/mL. The target spike mix concentrations can be changed to account for the rigidity in standard sources when using mixes. The concentration of PFBA may be at the same concentration as the other analytes in all solutions. If the sensitivity for this analyte at the lower concentrations is poor, the reporting limit will need to be adjusted. Also, other isotopically labeled compounds may be used as isotopically diluted internals as the number of available options is a rapidly changing landscape.

Deionized (DI) water taken from the source in the volatiles department as it has a carbon filter immediately preceding the tap.

Acetonitrile, LC/MS grade or equivalent (CAS # 75-05-8).

Methanol, LC/MS grade or equivalent (CAS# 67-56-1)

Isopropyl alcohol, LC/MS grade of equivalent (CAS # 67-63-0)

Ammonium hydroxide (CAS# 1336-21-6)

Ammonium acetate (CAS# 631-61-8)

Acetic acid (CAS # 64-19-7)

Polyfluoroalkyl sulfonates (PFAS)

- Absolute mix 64029 (PFOA-DOD)

Polyfluoroalkyl carboxylic acids (PFAC)

- Absolute mix 64029 (PFOA-DOD)

Polyfluorinated sulfonamides and sulfonamidoacetic acids

- Absolute mix 64029 (PFOA-DOD)

PFC mass labelled mix for isotopic dilution utilizing internal calibration for quantitation.

- Wellington mix MPFAC-24ES

Second source standard

- Wellington mix PFAC-30PAR

CAUTION: All standards must be kept away from PFC-containing packaging and materials used in preparation and storage. In order to prevent standard solutions from degrading, all standard solutions are stored at < 6º C in the refrigerator.

The instructions for the preparation of stock standards, spiking solutions, and QC batch samples are listed below.

The calibration levels and second source calibration check are prepared prior to calibration. Reagent blank and all batch QC are made for each batch of field samples. The CV may be taken from the appropriate calibration standard as monitoring the stability over time may provide necessary insight into sample behavior. The entire analysis with dilutions should be done within 14 days of sample preparation, if exceeded it shall flagged in the report. Should field and/or batch QC samples require re-analysis it will be included in a new batch with accompanying quality control. If a sample requires dilution it may be done from the already processed sample and the corresponding method blank and the reporting limit check should be run with it to verify instrument sensitivity. Alternatively, the reporting limit check from a new batch may be used if a new preparatory batch is being analyzed as the efficacy of the original preparation will have already been verified.

Surrogate spiking solution

- A surrogate spiking solution containing fourteen isotopically-labeled PFCs is added to all samples. This surrogate spiking solution is added to achieve a concentration of 160 ng/L in a 5 mL water sample (i.e. 40 µL of a 20 µg/L solution prepared in methanol is added to a 5 mL sample). Example dilution: The PFC surrogate mix solutions were purchased from Wellington and 40ul of the stock solution (1000ug/L) is added to 1960ul methanol producing a 20 µg/L spiking solution.

MS/MSD and LCS/LCSD spiking solution

- Each MS/MSD or LCS/LCSD sample is spiked with target PFCs to achieve a concentration of 100 ng/L in a 5 mL water sample. This is achieved by making a 5ug/L solution from the stock solution at 1000ug/L by adding 15ul of the stock solution to 2985ul of methanol and spiking 100ul of the 5ug/L solution into 5ml of water (sample or LCS).

Reporting limit check spiking solution

- The reporting limit check sample is prepared by spiking a 5 mL water sample with target analytes at the reporting limit. Using the 5ug/L working standard spike 10ul into 5ml of water. Also as the reporting limit for PFBA is 20ng/L it may be necessary to make a second reporting limit check sample at twice the spike amount as PFBA may not always pass the lower spike check.

Calibration standards

- Calibration standards are prepared as shown in Table 4. All calibration standards should contain 50:50 methanol and water with 0.1% acetic acid.

Second source calibration check solution

- A second source calibration check solution should be prepared and analyzed at a concentration inside the calibration curve and at the same composition of the calibration solvent.

- NOTE: The second source standard may contain PFOS and PFHxS as linear compounds as opposed to branched. PFOS and PFHxS are calibrated as branched compounds as that's how they are likely to appear in nature.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

For water, 5.0 mL grab samples are collected in 15 mL polypropylene containers. For soil, 2.0 g samples are collected in 15 mL polypropylene containers. Extra samples must be collected in order to analyze duplicate and matrix spike samples for QA/QC purposes upon client request.

CAUTION: PTFE containers and contact surfaces with PTFE must be avoided. Field blanks are needed to follow conventional sampling practices. Surface binding of target compounds to collection devices may bias data and must be minimized. Each QC sample must be collected in its own container, including matrix spike, matrix spike duplicate, and duplicate samples.

Sample containers will be checked for PFCs by lot prior to distributing to clients. The lab PFC free DI water, is tested prior to distribution and is tracked by lot.

Since surface binding of target compounds may bias data, it is best to collect a 5.0 mL sample in a graduated 15 mL polypropylene BD Falcon tube in the field so that the whole sample is processed in the lab.

CAUTION: Taking a sub-sample is not recommended in this SOP, whether in the field during sample collection, or in the lab at the bench.

In order to have accurate volumes, the weight of the 15 mL polypropylene BD Falcon tube should be taken before and after sample processing in order to calculate an exact volume or weight. The density of water is assumed to be 1.0 g/mL unless otherwise instructed by the client/sampler. Efforts are being made with distributors to provide pre-weighed tubes and this methodology is intended as an intermediate solution.

If a larger sample is collected in the field, a 5.0 mL or 2.0 g aliquot of that sample will be processed, not taking into account any PFCs that may adhere to the surface of the original container. This practice is not recommended. This section is in this SOP in the event that field samples are taken in large containers or for another project as the sampling protocol and containers used is still a subject of confusion for many. The use of such containers will be noted in the report.

All samples are iced or refrigerated at < 6°C from the time of collection until sample analysis. At the laboratory, prepared samples (diluted and filtered) are stored in the refrigerator at < 6°C at all times while not being analyzed. Holding times have not yet been established for these analytes in various matrices. A preliminary holding time of 28 days to extraction and 30 days from extraction to analysis is used as a guide until an extensive holding time study is completed.

7.0 PROCEDURE

CAUTION: PFC contamination at low levels is common in laboratory reagents, supplies, and equipment. A reagent blank (50:50 methanol and water solution containing 0.1 % acetic acid) should be prepared and analyzed prior to the preparation and analysis of samples to ensure an undetectable or negligible PFC presence that will not affect quantitation at the reporting limits.

A. Sample preparation

Each batch of samples (20 field samples plus QC) shall contain at least, a Method Blank, a Laboratory Control Sample and Laboratory Control Sample Duplicate, a Reporting Limit Check Sample and upon request a Duplicate, a Matrix Spike and Matrix Spike Duplicate, provided enough individual sample containers are submitted.

1. Reagent Blank

   A reagent blank (50:50 methanol and water solution containing 0.1 % acetic acid) should be prepared and analyzed prior to the preparation and analysis of samples to ensure an undetectable or negligible PFC presence that will not affect quantitation at the reporting limit. However, it is noted that this pre-emptive check is not always possible and is only mandatory when only one sample container is submitted, otherwise the method blank provides all of the appropriate information and detections outside of the project's acceptable limits will result in re-analysis utilizing a second sample container.
2. Method blank

   The method blank is prepared by measuring 5 mL of Deionized water or 2 g of blank sand in a 15 mL polypropylene tube, spiking with 100 µL of the surrogate spike solution, and then taking it through the sample preparation procedure.
3. Laboratory control sample/laboratory control sample duplicate

   Add 5 mL of Deionized water or 2 g of blank sand to each of two 15 mL polypropylene centrifuge tubes. The samples are spiked with 100 µL of surrogate spiking solution, 100 µL of the working spike solution (10ug/L) and then taking it through sample preparation.
4. Reporting limit check

   Add 5 mL of Deionized water or 2 g of blank sand to a 15 mL polypropylene centrifuge tube. The sample is spiked with 100 µL of surrogate spiking solution and 10 µL of the working spike solution (5ug/L) and then taking it through sample preparation.
5. Sample and sample duplicate

   The 5.0 mL water sample or 2.0 g soil sample collected in a 15 mL polypropylene centrifuge tube is allowed to warm to room temperature before spiking and sample processing. Each sample is spiked with 100 µL of surrogate spiking solution and then taking it through sample preparation.
6. Matrix spike/matrix spike duplicate

   Additional field-collected 5.0 mL water samples or 2.0 g soil sample in each of two 15 mL polypropylene centrifuge tubes are used for the MS and MSD The samples are spiked with 100 µL of surrogate spiking solution, 100 µL of the working spike solution (5ug/L) and then taking it through sample preparation.

B. Sample preparation – Step II

1. To all samples, add 5 mL of methanol and hand shake/vortex for ~ 2 minutes or tumble for 20 minutes. For soil samples, add 5 ml DI water, 5 ml MeOH, and 20 µL ammonium hydroxide and tumble for 60 minutes.
2. After vortexing, the pH of sludge samples is adjusted to pH ~ 9-10 with ammonium

hydroxide (~ 20 µL) and hand shaken/vortexed again for ~ 2 minutes. This step is not required for water, wastewater, influent, or effluent unless high percent solids are present or low recoveries were observed historically when no base was added.

3. The samples may be filtered through an Acrodisc GxF/0.2µm GHP membrane syringe-driven filter unit to remove particulates in the samples. 10 uL of acetic acid is then added to all water and 50 µL to all soil samples to adjust the pH ~ 3-4 after filtration. Approximately a 0.5 mL aliquot of that solution is transferred to a polypropylene or amber glass LC autosampler vial and may then be analyzed. The final volume of the solution is assesed by the graduated tube and dilution factor calculated. Soils are corrected for percent moisture.

CAUTION: Use only polyethylene caps to seal the LC autosampler vials. All prepared LC autosampler vials should only be injected once since some of the analytes or solvent may evaporate after the vial cap is pierced; the polyethylene caps are not self-sealing.

4. The Acrodisc filters are washed in conjunction with the disposable syringes with at least 20 mL of methanol prior to use.

C. Analytical procedure

1. Sample analysis procedure

Instrument conditions for LC/MS/MS are described in Figure 2. The target compounds are identified by comparing the dynamic multiple reaction monitoring (DMRM) transitions in the sample to the DMRM transitions in the standards. A confirmatory transition is available for most of the analytes. The retention time (RT) for the analytes of interest must also agree with the RT of the calibration verification standard by ±5%. The target compounds are quantitated using the primary DMRM transitions of the target compounds utilizing isotopic internal calibration.

If the absolute amount of a target compound in a sample exceeds the working calibration range, the sample must be diluted and re-analyzed. This should be done by diluting the sample with the associated method blank. It is acknowledged that this negates the fundamental benefits of Isotopic dilution but this is a known problem with such procedures and due to this potentiality, all efforts must be given to have as wide a calibration range as possible, accepting that results beyond this are by magnitude less accurate.

2. Qualitative and quantitative analysis

The quantitation of the target analytes and surrogates is accomplished with Masshunter software. An isotopic dilution internal calibration is used. The quantitation method is set as an internal calibration using the realative peak areas in ppt units (ng/L).

The DMRM analysis provides qualitative identification by isolating the precursor ion and fragmenting it into the product ions, which are then used to calculate ion ratios that can be compared between samples and standards to confirm the identification of the analyte. The retention times of the analytes are also monitored between samples and standards to further confirm the identification. The signal/noise ratio for all peaks shall be ≥ 3. If not, it should be investigated, the system re-optimized, and, if not corrected, the reporting limit must be raised to account for the lack of sensitivity and mentioned in the narrative.

If there are two or more analyses for a sample due to dilution, the analyst must determine which is best to report based on evaluation of all available data relevant to a given sample. The target compounds are identified by comparing the primary DMRM transition and its confirmatory DMRM transition in the sample to the DMRM transitions in the standards. Confirmatory transitions are available for most of the analytes. The primary/confirmatory DMRM ion ratio shall meet the criteria established by the most recent calibration verification by ± 30%. This ratio will vary depending on the instrument acquisition parameters. Due to sensitivity issues, some ion ratios may not meet the ± 30% ion ratio at the lower concentrations. Analyst experience is important in determining if outliers are due to indeterminate interference resulting in elevated reporting limits and an associated flag or report the result acknowledging these outliers.

NOTE: Depending on sensitivity and matrix interference issues, a confirmatory DMRM transition might be used as a primary DMRM transition for quantitation during the analysis. This shall be explained in the case narrative if these changes are made.

The confirmatory ion ratios in “weathered samples” may not match the ion ratios in the calibration standards for the target analytes that may contain isomeric mixtures. The complete isomer grouping shall be quantitated consistently for all samples. These differences for PFHxS and PFOS can be found in groundwater samples and may either be the cause of different compositions used, weathering, degradation, or the affinity of the branched isomers to be more soluble than the linear in water and leach into the water from the soil at a higher rate than the linear.

Regression fits should exclude the point of origin (X=0, Y= 0) and be weighted by 1/concentration in order to increase the accuracy of the curve at the lower concentrations. For linear regression to be used, the coefficient of determination, r^2, should be > 0.99 for each analyte, and for quadratic regression, the r^2 should be > 0.99. If the low and/or high points are excluded, a six-point curve is acceptable for quadratic fit and five point for a linear fit, but the calibration range and reporting limits must be modified to reflect this change. Points can be dropped from both the high and/or the low end of the curve as long as the reporting range is adjusted accordingly. The calculated calibration level concentrations used to generate the curve should be < ±30% deviation from the concentration of the generated curve; if this is exceeded, a new calibration curve must be generated or the data flagged accordingly.

The retention time window of the DMRM transitions must be within 5% of the retention time of the analyte in the calibration verification standard. If this is not true, the calibration curve needs to be re- analyzed to see if there was a shift in retention time during the analysis and the sample needs to be re-injected. If the retention time is still incorrect in the sample, the analyte is referred to as an unknown.
If there is no confirmatory transition for the analyte and the presence of the analyte in the sample cannot be confirmed with a primary transition and retention time, the analyte is listed as a non-detect or as having a matrix interference present.

D. Instrument mass calibration and standardization procedures

1. Mass calibration of mass spectrometer
   The Agilent 6470 is autotuned using the Agilent Masshunter software and tuning protocols. The autotune is set to unit resolution for both positive and negative polarities. The tuning solution used is the Agilent ESI-L low concentration tuning mix. Part #G1969-85000.

   A Check-tune should be run every 24 hours of operation. An example check-tune is in Figure 3.
2. Mass calibration criteria and parameters
   a) The instrument must be calibrated over the calibration range for all analytes.

   b) Instrument operating conditions: Analytical conditions (acquisition methods) are listed in Figure 2.

   c) Calibration

      i. **Initial calibration**: The initial calibration contains a ten-point curve. The sensitivity and calibration curve responses may vary. At a minimum, a five point linear or a six-point quadratic calibration curve will be utilized for all analytes. The calibration must be verified at the beginning and end of every 24 hour period. It is strongly advised to run intermediate ending calibration verifications when more than one set of batch qc and samples is run.

      ii. **Second source calibration check**: The second source calibration check, analyzed after an initial calibration at or near the midpoint of the calibration curve, should be run. The second source calibration check should yield measured concentrations within

± 30% of the expected concentrations for all target compounds present in the standard. If the measured concentration of any of these compounds varies from the expected concentration by > ± 30%, the results for the compounds exceeding these criteria are qualified accordingly.

iii. **Calibration verification (CV)**: At the beginning and end of any 24 hour period of analysis a calibration verification standard at or near the lower quadrant of the calibration curve must be run. If the high end calibration points are utilized the calibration verification should still be analyzed in the lower quadrant of the curve as this is closer to a concentration that is typically more project sensitive. If project goals dictate, a CV in the higher portion of the curve may also be analyzed or used as the ending CV. If the measured concentration of any of the analytes varies from the expected concentration by > 30%, the data for the failing analytes are qualified as estimated.

iv. **Autosampler schedule/analytical sequence**: Prepare a sequence that includes all relevant items. Beginning CV, Reporting limit check, LCS, LCSD, and Method Blank. (If a reagent blank is to be utilized prior to sample preparation this is run first.) Then all accompanying samples followed by and ending CV.

E. Equations

1. Example calculation of sample concentration reported

$$\frac{V_f}{V_i}(C_u) = C_f$$

Where:
V_f = Final Volume
V_i = Initial Volume
C_u= Uncorrected Concentration
C_f = Final Concentration (Corrected for Dilution)

2. Relative Percent Difference:

$$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

3. Spike Recovery Percent Recovery:

$$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (un-spiked) result
SA = Spike added

8.0 QUALITY CONTROL

Internals (Isotopic Dilution)

- All samples are spiked with an internal (isotopic dilution) standard spiking solution as described in Section 4. The recovery limits are set to 50-150% from the average of the initial calibration.
- The list of mass labelled compounds utilized is given in Table 8.

Method blank and reagent blank samples

- For every 20 field samples, a method blank will be prepared in reagent water to investigate for contamination throughout sample preparation, extraction, and analysis. A reagent blank is prepared each day with a 50:50 methanol and water solution containing 0.1 % acetic acid for every 20 samples (or a batch) to investigate for system/laboratory contamination.
- The concentration of target analytes in the blank shall be less than half the reporting limit or the associated data shall be qualified for high bias due to blank contamination. Alternatively, the reporting limit in the associated field sample(s) can be raised to three times the blank contamination concentration.

Reporting limit check samples

- For every 20 field samples, a reporting limit check sample will be prepared in reagent water and spiked at the reporting limit as described in Section 4. to verify that the target analytes are present and can be qualitatively identified at the reporting limit. The recovery criteria for the reporting limit check sample is 50-150%.
- If the target analytes are not present or biased low in the reporting limit check sample, the data for all non-detects are qualified if detected up to a passing LCS concentration level. If the recovery is biased high, non-detects in field samples are not qualified, but detects are qualified to the level of a passing LCS concentration.

Laboratory control samples

- For every 20 field samples, at least one LCS/LCSD pair will be prepared in reagent water and spiked at the LCS/LCSD level as described in Section 4. to monitor spike accuracy and method performance in a clean matrix. The percent recovery limits for each target compound are set to 70-130%.

Matrix spike and Dup samples

- Upon client request and with adequate sample containers every 20 field samples, at least one MS/MSD or MS/DUP pair will be prepared in a field sample matrix and spiked at the LCS/LCSD level as described in Section 4. to monitor spike accuracy and method performance in a sample matrix. The percent recovery limits for each target compound are set to 70-130%

9.0 METHOD PERFORMANCE

The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

Symptom: inadequate abundance or sensitivity
Dirty or contaminated ion source, electron multiplier, or quadrupole rod surfaces.
Potentials of ion source elements at wrong values due to open or short circuits.
Faulty ion source electronics, detector electronics, or power supply.

Symptom: improper isotope ratios
High "background" levels of undesired substances (contamination from earlier sample injections) which contribute additional abundance at the isotope mass. Bake out the ion source assembly and condition the column.
Resolution of adjacent masses set improperly/higher than normal ratios due to poor resolution (peaks too wide) or lower ratios due to over resolution (narrow peaks).

Symptom: poor reproducibility
Loose or intermittent connection either to a printed circuit or to one or more ion source or quadrupole elements inside the analyzer assembly.

Symptom: high background
Dirty or contaminated ion source, electron multiplier, or quadrupole rod surfaces.
"Yesterday's" samples - There is the possibility that some previously injected sample can still be present in the vacuum system long after it was thought to be evacuated. This phenomenon depends on sample volatility, temperature, etc.

Contamination in a recently cleaned vacuum system - After any venting of a vacuum system for maintenance, there is the potential for introducing new substances into the vacuum system. Some substances are normal and can be pumped out, while others require more cleaning or baking.
Solvents used in the cleaning process - These will be present for a while but should be pumped out as heat is applied to the vacuum system.
Water absorbed on the metal surfaces while vented - This will pump out with heat.
"Fingerprints" - Heavy organic substances from inadequate clean room procedures may not be pumped out and may require source cleaning.

Symptom: mass spectrometer does not respond.
The mass spectrometer electronics are not on; check the switch.
Secondary fuse blown - Check the secondary fuses on the rear of the mass spectrometer and replace the faulty fuse(s).
Board failure
Communication loss - reboot mass spectrometer, PC, and LC.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit’s Waste Management Plan and Handbook.

13.0 DEFINITIONS

Method Detection Limit (MDL): The minimum concentration of analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known 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. 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.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate 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 (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

ASTM Type I Water: Shall conform to ASTM Standard D1193 specifications.

Reagent Water: Reagent water is defined as water with no interferants at or near the RL for all reagent compounds. The in-house Milli-Q water has been found acceptable for use. It is tested for each batch of samples by using it as a Method Blank.

DMRM Transition: Dynamic multiple reaction monitoring transition.

14.0 REFERENCES

ASTM D7979-19

ASTM D7968-17a

Table 1. Method Parameters

Full Name	Acronym	Molecular Formula	CAS #	MDL (ppt)	RL (ppt)
Perfluorobutanoic Acid	PFBA	C_3F_7COOH	375-22-4	5.21	20
Perfluoropentanoic Acid	PFPeA	C_4F_9COOH	2706-90-3	4.86	10
4:2 Fluorotelomer Sulfonic Acid	4:2 FTSA	$C_4F_9CH_2CH_2SO_3$	757124-72-4	1.61	10
Perfluorohexanoic Acid	PFHxA	$C_5F_{11}COOH$	307-24-4	1.45	10
Perfluorobutane sulfonic Acid	PFBS	$C_4F_9SO_3H$	375-73-5	1.56	10
Perfluoroheptanoic Acid	PFHpA	$C_6F_{13}COOH$	375-85-9	2.14	10
Perfluoropentane Sulfonic Acid	PFPeS	$C_5F_{11}SO_3H$	2706-91-4	3.31	10
6:2 Fluorotelomer Sulfonic Acid	6:2 FTSA	$C_6F_{13}CH_2CH_2SO_3$	27619-97-2	2.95	10
Perfluorooctanoic Acid	PFOA	$C_7F_{15}COOH$	335-67-1	1.16	10
Perfluorohexane Sulfonic Acid	PFHxS	$C_6F_{13}SO_3H$	355-46-4	2.46	10
Perfluorohexane Sulfonic Acid - Linear	PFHxS-LN	$C_6F_{13}SO_3H$	355-46-4	2.46	10
Perfluorohexane Sulfonic Acid - Branched	PFHxS-BR	$C_6F_{13}SO_3H$	355-46-4	2.46	10
Perfluorononanoic Acid	PFNA	$C_8F_{17}COOH$	375-95-1	1.20	10
8:2 Fluorotelomer Sulfonic Acid	8:2 FTSA	$C_8F_{17}CH_2CH_2SO_3$	39108-34-4	4.02	10
Perfluoroheptane Sulfonic Acid	PFHpS	$C_7F_{15}SO_3$	375-92-8	5.52	10
Perfluorodecanoic Acid	PFDA	$C_9F_{19}COOH$	335-76-2	5.14	10
N-Methyl Perfluorooctane Sulfonamide	N-MeFOSA	$C_8F_{17}SO_2N(CH_3)CH_2COOH$	2355-31-9	3.58	10
N-Ethyl Perfluorooctane Sulfonamidoacetic Acid	EtFOSAA	$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$	2991-50-6	4.32	10
Perfluorooctane Sulfonic Acid	PFOS	$C_8F_{17}SO_3H$	1763-23-1	3.96	10
Perfluorooctane Sulfonic Acid - Linear	PFOS-LN	$C_8F_{17}SO_3H$	1763-23-1	3.96	10
Perfluorooctane Sulfonic Acid - Branched	PFOS-BR	$C_8F_{17}SO_3H$	1763-23-1	3.96	10
Perfluoroundecanoic Acid	PFUnDA	$C_{10}F_{21}COOH$	2058-94-8	1.05	10
Perfluorononane Sulfonic Acid	PFNS	$C_9F_{19}SO_3H$	68259-12-1	3.70	10
Perfluorododecanoic Acid	PFDoDA	$C_{11}F_{23}COOH$	307-55-1	1.85	10
Perfluorodecane Sulfonic Acid	PFDS	$C_{10}F_{21}SO_3H$	335-77-3	1.90	10
Perfluorotridecanoic Acid	PFTrDA	$C_{12}F_{25}COOH$	72629-94-8	2.06	10
Perfluorooctane Sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	754-91-6	2.44	10
Perfluorotetradecanoic Acid	PFTeDA	$C_{13}F_{27}COOH$	376-06-7	3.03	10
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	$C_{10}HF_{20}ClSO_4$	763051-92-9	2.4	10
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	C8HF16ClSO4	756426-58-1	2.2	10
4,8-dioxa-3H-perfluorononanoic acid	ADONA	C7H2F12O4	919005-14-4	2.8	10
Hexafluoropropylene oxide dimer acid	HFPO-DA	C6HF11O3	13252-13-6	2.5	10

Table 2. Quality Control

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
Tune Check	24 hour	±0.5 amu	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
Calibration Verification (CV)	At the beginning and end of any 24 hour period of analysis	70-130%	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
Reporting Limit (RL) check	20 samples	50-150%	Not Applicable
LCS and MS	20 samples	70-130%	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	30% RPD	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	<1/2 RL	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) should result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard (Isotopic Dilution)	All samples	50-150% (from average of initial calibration)	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate

Table 3. Standard Prep

PFA0118(10,000ng/L)	5ug/L
PFA0118	15ul
Meoh	2985ul

PLIS0118-1(20ug/L)	8ug/L
PLIS0118-1	240ul
Meoh	29.76ml

ICV	400ppt
PFA0917(1000ng/L)	480ul
PLIS0118-1(20ug/L)	20ul

Table 4. Preparation of Calibration Standards

1000ppt	5ml meoh	5ml H20	100ul (8ug/L) ISD	100ul (10:1 PFA)
	blank	**1000ppt**		
100ppt	450ul	50ul		
	blank	**1000ppt**		
1000ppt		pipette		
400ppt	300	200		
200ppt	400	100		
100ppt	450	50		
50ppt	475	25		
	blank	**100ppt**		
20ppt	400	100		
10ppt	450	50		
5ppt	475	25		
2ppt	490	10		
1ppt	495	5		
0.5ppt	497.5	2.5		
10000ppt	1980ul	PFA(1000ug/L) 20ul		
IPFA (10ug/L)	1980ul	IPFA(1000ug/L) 20ul		
ICV (400ppt)	480ul	IPFA(10ug/L) 20ul		
ISD mix (8ug/L)		Meoh 29.76ml	PLIS (1000ug/L) 240ul	
MS mix (5ug/L)		2985ul	PFA (1000ug/L) 15ul	

Table 5. Retention Times and MRM Ions

Analyte	**Primary/Confirmatory**	**MRM Transition**	**Retention Time (Minutes)**	**Primary/ Confirmatory SRM Area Ratio**
PFTeDA	Primary	713.0→669.0	13.577	7.5
	Confirmatory	713.0→169		
PFTrDA	Primary	663.0→619.0	12.925	10.7
	Confirmatory	663.0→169.0		
PFDoDA	Primary	613.0→569	12.210	17.2
	Confirmatory	613.0→268.7		
PFUnA	Primary	563.0→519	11.496	18.1
	Confirmatory	563.0→219		
PFDA	Primary	513.0→469.0	10.780	28.4
	Confirmatory	513.0→218.7		
PFDS	Primary	599.0→80.0	12.650	65.5
	Confirmatory	599.0→99.0		
PFOS	Primary	499.0→80.0	11.120	48.8
	Confirmatory	499.0→99.0		
PFNA	Primary	463.0→419.0	10.050	12.1
	Confirmatory	463.0→169.0		
PFNS	Primary	548.9→ 79.9	11.943	98.8
	Confirmatory	548.9→ 98.9		
PFOA	Primary	413.0→369	9.311	23.2
	Confirmatory	413.0→169		
PFHpS	Primary	448.9→ 79.7	10.435	101.8
	Confirmatory	448.9→ 98.7		
PFHxS	Primary	399.0→80.0	9.564	42.6
	Confirmatory	399.0→99.0		
PFHpA	Primary	363.0→319	8.531	63.9
	Confirmatory	363.0→169		
PFHxA	Primary	313.0→269	7.651	2.6
	Confirmatory	313.0→119.0		
PFBS	Primary	299.0→80.0	7.806	47.0
	Confirmatory	299.0→98.9		

Analyte	Primary/Confirmatory	MRM Transition	Retention Time (Minutes)	Primary/ Confirmatory SRM Area Ratio
PFPeA	Primary	263→218.9	6.607	NA
PFPeS	Primary	348.9→ 79.9	8.805	41.6
	Confirmatory	348.9→98.9		
PFBA	Primary	213.0→168.9	5.189	NA
4:2 FTS	Primary	327 → 306.9	7.300	32.9
	Confirmatory	327→ 80.9		
6:2 FTS	Primary	427→ 406.8	8.971	29.8
	Confirmatory	427→ 79.9		
8:2 FTS	Primary	527.0→506.8	10.372	67.0
	Confirmatory	527.0→80.9		
N-MeFOSAA	Primary	570.0→418.9	10.831	58.8
	Confirmatory	570.0→482.9		
N-EtFOSAA	Primary	584.0→418.9	11.133	91.0
	Confirmatory	584.0→525.9		
FOSA	Primary	497.9→77.9	13.150	3.2
	Confirmatory	497.9→47.9		
11Cl-PF3OUDs	Primary	631→451	13.16	NA
9Cl-PF3ONS	Primary	531→351	11.76	NA
ADONA	Primary	377→251	8.98	NA
HFPO-DA	Primary	285→169	8.13	NA

Table 6: ASTM7979 with isotopic dilution Merit Labs Accuracy/Precision Study

Number of replicates: 4

Name	RT	Transition	Spike (ng/L) in samples	Avg Recovery (ng/L) in samples	Std. Dev.	Avg Recovery (%)	Recovery RSD (%)	Avg. Resp	Resp. RSD
4:2FTSA	7.3	327.0 -> 306.9	200	187.518	3.1462	93.759	3.4	22445	3.8
6:2FTSA	8.95	427.0 -> 406.8	200	180.3418	4.3453	90.1709	4.8	7369	5.4
8:2FTSA	10.383	527.0 -> 506.8	200	180.5346	2.0636	90.2673	2.3	5066	9.7
EtFOSAA	11.144	584.0 -> 418.9	200	181.8404	1.8411	90.9202	2	7734	4.9
FOSA	13.128	497.9 -> 77.9	200	187.158	3.0297	93.579	3.2	9404	14.4
N-MeFOSAA	10.82	570.0 -> 418.9	200	186.1304	2.4463	93.0652	2.6	10092	10.4
PFBA	5.221	213.0 -> 168.9	200	186.32	1.1017	93.16	1.2	47224	3.4
PFBS	7.785	299.0 -> 80.0	200	183.9274	3.1345	91.9637	3.4	26358	2.5
PFDA	10.769	513.0 -> 469.0	200	176.4868	2.5653	88.2434	2.9	19447	2.7
PFDoDA	12.21	613.0 -> 569.0	200	187.5248	2.9355	93.7624	3.1	30104	5.6
PFDS	12.661	599.0 -> 80.0	200	182.841	6.04	91.4205	6.6	7875	2.2
PFHpA	8.531	363.0 -> 319.0	200	185.8474	2.3603	92.9237	2.5	19991	2.7
PFHpS	10.435	448.9 -> 79.7	200	193.6212	8.9705	96.8106	9.3	6685	7.3
PFHxA	7.64	313.0 -> 269.0	200	188.9808	1.7859	94.4904	1.9	99386	1.8
PFHxS	9.564	399.0 -> 80.0	200	192.7958	3.9106	96.3979	4.1	12264	2
PFNA	10.05	463.0 -> 419.0	200	187.2022	1.3674	93.6011	1.5	43124	1.1
PFNS	11.932	548.9 -> 79.9	200	184.8164	5.9682	92.4082	6.5	6498	4
PFOA	9.311	413.0 -> 369.0	200	184.3328	0.7553	92.1664	0.8	62121	2.3
PFOS	11.186	499.0 -> 80.0	200	182.5454	6.4313	91.2727	7	8276	2.9
PFPeA	6.585	263.0 -> 218.9	200	185.1206	1.6738	92.5603	1.8	63511	2.3
PFPeS	8.794	348.9 -> 79.9	200	190.3868	6.3863	95.1934	6.7	16815	3.5
PFTeDA	13.588	713.0 -> 669.0	200	187.873	2.5503	93.9365	2.7	31456	6.2
PFTrDA	12.925	663.0 -> 619.0	200	201.8056	4.363	100.9028	4.3	35066	6.9
PFUnDA	11.485	563.0 -> 519.0	200	183.4224	1.8898	91.7112	2.1	31097	2.9

Table 7: ASTM7979 with isotopic dilution Merit Labs Pond Accuracy/Precision Study
Values in ng/L, samples Spiked at 200 ng/L.

		Unspiked 1	Unspiked 2	Spiked 1	Spiked 2	Spiked 3	Spiked 4	Average recovery	% Average recovery	Standard Dev.	RSD (%)
Compound Name		PW180425-1	PW180425-2	PS180425-1	PS180425-2	PS180425-3	PS180425-4				
Name	Transition Ions	Final Conc.	Final Conc.	Final Conc.	Final Conc.	Final Conc.	Final Conc.				
4:2FTSA	327.0 -> 306.9	<RL	<RL	188.703	190.703	183.441	200.739	190.896	95.45	6.271	3.28
6:2FTSA	427.0 -> 406.8	<RL	<RL	185.769	217.398	185.636	199.388	197.048	98.52	13.010	6.60
8:2FTSA	527.0 -> 506.8	<RL	<RL	168.294	176.720	165.134	190.735	175.220	87.61	9.908	5.65
EtFOSAA	584.0 -> 418.9	<RL	<RL	207.503	211.867	172.420	219.461	202.812	101.41	18.061	8.91
FOSA	497.9 -> 77.9	<RL	<RL	196.092	200.073	187.684	194.713	194.640	97.32	4.473	2.30
N-MeFOSAA	570.0 -> 418.9	<RL	<RL	185.885	187.558	189.511	181.172	186.031	93.02	3.085	1.66
PFBA	213.0 -> 168.9	10.3442	10.3709	183.706	184.426	172.753	187.512	182.099	91.05	5.582	3.07
PFBS	299.0 -> 80.0	<RL	<RL	192.358	197.465	180.403	188.643	189.717	94.86	6.223	3.28
PFDA	513.0 -> 469.0	<RL	<RL	192.956	178.510	164.271	170.224	176.490	88.25	10.768	6.10
PFDoDA	613.0 -> 569.0	<RL	<RL	188.074	183.763	175.456	191.824	184.779	92.39	6.092	3.30
PFDS	599.0 -> 80.0	<RL	<RL	180.007	194.048	158.224	184.240	179.130	89.56	13.100	7.31
PFHpA	363.0 -> 319.0	<RL	<RL	191.571	193.644	177.097	190.885	188.299	94.15	6.547	3.48
PFHpS	448.9 -> 79.7	<RL	<RL	206.529	192.693	186.204	209.809	198.809	99.40	9.707	4.88
PFHxA	313.0 -> 269.0	<RL	<RL	199.454	191.446	180.688	195.420	191.752	95.88	6.987	3.64
PFHxS	399.0 -> 80.0	<RL	<RL	197.546	188.166	182.072	198.486	191.567	95.78	6.807	3.55
PFNA	463.0 -> 419.0	<RL	<RL	196.337	189.223	170.689	194.886	187.784	93.89	10.221	5.44
PFNS	548.9 -> 79.9	<RL	<RL	184.904	198.905	167.542	183.372	183.681	91.84	11.111	6.05
PFOA	413.0 -> 369.0	<RL	<RL	187.603	184.429	181.697	186.357	185.021	92.51	2.227	1.20
PFOS	499.0 -> 80.0	10.151	12.4419	197.136	201.454	169.003	177.093	186.172	93.09	13.518	7.26
PFPeA	263.0 -> 218.9	<RL	<RL	188.796	187.623	181.052	195.304	188.194	94.10	5.056	2.69
PFPeS	348.9 -> 79.9	<RL	<RL	186.896	197.872	195.596	193.946	193.577	96.79	4.102	2.12
PFTeDA	713.0 -> 669.0	<RL	<RL	179.528	185.891	173.665	189.006	182.022	91.01	5.912	3.25
PFTrDA	663.0 -> 619.0	<RL	<RL	193.320	205.260	185.940	200.672	196.298	98.15	7.342	3.74
PFUnDA	563.0 -> 519.0	<RL	<RL	180.067	190.676	170.779	184.263	181.447	90.72	7.225	3.98

Table 8: Isotopic Dilutions Mass Labeled Compounds

M2-4:2FTSA	13C2-4:2 Fluorotelomer sulfonate
M2-6:2FTSA	13C2-6:2 Fluorotelomer sulfonate
M2-8:2FTSA	13C2-8:2 Fluorotelomer sulfonate
M2PFTeDA	13C2-Perfluorotetradecanoic acid
M3PFBS	13C3-Perfluorobutane Sulfonate
M3PFHxS	13C3-Perfluorohexanesulfonic acid
M4PFHpA	13C4-Perfluoroheptanoic acid
M5PFHxA	13C5-Perfluorohexanoic acid
M5PFPeA	13C5-Perfluoropentanoic acid
M6PFDA	13C6-Perfluorodecanoic acid
M7PFUnDA	13C7-Perfluoroundecanoic acid
M8FOSA	13C8-Perfluorooctanesulfonamide
M8PFOA	CARBON 13 LABELED STANDARD PFOA, surr
M8PFOS	13C8-Perfluorooctanesulfonate
M9-PFNA	13C9-Perfluorononanoic acid
MPFBA	13C4-Perfluorobutanoic acid
MPFDoDA	13C2-Perfluorododecanoic acid
d3N-MeFOSAA	N-deuteriomethylperfluoro-1-octanesulfonamidoacetic acid
d5EtFOSAA	d5-N-ethylperfluoro-1-octanesulfonamidoacetic acid, surr

Table 9: Precision & Accuracy Study with additional compounds

	Spike	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**x (%) Accuracy**	**%RSD**
Compound	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)		
4:2FTSA	50.0	42.9846	42.559	36.7384	44.3253	55.8474	54.27	55.6228	57.7083	97.5%	16.330
6:2FTSA	50.0	45.7834	47.6763	43.0037	46.3058	59.5745	75.0645	58.6639	64.0801	110.0%	20.349
8:2FTSA	50.0	41.2949	37.7199	34.8033	34.0225	46.67	53.649	64.5894	55.4618	92.1%	23.992
EtFOSAA	50.0	40.2386	40.0924	41.9946	39.8023	48.0238	53.012	46.9258	54.942	91.3%	13.241
FOSA	50.0	41.376	40.5971	45.083	42.7015	49.7062	55.2342	51.8978	56.0639	95.7%	12.996
N-MeFOSAA	50.0	39.6634	38.2637	41.4616	42.2088	55.0629	56.2606	59.1118	55.0435	96.8%	17.994
PFBA	50.0	47.7945	46.3075	46.6032	48.4606	54.2203	58.985	55.4014	56.5675	103.6%	9.724
PFBS	50.0	41.3579	38.762	40.3733	41.7127	53.1459	52.9503	52.9029	55.6424	94.2%	15.101
PFDA	50.0	38.8953	39.3281	42.1683	41.1819	51.4692	52.6654	50.4936	54.7538	92.7%	14.188
PFDoDA	50.0	43.3486	35.6643	42.9282	40.1219	49.1069	60.0705	51.2188	54.0751	94.1%	17.013
PFDS	50.0	46.6212	42.8343	38.8438	47.5195	57.0201	57.7089	63.353	54.4751	102.1%	16.418
PFHpA	50.0	42.6778	40.4243	41.5696	40.9252	52.2388	54.773	55.0896	55.6513	95.8%	14.750
PFHpS	50.0	39.5543	38.827	43.7458	45.9568	53.8271	58.2775	47.5013	59.468	96.8%	16.528
PFHxA	50.0	39.819	40.2474	40.5795	42.8508	49.0609	55.2338	51.9636	55.5875	93.8%	14.545
PFHxS	50.0	41.6949	39.4868	41.5175	48.1715	55.3506	57.3189	52.6248	56.7311	98.2%	15.059
PFNA	50.0	42.1374	37.7289	45.6376	41.017	55.6852	48.9467	50.9622	63.246	96.3%	17.460
PFNS	50.0	45.2447	41.6084	42.7689	42.315	57.3302	54.7174	61.0767	59.6029	101.2%	16.583
PFOA	50.0	39.44	42.0962	46.6121	41.9228	56.3334	57.9651	54.2586	56.5781	98.8%	15.545
PFOS	50.0	46.6993	40.6347	39.3621	40.2535	55.2709	53.0935	61.6316	58.0516	98.7%	17.807
PFPeA	50.0	39.7979	40.187	42.1658	42.2198	50.8825	54.1761	53.2492	55.5553	94.6%	14.361
PFPeS	50.0	41.5994	36.5125	39.3338	42.3593	47.768	51.9297	49.8069	50.4503	89.9%	12.779
PFTeDA	50.0	45.583	40.083	43.7045	42.929	58.8311	57.9411	56.361	52.6672	99.5%	15.108
PFTrDA	50.0	42.685	40.6584	45.1447	42.2206	54.1332	64.6492	51.8293	61.4406	100.7%	18.233
PFUnDA	50.0	43.9843	37.8796	42.86	46.7865	53.1152	53.6215	57.4423	61.6227	99.3%	16.266
PFOS-BR	50.0	13.4026	10.6862	12.4698	11.2403	15.7079	14.1145	17.1993	19.5827	28.6%	21.293
PFOS-LN	50.0	32.2876	29.5682	26.7116	28.6819	39.2406	36.3701	45.2034	39.2076	69.3%	18.450
PFHxS-LN	50.0	35.7549	32.8924	34.722	41.0036	49.0067	48.4482	47.8858	50.2215	85.0%	17.038
PFHxS-BR	50.0	5.9619	6.5758	6.7352	7.0921	6.1767	6.7799	10.5223	8.3178	14.5%	20.548
11CL-PF3OUDS	50.0	42.7923	42.7218	41.0146	39.8722	56.3801	53.206	60.1184	57.0408	98.3%	16.943
9CL-PF3ONS	50.0	43.4217	37.4208	36.849	39.5165	53.758	47.6003	55.5511	53.5196	91.9%	16.786
ADONA	50.0	42.4503	41.3943	42.7558	40.2106	52.8526	54.4449	50.3438	58.6504	95.8%	14.692
HFPO-DA	50.0	42.1779	42.5186	42.244	43.8686	54.854	57.067	63.1655	60.7098	101.7%	17.770

Table 10: Precision & Accuracy Study Soil

	Spike	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**x (%) Accuracy**	**%RSD**
Compound	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)		
4:2FTSA	50.0	40.7754	41.2363	47.3719	48.1344	47.3894	43.6642	44.1264	44.7226	89.4%	6.272
6:2FTSA	50.0	48.4418	49.2271	57.9287	54.8633	58.7237	47.8804	49.9588	47.4069	103.6%	8.961
8:2FTSA	50.0	38.0052	42.4223	49.614	39.9095	36.9713	36.1929	38.3218	36.8316	79.6%	11.178
EtFOSAA	50.0	40.6253	43.8063	52.8093	51.0851	42.9783	46.2372	44.9175	50.034	93.1%	9.257
FOSA	50.0	43.7216	43.3058	47.0355	48.7235	45.0072	40.2226	43.238	42.5973	88.5%	6.011
N-MeFOSAA	50.0	39.0031	40.8935	49.3052	47.6915	54.0759	46.7427	49.2904	48.1359	93.8%	10.310
PFBA	50.0	43.1742	44.4345	52.3818	48.0903	57.022	54.8565	57.3079	54.4016	102.9%	10.783
PFBS	50.0	38.5823	41.8718	52.8962	46.7774	43.871	42.3977	43.7642	42.7965	88.2%	9.567
PFDA	50.0	38.6615	45.0218	49.4933	46.4066	46.4909	41.3286	40.2626	42.9755	87.7%	8.345
PFDoDA	50.0	41.079	40.3735	49.4451	46.7817	39.949	40.5231	40.846	42.414	85.4%	8.214
PFDS	50.0	40.5961	47.0006	52.5014	51.6747	56.6983	44.703	47.0264	48.6031	97.2%	10.274
PFHpA	50.0	43.3239	44.3847	55.2125	50.7101	47.3408	44.3264	43.4248	45.4388	93.5%	8.985
PFHpS	50.0	45.4585	41.2547	56.3273	48.3956	44.2189	47.6975	48.9783	47.6604	95.0%	9.243
PFHxA	50.0	39.7546	45.2885	43.3394	45.7944	43.0166	40.981	39.4099	43.2843	85.2%	5.576
PFHxS	50.0	46.6035	42.6077	57.0656	50.0369	41.5086	46.4929	50.1554	47.2948	95.4%	10.214
PFNA	50.0	48.1448	40.5686	58.3401	47.6069	42.8594	42.42	43.5925	42.7651	91.6%	12.452
PFNS	50.0	42.0527	42.5665	52.827	46.9307	57.2936	45.7512	46.2612	50.5992	96.1%	10.861
PFOA	50.0	45.7135	44.5738	55.5732	44.9519	48.7086	42.4589	42.3674	48.2908	93.2%	9.269
PFOS	50.0	42.7116	44.6671	48.6836	51.0611	52.9227	42.7508	48.6967	49.1862	95.2%	7.991
PFPeA	50.0	40.5008	41.5054	49.8913	47.2571	44.2715	42.1029	42.8048	43.1191	87.9%	7.179
PFPeS	50.0	41.5363	40.7016	49.349	48.1135	41.1943	39.8035	36.7701	41.6236	84.8%	9.972
PFTeDA	50.0	42.3899	49.8488	54.8383	49.9049	46.1164	46.4213	43.6276	45.5429	94.7%	8.486
PFTrDA	50.0	42.8213	45.699	51.9521	52.4935	46.0574	46.1471	50.4193	51.0692	96.7%	7.399
PFUnDA	50.0	40.6423	44.9513	62.0705	55.033	47.602	45.5942	47.4427	45.7512	97.3%	13.879
PFOS-BR	50.0	11.9384	13.1749	14.1152	13.5481	13.9109	13.8199	17.9033	15.9803	28.6%	12.850
PFOS-LN	50.0	29.9339	30.9399	34.3406	36.0711	33.6156	26.9222	28.2209	28.5124	62.1%	10.560
PFHxS-LN	50.0	39.5385	36.1586	48.5867	42.3187	33.6051	38.9848	35.2644	38.6889	78.3%	11.993
PFHxS-BR	50.0	6.852	6.5494	8.4694	7.5834	5.927	7.278	9.751	8.1977	15.2%	16.013
11CL-PF3OUDS	50.0	38.6548	42.4327	52.2196	49.2085	52.7401	42.3079	47.9545	49.5512	93.8%	10.962
9CL-PF3ONS	50.0	39.8117	41.6076	48.3828	46.9065	49.3514	41.2458	43.0633	47.0205	89.3%	8.182
ADONA	50.0	40.9247	43.8968	51.7781	48.5555	47.1625	41.7685	40.6551	45.0694	90.0%	8.830
HFPO-DA	50.0	44.8487	49.4065	57.7374	48.8048	47.8443	45.1833	47.3804	48.6833	97.5%	8.202

Figure 1: ASTM Prep Benchsheet

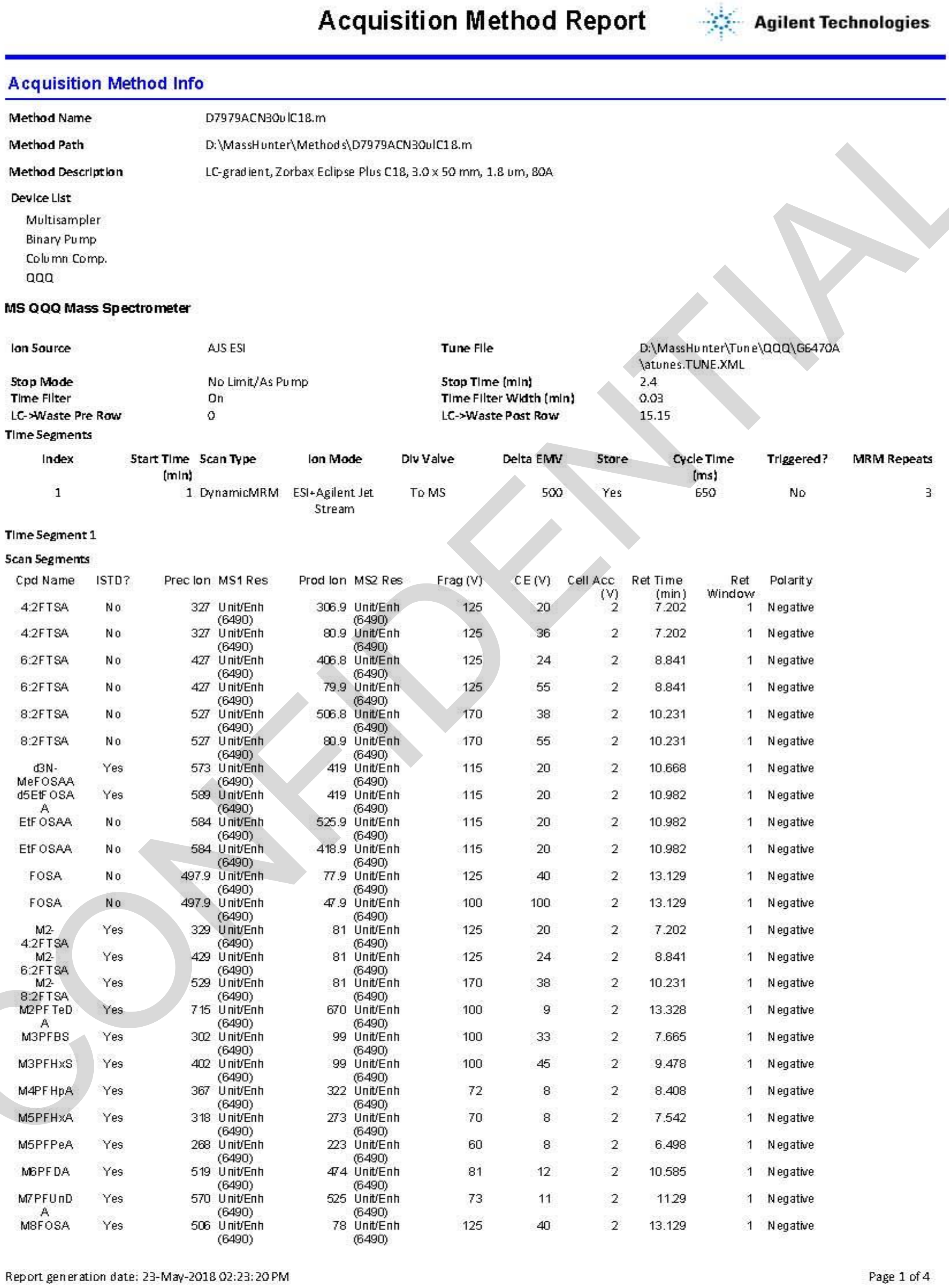
PFAS Extraction/Dilution
Method ASTMD7979

MeOH Lot #: _______________
Reagent H2O Source Lot #: _______________
Acetic acid Lot #: ____________________
Base #: ____________________
ISD #: ____________________
Spike #: _________________ **Filter lot #**_____________

Analyst: ____________________
Date: _____________________
Time Started: _______________
Time Ended: ________________
Batch ID#: _________________

#	Merit #	Matrix	Sample Volume (ml)	Initial tube weight (g)	Final tube weight (g)	MeOH Vol (ml)	Final Vol (ml)	ISD Vol (ul)	Spike Vol (ul)	Shake/Tumble time (min)	Acetic acid volume (ul)	Notes
Initial Q.C.	BLANK		5			5	10	40	---	2	10	
	LCS		5			5	10	40	50	2	10	
	LCSD		5			5	10	40	50	2	10	
	RL check		5			5	10	40	5	2	10	
	RL check		5			5	10	40	10	2	10	
	Daily Reagent BLK	W	5			5	10	40	---	2	10	[ ]
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												

Figure 2: Acquisition Method Report for ASTM D7979



Acquisition Method Report

Agilent Technologies

Acquisition Method Info

Method Name	D7979ACN30ulC18.m
Method Path	D:\MassHunter\Methods\D7979ACN30ulC18.m
Method Description	LC-gradient, Zorbax Eclipse Plus C18, 3.0 x 50 mm, 1.8 um, 80A

Device List

- Multisampler
- Binary Pump
- Column Comp.
- QQQ

MS QQQ Mass Spectrometer

Ion Source	AJS ESI	**Tune File**	D:\MassHunter\Tune\QQQ\G6470A \atunes.TUNE.XML
Stop Mode	No Limit/As Pump	**Stop Time (min)**	2.4
Time Filter	On	**Time Filter Width (min)**	0.03
LC->Waste Pre Row	0	**LC->Waste Post Row**	15.15

Time Segments

Index	Start Time (min)	Scan Type	Ion Mode	Div Valve	Delta EMV	Store	Cycle Time (ms)	Triggered?	MRM Repeats
1	1	DynamicMRM	ESI+Agilent Jet Stream	To MS	500	Yes	650	No	3

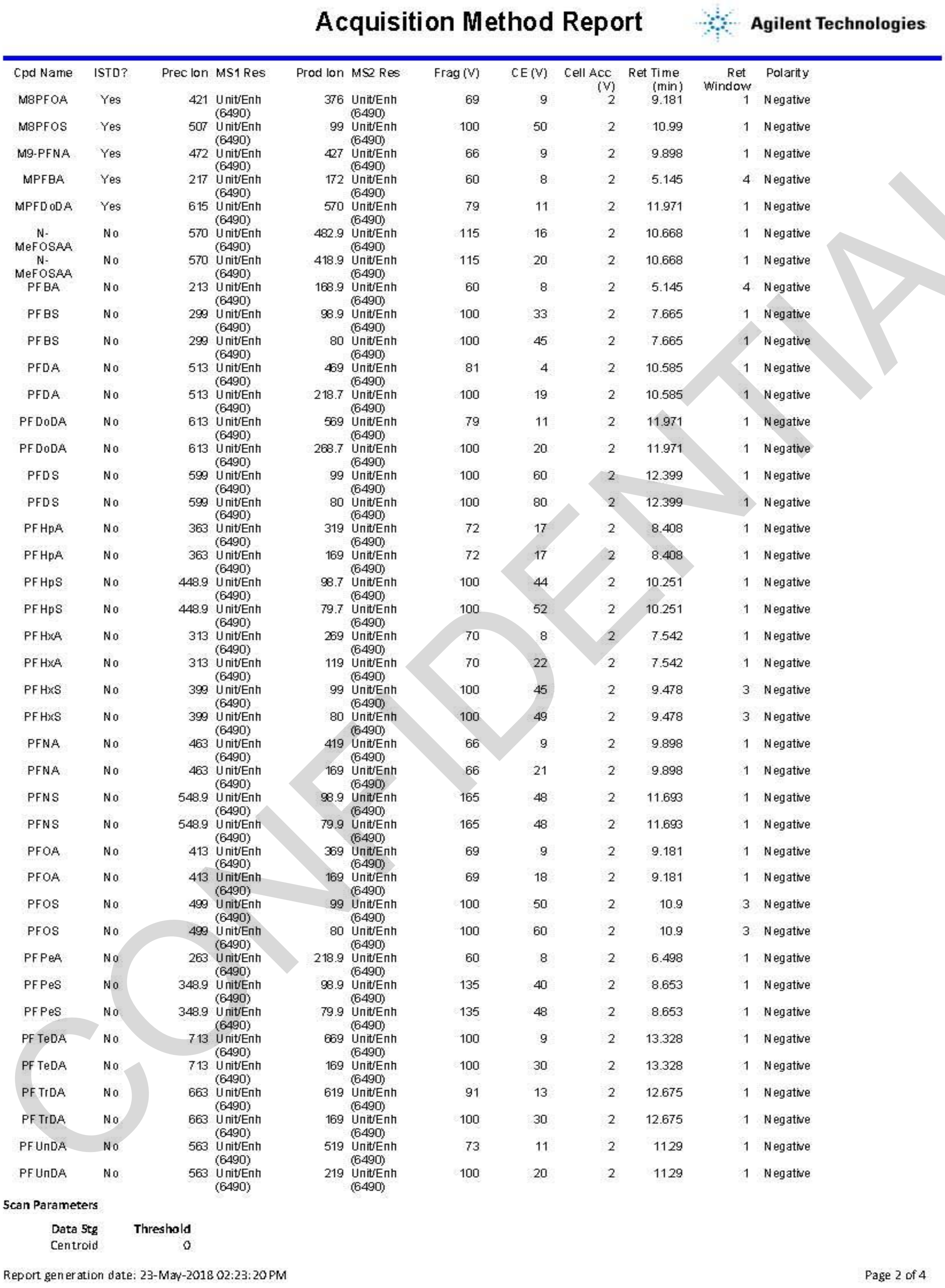
Time Segment 1

Scan Segments

Cpd Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Frag (V)	CE (V)	Cell Acc (V)	Ret Time (min)	Ret Window	Polarity
4:2FTSA	No	327	Unit/Enh (6490)	306.9	Unit/Enh (6490)	125	20	2	7.202	1	Negative
4:2FTSA	No	327	Unit/Enh (6490)	80.9	Unit/Enh (6490)	125	36	2	7.202	1	Negative
6:2FTSA	No	427	Unit/Enh (6490)	406.8	Unit/Enh (6490)	125	24	2	8.841	1	Negative
6:2FTSA	No	427	Unit/Enh (6490)	79.9	Unit/Enh (6490)	125	55	2	8.841	1	Negative
8:2FTSA	No	527	Unit/Enh (6490)	506.8	Unit/Enh (6490)	170	38	2	10.231	1	Negative
8:2FTSA	No	527	Unit/Enh (6490)	80.9	Unit/Enh (6490)	170	55	2	10.231	1	Negative
d3N-MeFOSAA	Yes	573	Unit/Enh (6490)	419	Unit/Enh (6490)	115	20	2	10.668	1	Negative
d5EtFOSAA	Yes	589	Unit/Enh (6490)	419	Unit/Enh (6490)	115	20	2	10.982	1	Negative
EtFOSAA	No	584	Unit/Enh (6490)	525.9	Unit/Enh (6490)	115	20	2	10.982	1	Negative
EtFOSAA	No	584	Unit/Enh (6490)	418.9	Unit/Enh (6490)	115	20	2	10.982	1	Negative
FOSA	No	497.9	Unit/Enh (6490)	77.9	Unit/Enh (6490)	125	40	2	13.129	1	Negative
FOSA	No	497.9	Unit/Enh (6490)	47.9	Unit/Enh (6490)	100	100	2	13.129	1	Negative
M2-4:2FTSA	Yes	329	Unit/Enh (6490)	81	Unit/Enh (6490)	125	20	2	7.202	1	Negative
M2-6:2FTSA	Yes	429	Unit/Enh (6490)	81	Unit/Enh (6490)	125	24	2	8.841	1	Negative
M2-8:2FTSA	Yes	529	Unit/Enh (6490)	81	Unit/Enh (6490)	170	38	2	10.231	1	Negative
M2PFTeDA	Yes	715	Unit/Enh (6490)	670	Unit/Enh (6490)	100	9	2	13.328	1	Negative
M3PFBS	Yes	302	Unit/Enh (6490)	99	Unit/Enh (6490)	100	33	2	7.665	1	Negative
M3PFHxS	Yes	402	Unit/Enh (6490)	99	Unit/Enh (6490)	100	45	2	9.478	1	Negative
M4PFHpA	Yes	367	Unit/Enh (6490)	322	Unit/Enh (6490)	72	8	2	8.408	1	Negative
M5PFHxA	Yes	318	Unit/Enh (6490)	273	Unit/Enh (6490)	70	8	2	7.542	1	Negative
M5PFPeA	Yes	268	Unit/Enh (6490)	223	Unit/Enh (6490)	60	8	2	6.498	1	Negative
M6PFDA	Yes	519	Unit/Enh (6490)	474	Unit/Enh (6490)	81	12	2	10.585	1	Negative
M7PFUnDA	Yes	570	Unit/Enh (6490)	525	Unit/Enh (6490)	73	11	2	11.29	1	Negative
M8FOSA	Yes	506	Unit/Enh (6490)	78	Unit/Enh (6490)	125	40	2	13.129	1	Negative

Report generation date: 23-May-2018 02:23:20 PM

Page 1 of 4



Acquisition Method Report

Agilent Technologies

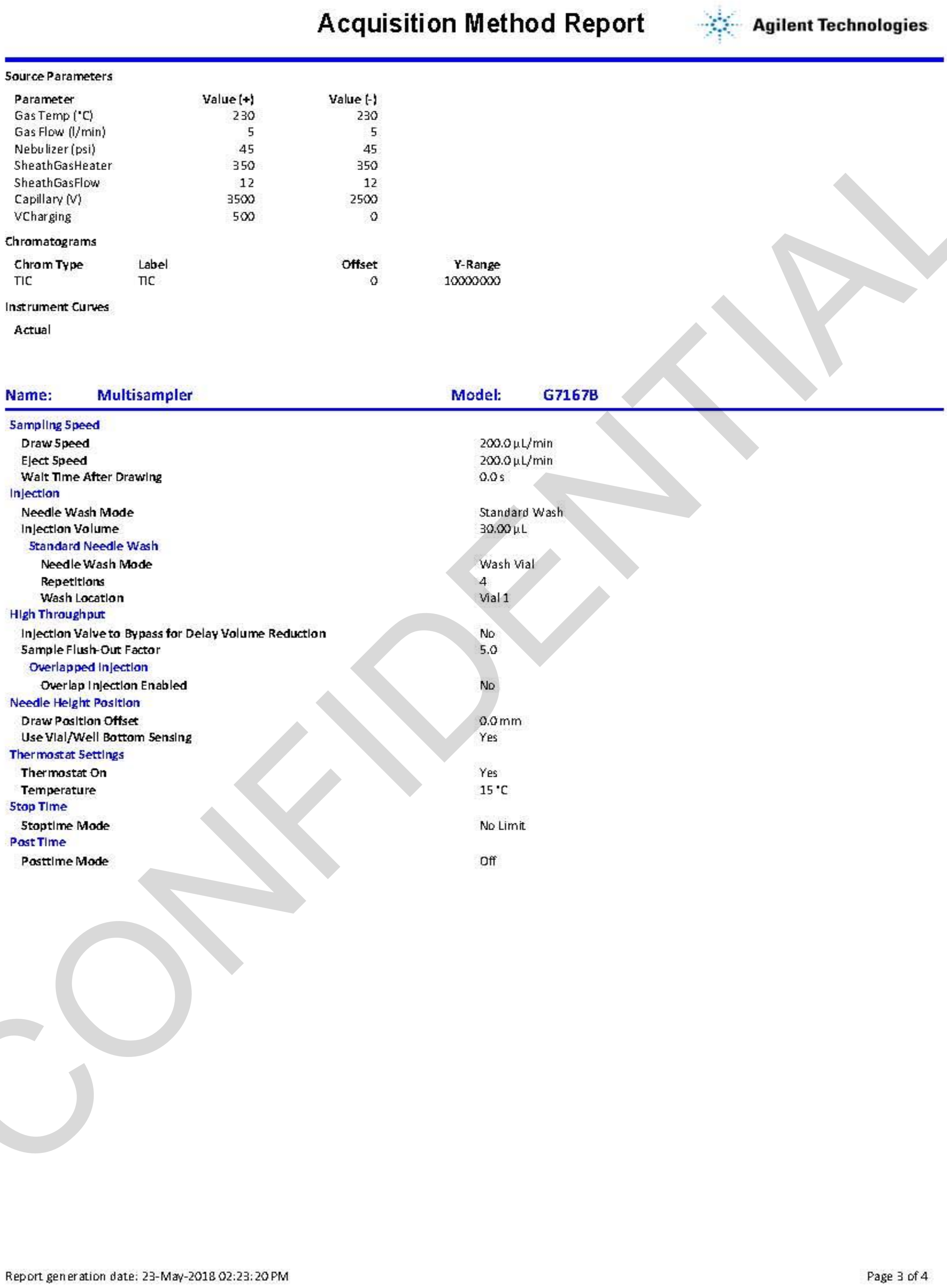
Cpd Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Frag (V)	CE (V)	Cell Acc (V)	Ret Time (min)	Ret Window	Polarity
M8PFOA	Yes	421	Unit/Enh (6490)	376	Unit/Enh (6490)	69	9	2	9.181	1	Negative
M8PFOS	Yes	507	Unit/Enh (6490)	99	Unit/Enh (6490)	100	50	2	10.99	1	Negative
M9-PFNA	Yes	472	Unit/Enh (6490)	427	Unit/Enh (6490)	66	9	2	9.898	1	Negative
MPFBA	Yes	217	Unit/Enh (6490)	172	Unit/Enh (6490)	60	8	2	5.145	4	Negative
MPFDoDA	Yes	615	Unit/Enh (6490)	570	Unit/Enh (6490)	79	11	2	11.971	1	Negative
N-MeFOSAA	No	570	Unit/Enh (6490)	482.9	Unit/Enh (6490)	115	16	2	10.668	1	Negative
N-MeFOSAA	No	570	Unit/Enh (6490)	418.9	Unit/Enh (6490)	115	20	2	10.668	1	Negative
PFBA	No	213	Unit/Enh (6490)	168.9	Unit/Enh (6490)	60	8	2	5.145	4	Negative
PFBS	No	299	Unit/Enh (6490)	98.9	Unit/Enh (6490)	100	33	2	7.665	1	Negative
PFBS	No	299	Unit/Enh (6490)	80	Unit/Enh (6490)	100	45	2	7.665	1	Negative
PFDA	No	513	Unit/Enh (6490)	469	Unit/Enh (6490)	81	4	2	10.585	1	Negative
PFDA	No	513	Unit/Enh (6490)	218.7	Unit/Enh (6490)	100	19	2	10.585	1	Negative
PFDoDA	No	613	Unit/Enh (6490)	569	Unit/Enh (6490)	79	11	2	11.971	1	Negative
PFDoDA	No	613	Unit/Enh (6490)	268.7	Unit/Enh (6490)	100	20	2	11.971	1	Negative
PFDS	No	599	Unit/Enh (6490)	99	Unit/Enh (6490)	100	60	2	12.399	1	Negative
PFDS	No	599	Unit/Enh (6490)	80	Unit/Enh (6490)	100	80	2	12.399	1	Negative
PFHpA	No	363	Unit/Enh (6490)	319	Unit/Enh (6490)	72	17	2	8.408	1	Negative
PFHpA	No	363	Unit/Enh (6490)	169	Unit/Enh (6490)	72	17	2	8.408	1	Negative
PFHpS	No	448.9	Unit/Enh (6490)	98.7	Unit/Enh (6490)	100	44	2	10.251	1	Negative
PFHpS	No	448.9	Unit/Enh (6490)	79.7	Unit/Enh (6490)	100	52	2	10.251	1	Negative
PFHxA	No	313	Unit/Enh (6490)	269	Unit/Enh (6490)	70	8	2	7.542	1	Negative
PFHxA	No	313	Unit/Enh (6490)	119	Unit/Enh (6490)	70	22	2	7.542	1	Negative
PFHxS	No	399	Unit/Enh (6490)	99	Unit/Enh (6490)	100	45	2	9.478	3	Negative
PFHxS	No	399	Unit/Enh (6490)	80	Unit/Enh (6490)	100	49	2	9.478	3	Negative
PFNA	No	463	Unit/Enh (6490)	419	Unit/Enh (6490)	66	9	2	9.898	1	Negative
PFNA	No	463	Unit/Enh (6490)	169	Unit/Enh (6490)	66	21	2	9.898	1	Negative
PFNS	No	548.9	Unit/Enh (6490)	98.9	Unit/Enh (6490)	165	48	2	11.693	1	Negative
PFNS	No	548.9	Unit/Enh (6490)	79.9	Unit/Enh (6490)	165	48	2	11.693	1	Negative
PFOA	No	413	Unit/Enh (6490)	369	Unit/Enh (6490)	69	9	2	9.181	1	Negative
PFOA	No	413	Unit/Enh (6490)	169	Unit/Enh (6490)	69	18	2	9.181	1	Negative
PFOS	No	499	Unit/Enh (6490)	99	Unit/Enh (6490)	100	50	2	10.9	3	Negative
PFOS	No	499	Unit/Enh (6490)	80	Unit/Enh (6490)	100	60	2	10.9	3	Negative
PFPeA	No	263	Unit/Enh (6490)	218.9	Unit/Enh (6490)	60	8	2	6.498	1	Negative
PFPeS	No	348.9	Unit/Enh (6490)	98.9	Unit/Enh (6490)	135	40	2	8.653	1	Negative
PFPeS	No	348.9	Unit/Enh (6490)	79.9	Unit/Enh (6490)	135	48	2	8.653	1	Negative
PFTeDA	No	713	Unit/Enh (6490)	669	Unit/Enh (6490)	100	9	2	13.328	1	Negative
PFTeDA	No	713	Unit/Enh (6490)	169	Unit/Enh (6490)	100	30	2	13.328	1	Negative
PFTrDA	No	663	Unit/Enh (6490)	619	Unit/Enh (6490)	91	13	2	12.675	1	Negative
PFTrDA	No	663	Unit/Enh (6490)	169	Unit/Enh (6490)	100	30	2	12.675	1	Negative
PFUnDA	No	563	Unit/Enh (6490)	519	Unit/Enh (6490)	73	11	2	11.29	1	Negative
PFUnDA	No	563	Unit/Enh (6490)	219	Unit/Enh (6490)	100	20	2	11.29	1	Negative

Scan Parameters

Data Stg	Threshold
Centroid	0

Report generation date: 23-May-2018 02:23:20 PM

Page 2 of 4



Acquisition Method Report

Agilent Technologies

Source Parameters

Parameter	Value (+)	Value (-)
Gas Temp (°C)	230	230
Gas Flow (l/min)	5	5
Nebulizer (psi)	45	45
SheathGasHeater	350	350
SheathGasFlow	12	12
Capillary (V)	3500	2500
VCharging	500	0

Chromatograms

Chrom Type	Label	Offset	Y-Range
TIC	TIC	0	10000000

Instrument Curves

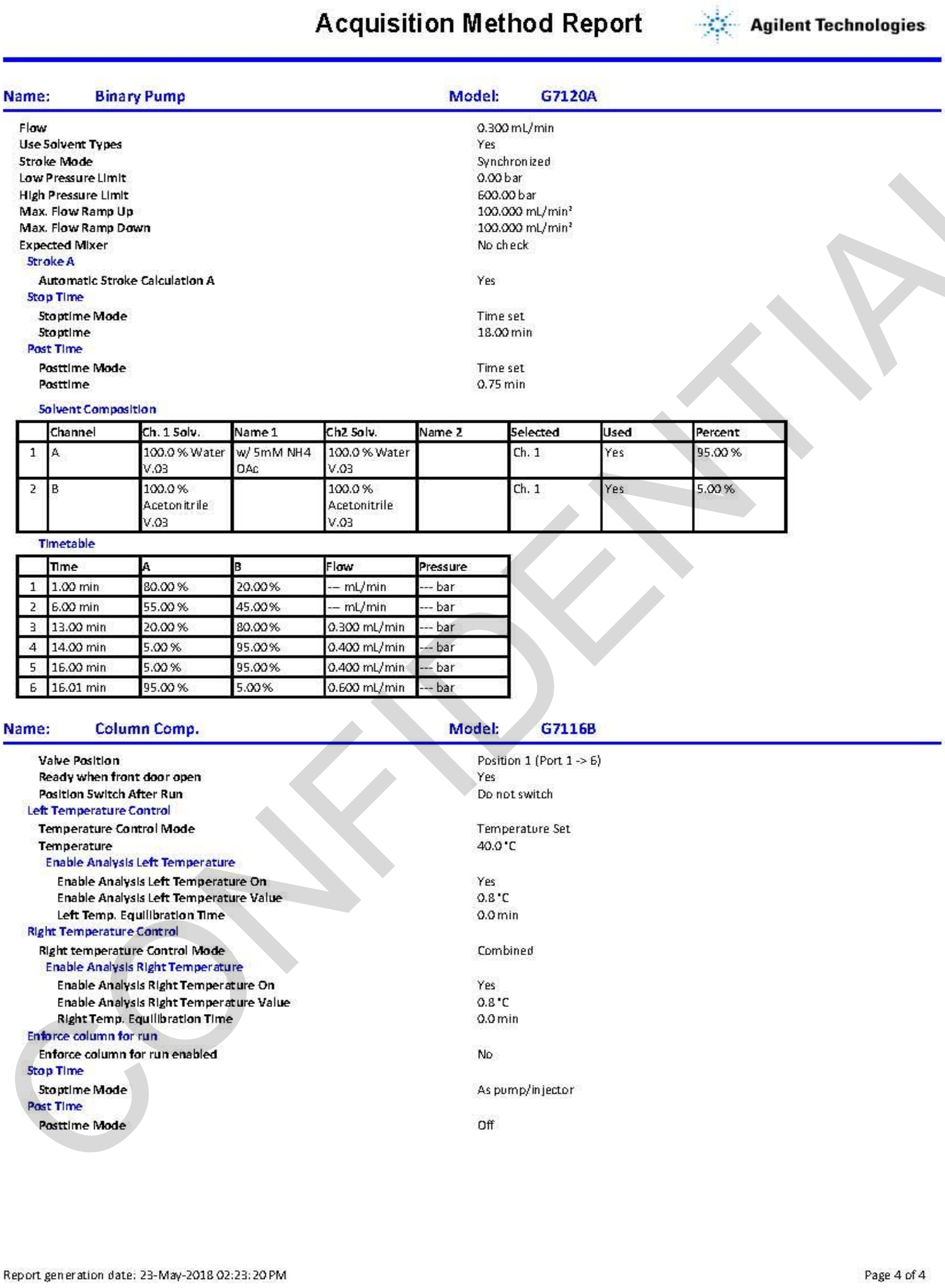
Actual

Name: Multisampler **Model: G7167B**

Sampling Speed	
Draw Speed	200.0 µL/min
Eject Speed	200.0 µL/min
Wait Time After Drawing	0.0 s
Injection	
Needle Wash Mode	Standard Wash
Injection Volume	30.00 µL
Standard Needle Wash	
Needle Wash Mode	Wash Vial
Repetitions	4
Wash Location	Vial 1
High Throughput	
Injection Valve to Bypass for Delay Volume Reduction	No
Sample Flush-Out Factor	5.0
Overlapped Injection	
Overlap Injection Enabled	No
Needle Height Position	
Draw Position Offset	0.0 mm
Use Vial/Well Bottom Sensing	Yes
Thermostat Settings	
Thermostat On	Yes
Temperature	15 °C
Stop Time	
Stoptime Mode	No Limit
Post Time	
Posttime Mode	Off

Report generation date: 23-May-2018 02:23:20 PM

Page 3 of 4



Acquisition Method Report

Agilent Technologies

Name: Binary Pump **Model:** G7120A

Flow	0.300 mL/min
Use Solvent Types	Yes
Stroke Mode	Synchronized
Low Pressure Limit	0.00 bar
High Pressure Limit	600.00 bar
Max. Flow Ramp Up	100.000 mL/min²
Max. Flow Ramp Down	100.000 mL/min²
Expected Mixer	No check
Stroke A	
Automatic Stroke Calculation A	Yes
Stop Time	
Stoptime Mode	Time set
Stoptime	18.00 min
Post Time	
Posttime Mode	Time set
Posttime	0.75 min

Solvent Composition

	Channel	Ch. 1 Solv.	Name 1	Ch2 Solv.	Name 2	Selected	Used	Percent
1	A	100.0 % Water V.03	w/ 5mM NH4 OAc	100.0 % Water V.03		Ch. 1	Yes	95.00 %
2	B	100.0 % Acetonitrile V.03		100.0 % Acetonitrile V.03		Ch. 1	Yes	5.00 %

Timetable

	Time	A	B	Flow	Pressure
1	1.00 min	80.00 %	20.00 %	--- mL/min	--- bar
2	6.00 min	55.00 %	45.00 %	--- mL/min	--- bar
3	13.00 min	20.00 %	80.00 %	0.300 mL/min	--- bar
4	14.00 min	5.00 %	95.00 %	0.400 mL/min	--- bar
5	16.00 min	5.00 %	95.00 %	0.400 mL/min	--- bar
6	16.01 min	95.00 %	5.00 %	0.600 mL/min	--- bar

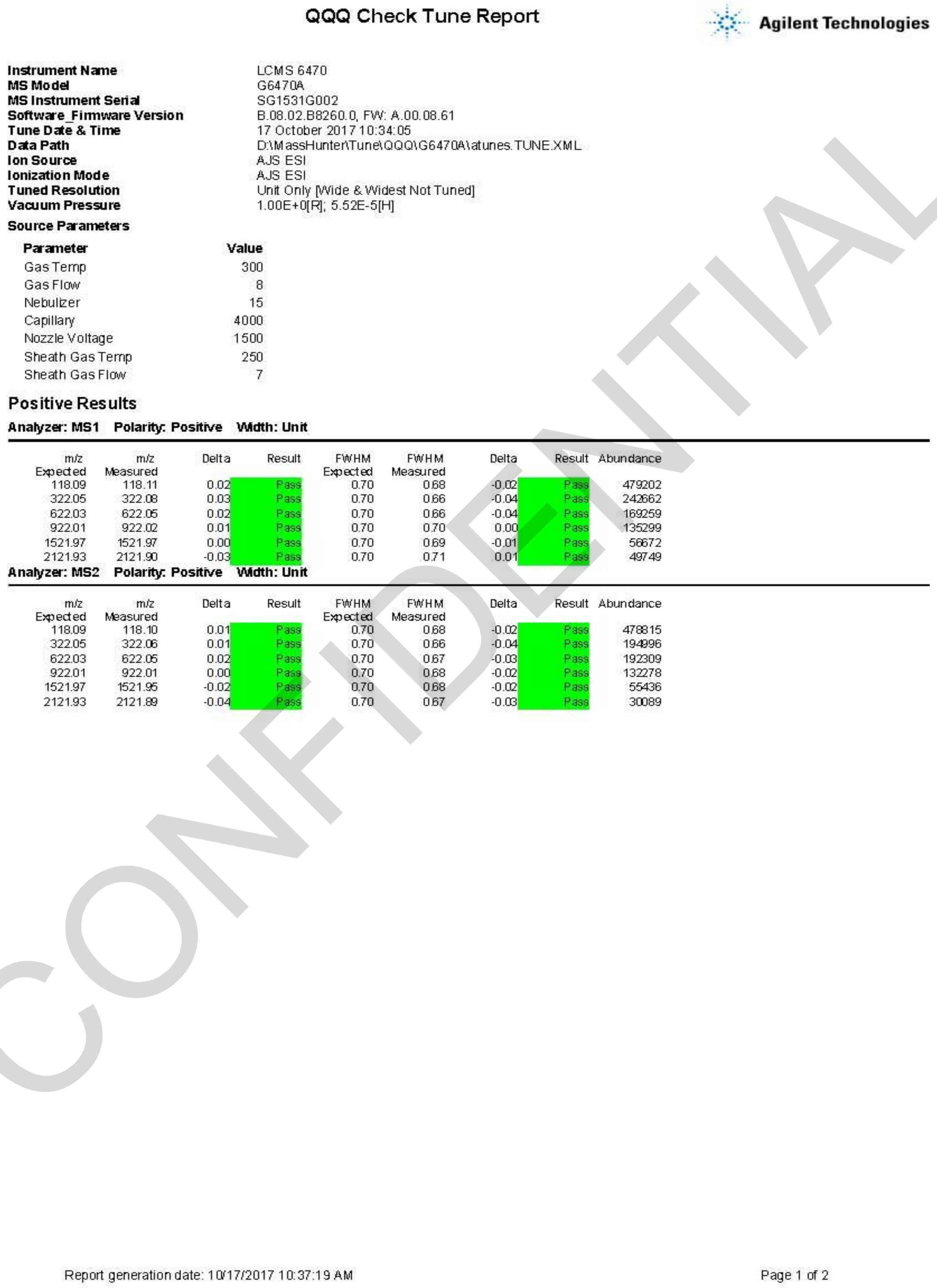
Name: Column Comp. **Model:** G7116B

Valve Position	Position 1 (Port 1 -> 6)
Ready when front door open	Yes
Position Switch After Run	Do not switch
Left Temperature Control	
Temperature Control Mode	Temperature Set
Temperature	40.0 °C
Enable Analysis Left Temperature	
Enable Analysis Left Temperature On	Yes
Enable Analysis Left Temperature Value	0.8 °C
Left Temp. Equilibration Time	0.0 min
Right Temperature Control	
Right temperature Control Mode	Combined
Enable Analysis Right Temperature	
Enable Analysis Right Temperature On	Yes
Enable Analysis Right Temperature Value	0.8 °C
Right Temp. Equilibration Time	0.0 min
Enforce column for run	
Enforce column for run enabled	No
Stop Time	
Stoptime Mode	As pump/injector
Post Time	
Posttime Mode	Off

Report generation date: 23-May-2018 02:23:20 PM

Page 4 of 4

Figure 3 Check Tune Report



QQQ Check Tune Report

Agilent Technologies

Instrument Name	LCMS 6470
MS Model	G6470A
MS Instrument Serial	SG1531G002
Software_Firmware Version	B.08.02.B8260.0, FW: A.00.08.61
Tune Date & Time	17 October 2017 10:34:05
Data Path	D:\MassHunter\Tune\QQQ\G6470A\atunes.TUNE.XML
Ion Source	AJS ESI
Ionization Mode	AJS ESI
Tuned Resolution	Unit Only [Wide & Widest Not Tuned]
Vacuum Pressure	1.00E+0[R]; 5.52E-5[H]

Source Parameters

Parameter	Value
Gas Temp	300
Gas Flow	8
Nebulizer	15
Capillary	4000
Nozzle Voltage	1500
Sheath Gas Temp	250
Sheath Gas Flow	7

Positive Results

Analyzer: MS1 Polarity: Positive Width: Unit

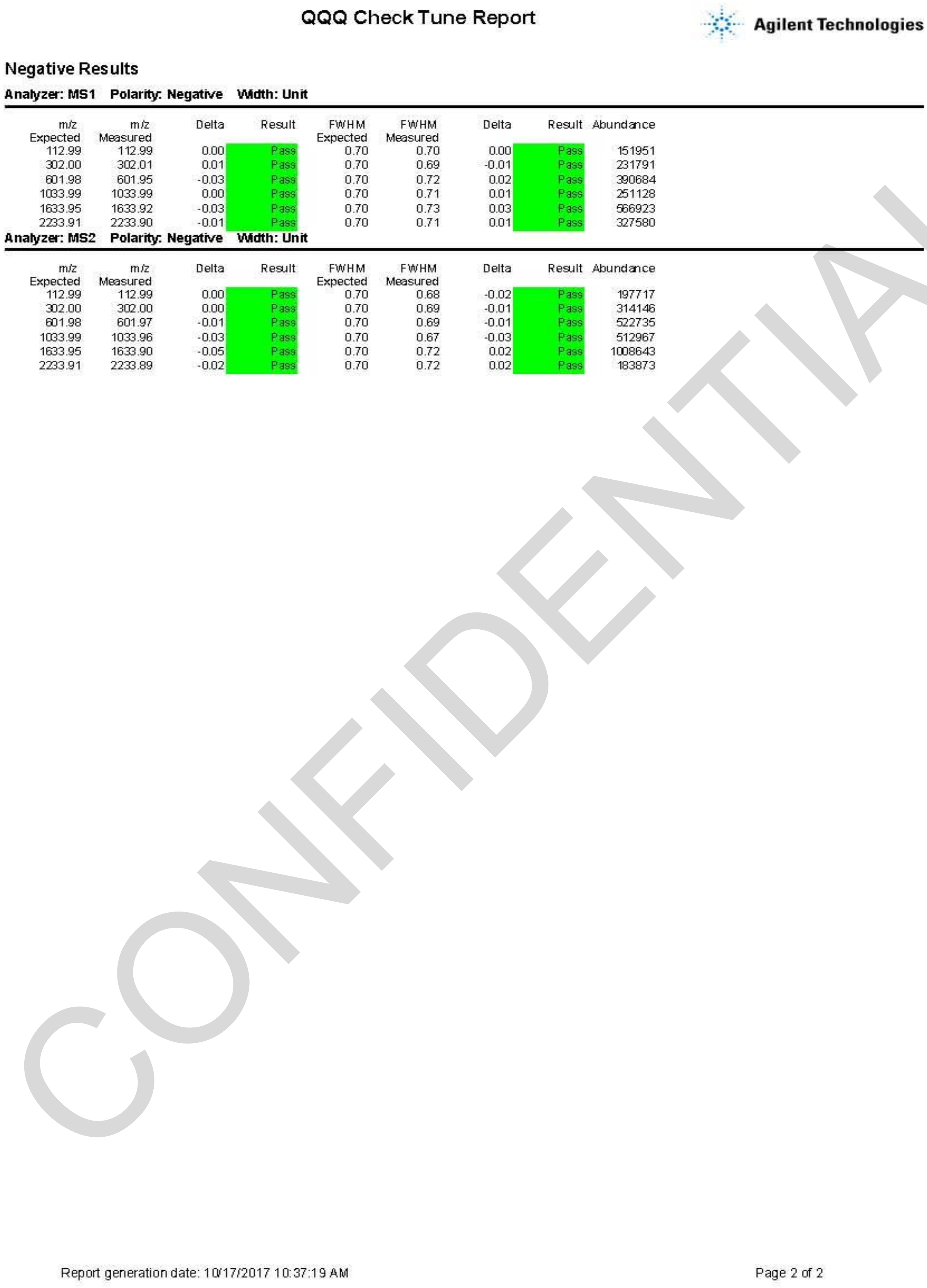
m/z Expected	m/z Measured	Delta	Result	FWHM Expected	FWHM Measured	Delta	Result	Abundance
118.09	118.11	0.02	Pass	0.70	0.68	-0.02	Pass	479202
322.05	322.08	0.03	Pass	0.70	0.66	-0.04	Pass	242662
622.03	622.05	0.02	Pass	0.70	0.66	-0.04	Pass	169259
922.01	922.02	0.01	Pass	0.70	0.70	0.00	Pass	135299
1521.97	1521.97	0.00	Pass	0.70	0.69	-0.01	Pass	56672
2121.93	2121.90	-0.03	Pass	0.70	0.71	0.01	Pass	49749

Analyzer: MS2 Polarity: Positive Width: Unit

m/z Expected	m/z Measured	Delta	Result	FWHM Expected	FWHM Measured	Delta	Result	Abundance
118.09	118.10	0.01	Pass	0.70	0.68	-0.02	Pass	478815
322.05	322.06	0.01	Pass	0.70	0.66	-0.04	Pass	194996
622.03	622.05	0.02	Pass	0.70	0.67	-0.03	Pass	192309
922.01	922.01	0.00	Pass	0.70	0.68	-0.02	Pass	132278
1521.97	1521.95	-0.02	Pass	0.70	0.68	-0.02	Pass	55436
2121.93	2121.89	-0.04	Pass	0.70	0.67	-0.03	Pass	30089

Report generation date: 10/17/2017 10:37:19 AM

Page 1 of 2



QQQ Check Tune Report

Negative Results

Analyzer: MS1 Polarity: Negative Width: Unit

m/z Expected	m/z Measured	Delta	Result	FWHM Expected	FWHM Measured	Delta	Result	Abundance
112.99	112.99	0.00	Pass	0.70	0.70	0.00	Pass	151951
302.00	302.01	0.01	Pass	0.70	0.69	-0.01	Pass	231791
601.98	601.95	-0.03	Pass	0.70	0.72	0.02	Pass	390684
1033.99	1033.99	0.00	Pass	0.70	0.71	0.01	Pass	251128
1633.95	1633.92	-0.03	Pass	0.70	0.73	0.03	Pass	566923
2233.91	2233.90	-0.01	Pass	0.70	0.71	0.01	Pass	327580

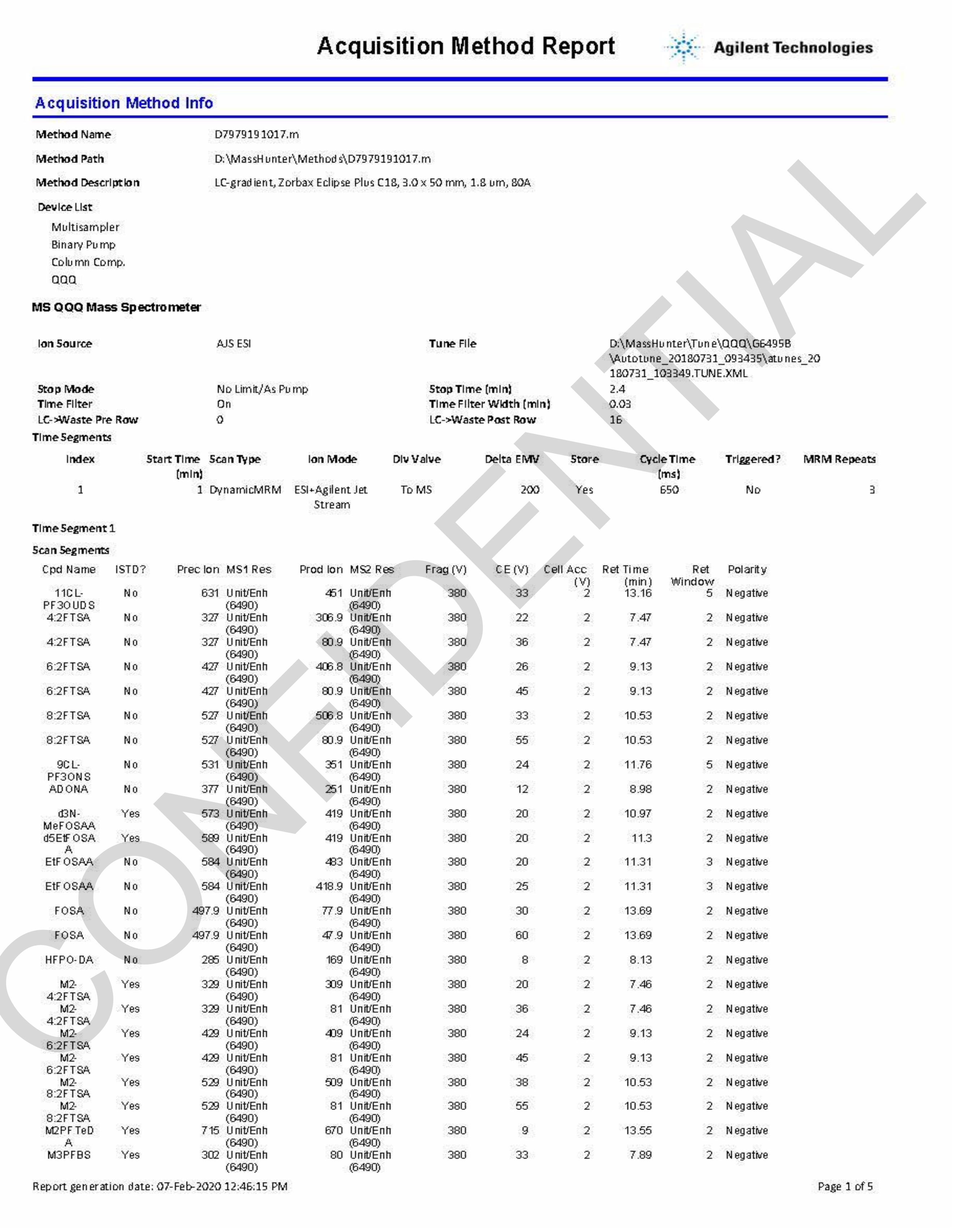
Analyzer: MS2 Polarity: Negative Width: Unit

m/z Expected	m/z Measured	Delta	Result	FWHM Expected	FWHM Measured	Delta	Result	Abundance
112.99	112.99	0.00	Pass	0.70	0.68	-0.02	Pass	197717
302.00	302.00	0.00	Pass	0.70	0.69	-0.01	Pass	314146
601.98	601.97	-0.01	Pass	0.70	0.69	-0.01	Pass	522735
1033.99	1033.96	-0.03	Pass	0.70	0.67	-0.03	Pass	512967
1633.95	1633.90	-0.05	Pass	0.70	0.72	0.02	Pass	1008643
2233.91	2233.89	-0.02	Pass	0.70	0.72	0.02	Pass	183873

Report generation date: 10/17/2017 10:37:19 AM

Page 2 of 2

Figure 4: Acquisition Method Report for ASTM D7979



Acquisition Method Report

Agilent Technologies

Acquisition Method Info

Method Name	D7979191017.m
Method Path	D:\MassHunter\Methods\D7979191017.m
Method Description	LC-gradient, Zorbax Eclipse Plus C18, 3.0 x 50 mm, 1.8 um, 80A

Device List

- Multisampler
- Binary Pump
- Column Comp.
- QQQ

MS QQQ Mass Spectrometer

Ion Source	AJS ESI	**Tune File**	D:\MassHunter\Tune\QQQ\G6495B \Autotune_20180731_093435\atunes_20 180731_103349.TUNE.XML
Stop Mode	No Limit/As Pump	**Stop Time (min)**	2.4
Time Filter	On	**Time Filter Width (min)**	0.03
LC->Waste Pre Row	0	**LC->Waste Post Row**	16

Time Segments

Index	Start Time (min)	Scan Type	Ion Mode	Div Valve	Delta EMV	Store	Cycle Time (ms)	Triggered?	MRM Repeats
1	1	DynamicMRM	ESI+Agilent Jet Stream	To MS	200	Yes	650	No	3

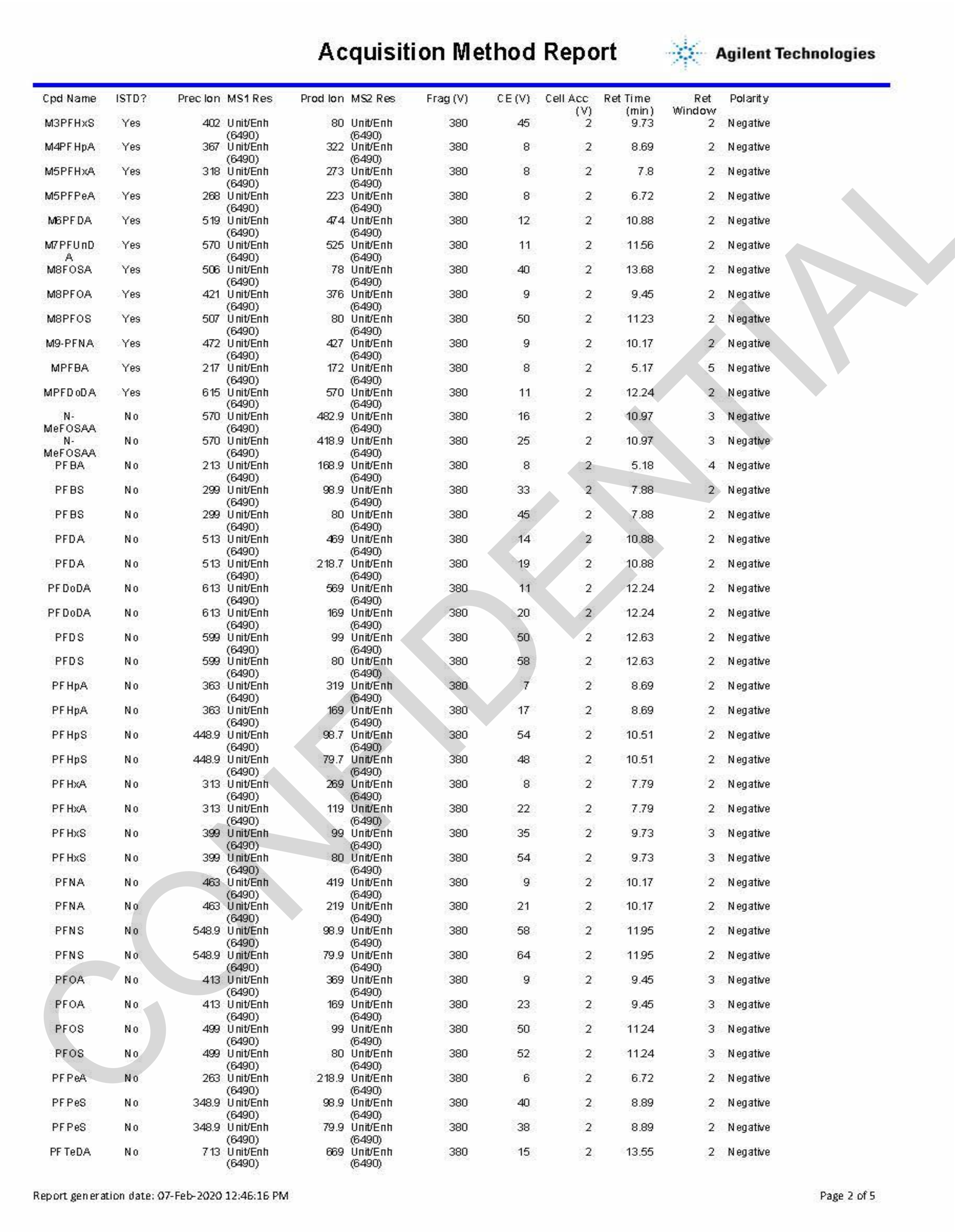
Time Segment 1

Scan Segments

Cpd Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Frag (V)	CE (V)	Cell Acc (V)	Ret Time (min)	Ret Window	Polarity
11CL-PF3OUDS	No	631	Unit/Enh (6490)	451	Unit/Enh (6490)	380	33	2	13.16	5	Negative
4:2FTSA	No	327	Unit/Enh (6490)	306.9	Unit/Enh (6490)	380	22	2	7.47	2	Negative
4:2FTSA	No	327	Unit/Enh (6490)	80.9	Unit/Enh (6490)	380	36	2	7.47	2	Negative
6:2FTSA	No	427	Unit/Enh (6490)	406.8	Unit/Enh (6490)	380	26	2	9.13	2	Negative
6:2FTSA	No	427	Unit/Enh (6490)	80.9	Unit/Enh (6490)	380	45	2	9.13	2	Negative
8:2FTSA	No	527	Unit/Enh (6490)	506.8	Unit/Enh (6490)	380	33	2	10.53	2	Negative
8:2FTSA	No	527	Unit/Enh (6490)	80.9	Unit/Enh (6490)	380	55	2	10.53	2	Negative
9CL-PF3ONS	No	531	Unit/Enh (6490)	351	Unit/Enh (6490)	380	24	2	11.76	5	Negative
ADONA	No	377	Unit/Enh (6490)	251	Unit/Enh (6490)	380	12	2	8.98	2	Negative
d3N-MeFOSAA	Yes	573	Unit/Enh (6490)	419	Unit/Enh (6490)	380	20	2	10.97	2	Negative
d5EtFOSAA	Yes	589	Unit/Enh (6490)	419	Unit/Enh (6490)	380	20	2	11.3	2	Negative
EtFOSAA	No	584	Unit/Enh (6490)	483	Unit/Enh (6490)	380	20	2	11.31	3	Negative
EtFOSAA	No	584	Unit/Enh (6490)	418.9	Unit/Enh (6490)	380	25	2	11.31	3	Negative
FOSA	No	497.9	Unit/Enh (6490)	77.9	Unit/Enh (6490)	380	30	2	13.69	2	Negative
FOSA	No	497.9	Unit/Enh (6490)	47.9	Unit/Enh (6490)	380	60	2	13.69	2	Negative
HFPO-DA	No	285	Unit/Enh (6490)	169	Unit/Enh (6490)	380	8	2	8.13	2	Negative
M2-4:2FTSA	Yes	329	Unit/Enh (6490)	309	Unit/Enh (6490)	380	20	2	7.46	2	Negative
M2-4:2FTSA	Yes	329	Unit/Enh (6490)	81	Unit/Enh (6490)	380	36	2	7.46	2	Negative
M2-6:2FTSA	Yes	429	Unit/Enh (6490)	409	Unit/Enh (6490)	380	24	2	9.13	2	Negative
M2-6:2FTSA	Yes	429	Unit/Enh (6490)	81	Unit/Enh (6490)	380	45	2	9.13	2	Negative
M2-8:2FTSA	Yes	529	Unit/Enh (6490)	509	Unit/Enh (6490)	380	38	2	10.53	2	Negative
M2-8:2FTSA	Yes	529	Unit/Enh (6490)	81	Unit/Enh (6490)	380	55	2	10.53	2	Negative
M2PFTeDA	Yes	715	Unit/Enh (6490)	670	Unit/Enh (6490)	380	9	2	13.55	2	Negative
M3PFBS	Yes	302	Unit/Enh (6490)	80	Unit/Enh (6490)	380	33	2	7.89	2	Negative

Report generation date: 07-Feb-2020 12:46:15 PM

Page 1 of 5

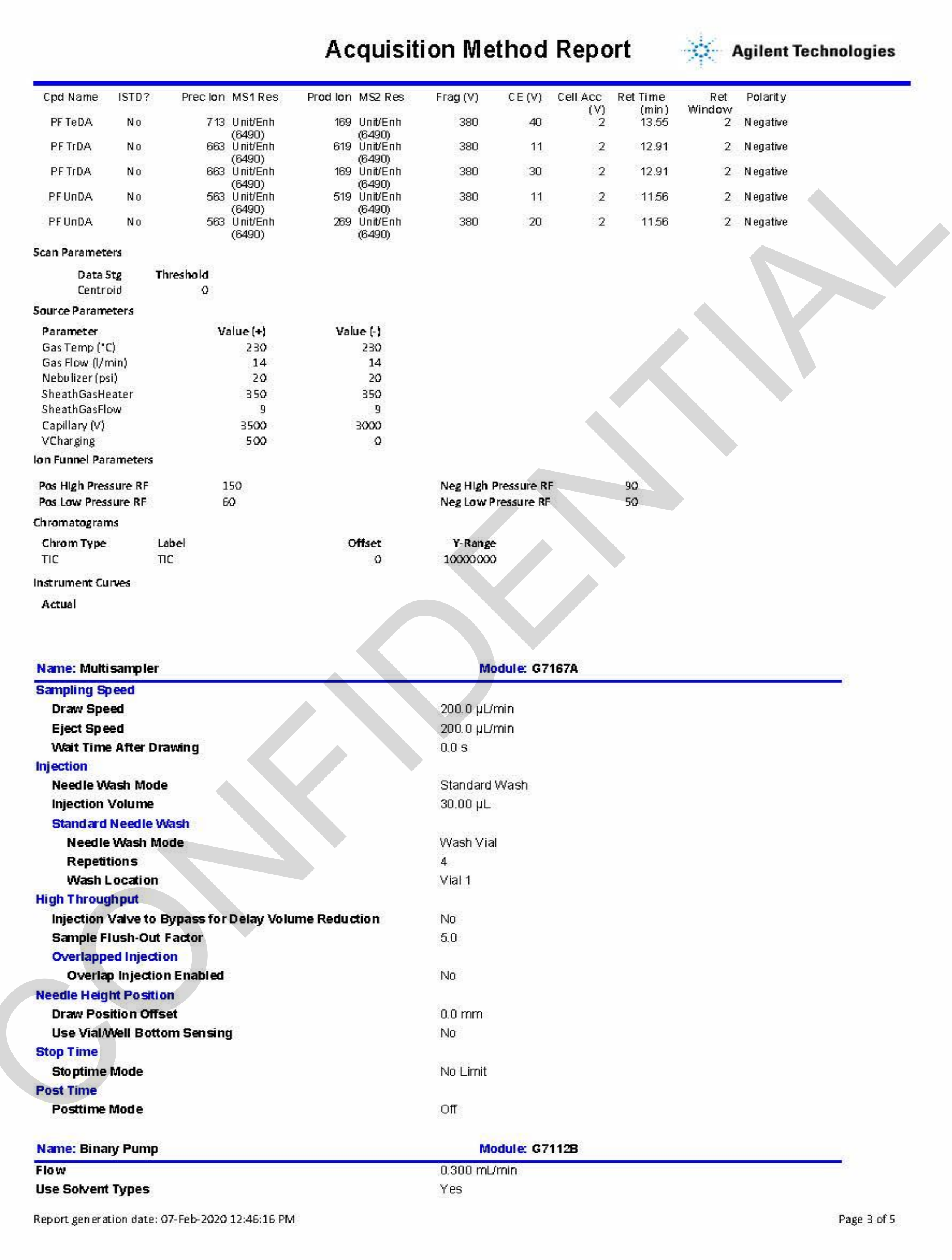


Acquisition Method Report

Agilent Technologies

Cpd Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Frag (V)	CE (V)	Cell Acc (V)	Ret Time (min)	Ret Window	Polarity
M3PFHxS	Yes	402	Unit/Enh (6490)	80	Unit/Enh (6490)	380	45	2	9.73	2	Negative
M4PFHpA	Yes	367	Unit/Enh (6490)	322	Unit/Enh (6490)	380	8	2	8.69	2	Negative
M5PFHxA	Yes	318	Unit/Enh (6490)	273	Unit/Enh (6490)	380	8	2	7.8	2	Negative
M5PFPeA	Yes	268	Unit/Enh (6490)	223	Unit/Enh (6490)	380	8	2	6.72	2	Negative
M6PFDA	Yes	519	Unit/Enh (6490)	474	Unit/Enh (6490)	380	12	2	10.88	2	Negative
M7PFUnDA	Yes	570	Unit/Enh (6490)	525	Unit/Enh (6490)	380	11	2	11.56	2	Negative
M8FOSA	Yes	506	Unit/Enh (6490)	78	Unit/Enh (6490)	380	40	2	13.68	2	Negative
M8PFOA	Yes	421	Unit/Enh (6490)	376	Unit/Enh (6490)	380	9	2	9.45	2	Negative
M8PFOS	Yes	507	Unit/Enh (6490)	80	Unit/Enh (6490)	380	50	2	11.23	2	Negative
M9-PFNA	Yes	472	Unit/Enh (6490)	427	Unit/Enh (6490)	380	9	2	10.17	2	Negative
MPFBA	Yes	217	Unit/Enh (6490)	172	Unit/Enh (6490)	380	8	2	5.17	5	Negative
MPFDoDA	Yes	615	Unit/Enh (6490)	570	Unit/Enh (6490)	380	11	2	12.24	2	Negative
N-MeFOSAA	No	570	Unit/Enh (6490)	482.9	Unit/Enh (6490)	380	16	2	10.97	3	Negative
N-MeFOSAA	No	570	Unit/Enh (6490)	418.9	Unit/Enh (6490)	380	25	2	10.97	3	Negative
PFBA	No	213	Unit/Enh (6490)	168.9	Unit/Enh (6490)	380	8	2	5.18	4	Negative
PFBS	No	299	Unit/Enh (6490)	98.9	Unit/Enh (6490)	380	33	2	7.88	2	Negative
PFBS	No	299	Unit/Enh (6490)	80	Unit/Enh (6490)	380	45	2	7.88	2	Negative
PFDA	No	513	Unit/Enh (6490)	469	Unit/Enh (6490)	380	14	2	10.88	2	Negative
PFDA	No	513	Unit/Enh (6490)	218.7	Unit/Enh (6490)	380	19	2	10.88	2	Negative
PFDoDA	No	613	Unit/Enh (6490)	569	Unit/Enh (6490)	380	11	2	12.24	2	Negative
PFDoDA	No	613	Unit/Enh (6490)	169	Unit/Enh (6490)	380	20	2	12.24	2	Negative
PFDS	No	599	Unit/Enh (6490)	99	Unit/Enh (6490)	380	50	2	12.63	2	Negative
PFDS	No	599	Unit/Enh (6490)	80	Unit/Enh (6490)	380	58	2	12.63	2	Negative
PFHpA	No	363	Unit/Enh (6490)	319	Unit/Enh (6490)	380	7	2	8.69	2	Negative
PFHpA	No	363	Unit/Enh (6490)	169	Unit/Enh (6490)	380	17	2	8.69	2	Negative
PFHpS	No	448.9	Unit/Enh (6490)	98.7	Unit/Enh (6490)	380	54	2	10.51	2	Negative
PFHpS	No	448.9	Unit/Enh (6490)	79.7	Unit/Enh (6490)	380	48	2	10.51	2	Negative
PFHxA	No	313	Unit/Enh (6490)	269	Unit/Enh (6490)	380	8	2	7.79	2	Negative
PFHxA	No	313	Unit/Enh (6490)	119	Unit/Enh (6490)	380	22	2	7.79	2	Negative
PFHxS	No	399	Unit/Enh (6490)	99	Unit/Enh (6490)	380	35	2	9.73	3	Negative
PFHxS	No	399	Unit/Enh (6490)	80	Unit/Enh (6490)	380	54	2	9.73	3	Negative
PFNA	No	463	Unit/Enh (6490)	419	Unit/Enh (6490)	380	9	2	10.17	2	Negative
PFNA	No	463	Unit/Enh (6490)	219	Unit/Enh (6490)	380	21	2	10.17	2	Negative
PFNS	No	548.9	Unit/Enh (6490)	98.9	Unit/Enh (6490)	380	58	2	11.95	2	Negative
PFNS	No	548.9	Unit/Enh (6490)	79.9	Unit/Enh (6490)	380	64	2	11.95	2	Negative
PFOA	No	413	Unit/Enh (6490)	369	Unit/Enh (6490)	380	9	2	9.45	3	Negative
PFOA	No	413	Unit/Enh (6490)	169	Unit/Enh (6490)	380	23	2	9.45	3	Negative
PFOS	No	499	Unit/Enh (6490)	99	Unit/Enh (6490)	380	50	2	11.24	3	Negative
PFOS	No	499	Unit/Enh (6490)	80	Unit/Enh (6490)	380	52	2	11.24	3	Negative
PFPeA	No	263	Unit/Enh (6490)	218.9	Unit/Enh (6490)	380	6	2	6.72	2	Negative
PFPeS	No	348.9	Unit/Enh (6490)	98.9	Unit/Enh (6490)	380	40	2	8.89	2	Negative
PFPeS	No	348.9	Unit/Enh (6490)	79.9	Unit/Enh (6490)	380	38	2	8.89	2	Negative
PFTeDA	No	713	Unit/Enh (6490)	669	Unit/Enh (6490)	380	15	2	13.55	2	Negative

Report generation date: 07-Feb-2020 12:46:16 PM



Acquisition Method Report

Agilent Technologies

Cpd Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Frag (V)	CE (V)	Cell Acc (V)	Ret Time (min)	Ret Window	Polarity
PF TeDA	No	713	Unit/Enh (6490)	169	Unit/Enh (6490)	380	40	2	13.55	2	Negative
PF TrDA	No	663	Unit/Enh (6490)	619	Unit/Enh (6490)	380	11	2	12.91	2	Negative
PF TrDA	No	663	Unit/Enh (6490)	169	Unit/Enh (6490)	380	30	2	12.91	2	Negative
PF UnDA	No	563	Unit/Enh (6490)	519	Unit/Enh (6490)	380	11	2	11.56	2	Negative
PF UnDA	No	563	Unit/Enh (6490)	269	Unit/Enh (6490)	380	20	2	11.56	2	Negative

Scan Parameters

Data Stg	Threshold
Centroid	0

Source Parameters

Parameter	Value (+)	Value (-)
Gas Temp (°C)	230	230
Gas Flow (l/min)	14	14
Nebulizer (psi)	20	20
SheathGasHeater	350	350
SheathGasFlow	9	9
Capillary (V)	3500	3000
VCharging	500	0

Ion Funnel Parameters

Pos High Pressure RF	150	Neg High Pressure RF	90
Pos Low Pressure RF	60	Neg Low Pressure RF	50

Chromatograms

Chrom Type	Label	Offset	Y-Range
TIC	TIC	0	10000000

Instrument Curves

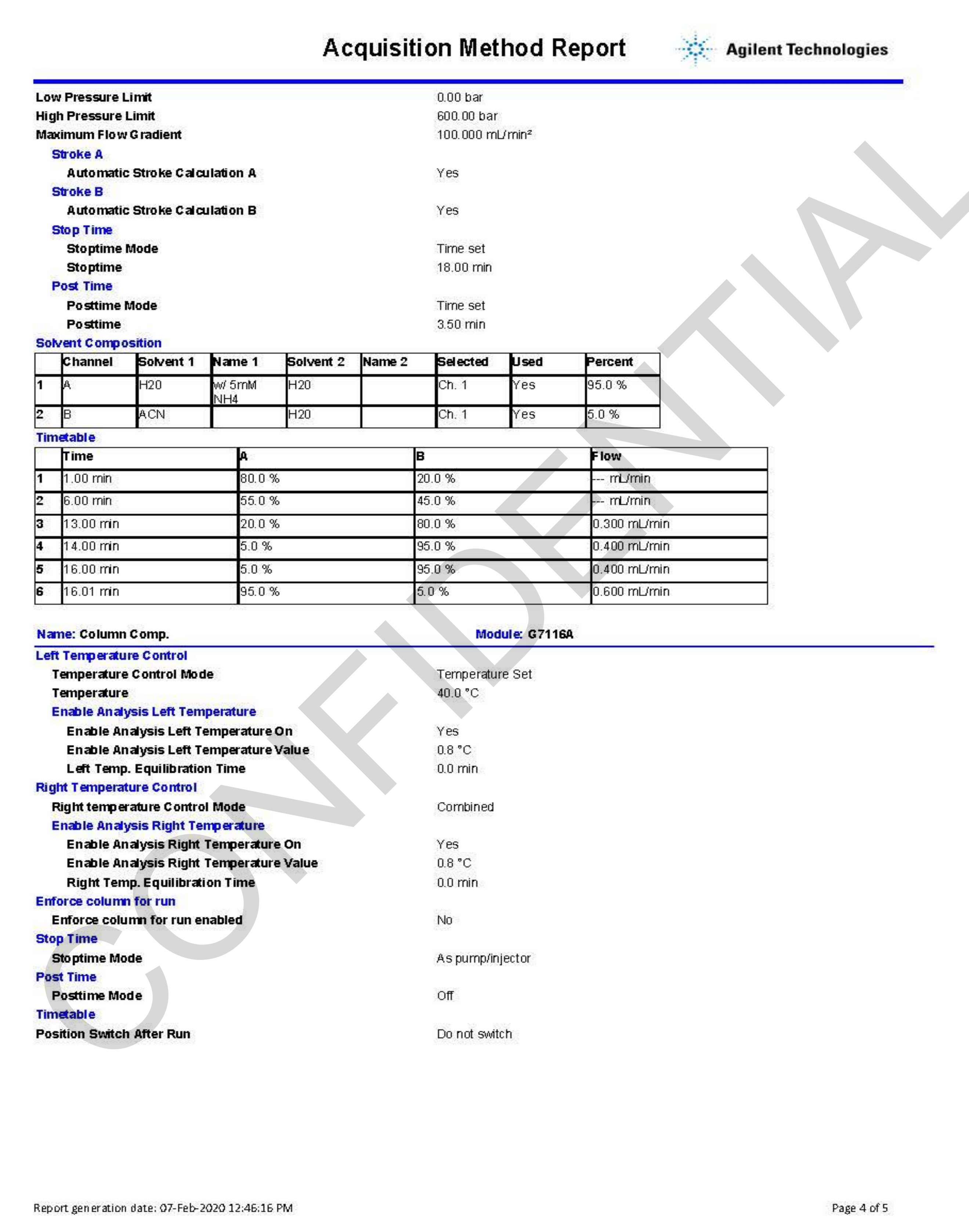
Actual

Name: Multisampler	**Module:** G7167A
Sampling Speed	
Draw Speed	200.0 µL/min
Eject Speed	200.0 µL/min
Wait Time After Drawing	0.0 s
Injection	
Needle Wash Mode	Standard Wash
Injection Volume	30.00 µL
Standard Needle Wash	
Needle Wash Mode	Wash Vial
Repetitions	4
Wash Location	Vial 1
High Throughput	
Injection Valve to Bypass for Delay Volume Reduction	No
Sample Flush-Out Factor	5.0
Overlapped Injection	
Overlap Injection Enabled	No
Needle Height Position	
Draw Position Offset	0.0 mm
Use Vial/Well Bottom Sensing	No
Stop Time	
Stoptime Mode	No Limit
Post Time	
Posttime Mode	Off

Name: Binary Pump	**Module:** G7112B
Flow	0.300 mL/min
Use Solvent Types	Yes

Report generation date: 07-Feb-2020 12:46:16 PM

Page 3 of 5



Acquisition Method Report

Agilent Technologies

Low Pressure Limit	0.00 bar
High Pressure Limit	600.00 bar
Maximum Flow Gradient	100.000 mL/min²
Stroke A	
Automatic Stroke Calculation A	Yes
Stroke B	
Automatic Stroke Calculation B	Yes
Stop Time	
Stoptime Mode	Time set
Stoptime	18.00 min
Post Time	
Posttime Mode	Time set
Posttime	3.50 min

Solvent Composition

	Channel	Solvent 1	Name 1	Solvent 2	Name 2	Selected	Used	Percent
1	A	H20	w/ 5mM NH4	H20		Ch. 1	Yes	95.0 %
2	B	ACN		H20		Ch. 1	Yes	5.0 %

Timetable

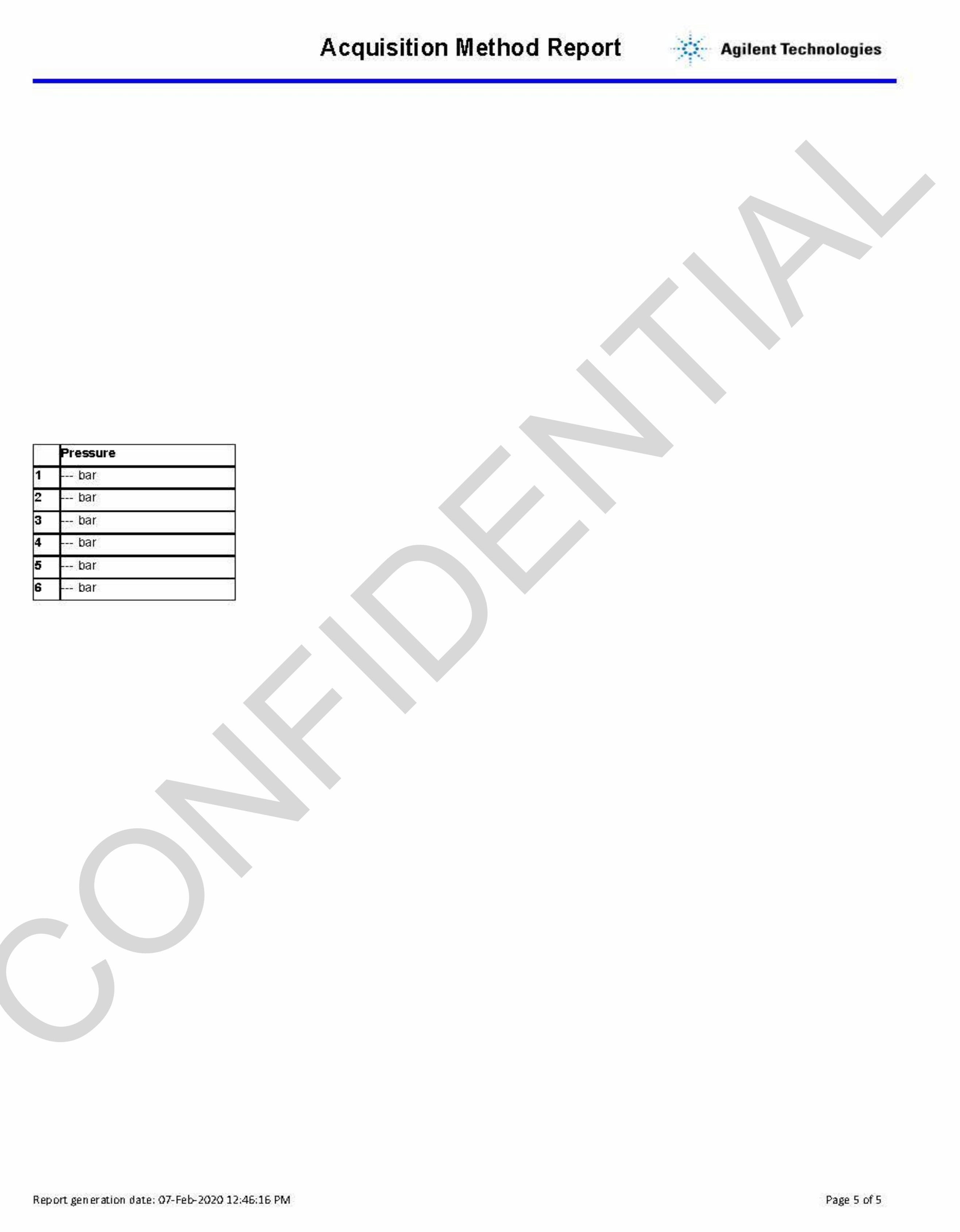
	Time	A	B	Flow
1	1.00 min	80.0 %	20.0 %	--- mL/min
2	6.00 min	55.0 %	45.0 %	--- mL/min
3	13.00 min	20.0 %	80.0 %	0.300 mL/min
4	14.00 min	5.0 %	95.0 %	0.400 mL/min
5	16.00 min	5.0 %	95.0 %	0.400 mL/min
6	16.01 min	95.0 %	5.0 %	0.600 mL/min

Name: Column Comp. **Module:** G7116A

Left Temperature Control	
Temperature Control Mode	Temperature Set
Temperature	40.0 °C
Enable Analysis Left Temperature	
Enable Analysis Left Temperature On	Yes
Enable Analysis Left Temperature Value	0.8 °C
Left Temp. Equilibration Time	0.0 min
Right Temperature Control	
Right temperature Control Mode	Combined
Enable Analysis Right Temperature	
Enable Analysis Right Temperature On	Yes
Enable Analysis Right Temperature Value	0.8 °C
Right Temp. Equilibration Time	0.0 min
Enforce column for run	
Enforce column for run enabled	No
Stop Time	
Stoptime Mode	As pump/injector
Post Time	
Posttime Mode	Off
Timetable	
Position Switch After Run	Do not switch

Report generation date: 07-Feb-2020 12:46:16 PM

Page 4 of 5



Acquisition Method Report

Agilent Technologies

	Pressure
1	--- bar
2	--- bar
3	--- bar
4	--- bar
5	--- bar
6	--- bar

Report generation date: 07-Feb-2020 12:46:16 PM

Page 5 of 5

STANDARD OPERATING PROCEDURE

INTERNAL AUDIT

APPROVALS:

Barbara Ball

03/06/13

QA Officer Date

03/06/13

Technical Director Date

Number	Description of Change	Date
001-003	Previous changes were not documented	
004	Updated to comply with DoD QSM and ISO 17025 standards.	03/31/11
005	Login/Sample Receiving audit checklist added and SOP/Test Method checklist updated	03/05/12
006	Minor changes needed due to extra certification requirements	03/06/13
007		
008		
009		
010		
011		
012		
013		
014		

1.0 SCOPE AND APPLICATION

This SOP sets the procedure for conducting internal audits. All employees are subject to the internal audit. All certifying bodies and many clients require annual internal audits.

2.0 SUMMARY OF METHOD

An annual internal audit is required by NELAC, DoD QSM, other certifying bodies, and clients. The Quality Assurance Officer is responsible for scheduling and executing the audit. The task of carrying out audits may be delegated to other staff with appropriate technical training and familiarity with the Quality Assurance System. Each department of the lab must be audited to ensure they follow the quality system and appropriate SOPs, that SOPs match methods when appropriate and required, and that the procedures and documentation produce scientifically and legally defensible results.

3.0 INTERFERENCES

Not applicable.

4.0 APPARATUS AND MATERIALS

Computer.

VLIMs.

Internal Audit Checklists.

SOPs.

Methods.

Quality system documentation provided by all certifying bodies and clients.

5.0 REAGENTS

Not applicable.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Not applicable.

7.0 PROCEDURE

1. The audit is performed annually and documents are kept to verify its successful completion. The goal of the audit is to ensure that lab functions are within the requirements of the quality system and that the quality system meets the requirements of all certifications and clients.

2. The QA Officer along with the QA Officer deputies must carry out these audits. Analysts cannot audit their own operations.

3. Review of Quality Assurance Manual. In particular to make sure all appendixes are up to date that the manual reflects what is done in the lab and also up to date with the most recent changes in regulations and certification requirements.

4. Review of Quality Assurance System. Quality Assurance System checklist (Figure 1) is used annually for this review. All points must be addressed.

5. SOP/Test Method Review.

    - SOP/Test Method Checklist (Figure 2) is used for every SOP/Test Method during the annual internal audit.
    - All information on checklist must be completed.
    - Proficiency Testing (PT) Samples (see SOP # QA-018 for more information)
        - Applicable matrix/analyte PT samples performed based on certifications.
        - Diluted per PT provider instructions.
        - Extracted or digested for appropriate analyses.
        - Handled and run in the same manner as real environmental samples.
        - Not analyzed multiple times unless real environmental samples are.
        - Concentration same as real environmental samples.
        - Frequency of quality control samples analyzed is same as real environmental samples.
        - Results are recorded in VLIMs and PT provider results book.
        - PT results reviewed when received from PT provider.
        - Failed/Not Acceptable results have corrective action with supporting documentation.
        - PT results are placed in analyst training record with new continuing Demonstration of Capability.
    - Corrective actions and follow-ups must be reviewed from the past year including Proficiency Test study results.

- Follow-up on any audit responses from recent external audits.
- Follow-up on any issue from the past year's internal audit.
- General Information Section includes all logbook checks and annual requirements.
  - All logbooks must be checked for the following information:
    - Unique ID, Title/Description and Date of Issue on outside cover.
    - Entries must be checked for date, name (Signature or Initials), what was done, and is it current.
    - Balance Logbooks need to be checked for the following:
      - Weight Serial #
      - Acceptance Criteria
      - Check performed everyday of use
    - Maintenance Logbooks need to be checked for the following:
      - All preventive maintenance is recorded.
      - All maintenance performed is documented.
      - Signed off by Laboratory Manager or Superintendent of Operations.
    - Reagent/Standard Logbooks need to be checked for the following:
      - Date of Receipt
      - Source
      - Lot #
      - Concentration (initial and final)
      - Unique Name
      - Weight or volume (initial and final)
      - Solvent/Reagent used with Lot #
      - Recipe/Formula for making reagent/standard
      - Analyst's Initials

        - Date Prepared
        - Expiration Date
    - Nonconformance/Preventive Action Logbook needs to be checked. SOP # QA-004 can be used for guidance.
- Annual QC requirements See SOP # QA-009 for specific requirements.
    - Method Detection Limit
        - Must be completed within last 12 months.
        - Prepared, extracted, or digested like normal samples.
        - Run for all analytes, matrices, and instruments.
        - 7 replicates must be run.
        - Follow MDL spike requirements.
        - All documentation must be retained.
    - Limit of Detection (LOD)
        - Must be completed within last 12 months. If DoD analyte, LOD must be completed quarterly.
        - Prepared, extracted, or digested like normal samples.
        - Run for all analytes, matrices, and instruments.
        - Run at 2-3 times the detection limit for single analyte standards or 1-4 times the detection limit for multi-analyte standards.
        - Qualitative identification greater than blank.
        - All documentation must be retained.
    - Limit of Quantitation (LOQ)
        - Must be completed within last 12 months. If DoD analyte, LOQ must be completed quarterly.
        - Prepared, extracted, or digested like normal samples.
        - Run for all analytes, matrices, and instruments.
        - Must be at or above the lowest initial calibration point and above the LOD.

        - Must be within acceptable recoveries.
        - All documentation must be retained.
    - Check the date of the last Control Check and/or Linear Range.
    - Check the date of the last Retention Time Window Study for Organics and Ion Chromotography.
    - Check that all supplies are labeled with date received, date opened, and expiration date.

- Data chase is performed by randomly selecting a sample relevant to each analysis. The sample is to be followed from entry into the department until final result or exit from the department.
    - Sample chosen must also be chosen for co-dependent analysis (i.e. PCB Extraction and PCBs).
    - QC Prep and Run Batches must be reviewed and verified that all qc samples were completed and within requirements.
    - Identify all reagents and standards associated with sample and calibration batch.
    - Reagent traceability is performed to trace the reagent back to the stock standards received.
        - The reagent/standard logbook and unique identifier is used to follow reagents back to stock standards and stock standards back to certification.
    - General notes section needs to include any information that could effect the outcome of the analysis (i.e. holding time issue, incorrect preservation, dilutions, etc.)
    - Is all raw data (i.e. benchsheet, instrument printouts, electronic instrument reports, etc.) available?
    - Associated calibration and MDL was completed within the last 12 months and was within quality control/method requirements?

- Calibrations
  - Record all standards and reagents used in the calibration for the randomly selected sample.
    - Record standard or reagent ID, lot #'s, preparation date, and expiration date for the prepared standard and standard as received.
    - Check to make sure a certificate of analysis is available.
  - Must be completed within last 12 months.
  - Second source standard is used.
  - R value must meet method requirements.
  - Curve Fit must meet method requirements.
  - Correct number of points used.
  - Lowest point must be below reporting limit.

- Preparation Check (i.e. extraction or digestion)
  - Record all standards and reagents used in the preparation batch.
    - Record standard or reagent ID, lot #'s, preparation date, and expiration date for the prepared standard and standard as received.
    - Check to make sure a certificate of analysis is available.

- Bench Sheet check for the following information to be recorded:
  - Analysis Information
    - Name of Analysis
    - Method #
    - Detection Limits
    - Wavelength
    - Program
    - Instrumentation

- Batch Information
  - Start Date & Time
  - End Date & Time
  - Analyst
  - Batch ID
  - Calibration ID
- Reagent/Standard Information
  - Standard Lot #(s)
  - Reagent Lot #(s)
- Sample Information
  - Lab Sample Ids
  - Matrix
  - QC Samples
  - Solvents
  - Spike Concentrations
  - Spike IDs
  - pH Checks Recorded
  - Dilution Factor
  - % Total Solids
  - Initial Volume/Weight used
  - Final Volume/Weight
  - Absorbance
  - Calculations
  - Results
  - Notes

        - Peer Review
    - Is subsampling procedure described in SOP #SAD-011 being followed?
        - Volumes are they being targeted.
    - Does benchsheet include an effective date?
        - Is the benchsheet being used a current controlled copy?
    - Is the benchsheet a clean legible copy?
        - Are any corrections addressed in appropriate fashion?
- Prep Batch QC Check
    - Identify what items are being performed with the prep batch.
    - Record the frequency that the QC item is being performed.
    - Are the QC items being performed at the appropriate frequency?
- Raw Data Check for the following information to be recorded
    - Analysis Information (same as benchsheet check)
    - Batch Information (same as benchsheet check)
    - Reagent/Standard Information (same as benchsheet check)
    - Sample Information (same as benchsheet check)
    - Manual Integrations check see SOP #ORL-003 for more information
        - Are project/certification requirements being followed?
            - Before and after pictures retained?
        - Records initialed and date by analyst.
        - Are manual integrations identified with appropriate codes?
- Run Batch Quality Control Sample Review
    - QC Sample Type performed with each batch
    - Frequency that the QC item is being performed
    - Acceptance Limits
    - Is QC item within acceptance limit?

  - SOP Requirements
  - Method Requirements
  - Project/Certification Specific Requirements
- Data Review
  - Is SOP # QA-007 being followed?
  - Analyst Review
  - Peer Review
- SOP Check
  - Check that all required sections are included in SOP.
  - Are all sections in the SOP followed?
  - Do all sections in the SOP agree with method?
  - Record all revisions needed for current SOP.
  - Analysts' methods and procedures must be checked against SOPs. If the two are inconsistent and the analysts' procedure is acceptable the SOP must be changed to reflect what is done. If the analysts' procedure is not acceptable the corrective action procedure must be implemented.
  - Verify that the SOP meets all requirements of the most recent revision of the method. All method QC requirements must be met or exceeded.

6. Log-In/Sample Receiving Checklist

- Log-In/Sampling Receiving Checklist (Figure 3) is used for the Log-In/Sample Receiving department during the annual internal audit.
- All information on checklist must be completed.
- Corrective actions and follow-ups must be reviewed from the past year including Proficiency Test study results.
- Follow-up on any audit responses from recent external audits.
- Follow-up on any issue from the past year's internal audit.
- General Checklist information:

  - Nonconformance/Preventive Action Logbook needs to be checked. SOP # QA-004 can be used for guidance.
  - Check that all supplies are labeled with date received, date opened, and expiration date.
  - Check that the sample acceptance policy is clearly posted and available to all staff and clients.

- Data Chase:
  - Record Merit ID, Log-In Date, and COC #.
  - Sample Receiving Check section:
    - Is the Chain of Custody adequately filled out, signed and relinquished to the lab?
    - Are samples uniquely labeled?
    - Are all containers received in the laboratory assigned a unique identification?
    - Are durable labels used on samples?
    - When receiving samples, is the condition of the sample recorded?
    - Did samples arrive at the require temperature?
    - Chemical preservation of samples checked and recorded?
    - Is data from any sample that does not meet requirements flagged appropriately?
    - Are samples stored in appropriate conditions?
  - Subcontracting section:
    - Is the client notified when analyses need to be subcontracted?
    - Is a certified laboratory used for subcontracting when needed?
    - Is subcontracting laboratory registry complete and up-to-date?
  - Service to Client section:
    - Are records of complaints and subsequent actions maintained?
    - All correspondence pertaining to samples kept?
    - Is client confidentiality maintained?

- Records section:
  - Is the Chain of Custody adequately filled out, signed and relinquished to the lab? Chain of custody retained and stored in vLIMS?
  - Is field sheet completed for samples collected by Merit personnel? Field sheet retained and stored in vLIMS?
  - Is sample receiving checklist completed, retained and stored in vLIMS?
  - Is sample preservation checklist completed, retained and stored in vLIMS?
- Reporting:
  - Is client confidentiality maintained?
  - Are data qualifiers explained?
  - Are any amendments or revisions to analytical report clearly identified?
  - When analyses are completed by a subcontracting laboratory, are the results clearly identified as subcontracted? Is subcontractor's report available?
  - When new report is issued, is it uniquely identified?
- SOP Check
  - Check that all required sections are included in SOP.
  - Are all sections in the SOP followed?
  - Do all sections in the SOP agree with method?
  - Record all revisions needed for current SOP.

7. Guidance for expanding the internal audit can be found in the Reference Section.
8. Internal audit findings must be shared with the Technical Director and the Laboratory Manager.
9. A final report of the internal audit is then given to upper management (i.e. President, Vice President, etc.).

8.0 QUALITY CONTROL

Not applicable.

9.0 METHOD PERFORMANCE

Not applicable.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Not applicable.

11.0 SAFETY

Follow safety requirements listed in the specific SOP that is being audited.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

Not applicable.

13.0 DEFINITIONS

Not applicable.

14.0 REFERENCES

2003 NELAC Standard.

http://www.nelac-institute.org/standards.php#pab1_1

ELAP Certification Manual.

http://www.wadsworth.org/labcert/elapcert/certmanual/index.html

General Audit Checklist.

http://www.wadsworth.org/labcert/elapcert/forms/general_checklist.pdf

SW-846 Chapter 1.

http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/chap1.pdf

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.2, October 25, 2010.

Relevant Aspect of Standards	Y	N	N/A	Comments
PT Studies				
Are all PT samples are handled (i.e., managed, analyzed, and reported) in the same manner as real environmental samples utilizing the same staff, methods as used for routine analysis of that analyte, procedures, equipment, facilities, and frequency of analysis?				
Satisfactorily analyze at least one proficiency test sample per analyte per year for every accredited Potable Water Method?				
Perform proficiency testing two times per year per analyte per matrix per program from a NELAC approved provider?				
Personnel				
Has managerial staff with the authority and resources needed to discharge their duties?				
Have processes to ensure its personnel are free from any commercial, financial and other undue pressures, which might adversely affect the quality of the work?				
Organized in such a way that confidence in its independence of judgment and integrity is maintained at all times?				
Specify and document the responsibility, authority, and interrelation of all personnel who manage, perform or verify work affecting the quality of calibrations and tests in job descriptions for all positions.				
Does the documentation clearly described the lines of responsibility in the laboratory and shall be proportioned such that adequate supervision is maintained?				
Is supervision provided by persons familiar with the calibration or test methods and procedures, and the objective of the calibration or test and the assessment of the results.				
Does the Technical Director document the certification of the personnel performing all tests for which the laboratory is accredited have the appropriate educational and/or technical backgrounds?				
Do the technical director have overall responsibility for the technical operation of the environmental testing laboratory?				
Quality assurance officer: ___ensure that the quality system is implemented and followed at all times? ___have direct access to the highest level of management at which decisions are taken on laboratory policy or resources, and to the technical director? ___serve as the focal point for QA/QC?				

Relevant Aspect of Standards	Y	N	N/A	Comments
___responsible for the oversight and/or review of quality control data? ___functions independent from laboratory operations where QA oversight is provided? ___evaluate data objectively and perform assessments without outside (e.g., managerial) influence? ___have documented training and/or experience in QA/QC procedures? ___have a general knowledge of the analytical methods for which data review is performed?				
Are deputies nominated in the case of absence of the technical director or QA officer?				
Are records maintained to indicate that it has sufficient personnel, having the necessary education, training, technical knowledge and experience for their assigned functions?				
Are personnel responsible for complying with all quality assurance/quality control requirements that pertain to their organizational/technical function?				
Does each technical staff member have a combination of experience and education to adequately demonstrate: __a specific knowledge of their particular function; and __a general knowledge of laboratory operations, analytical methods, QA/QC procedures and records management?				
Does management ensure that staff who are undergoing training are provided with appropriate supervision?				
Does management formulate goals with respect to the education, training and skills for laboratory personnel?				
Have a policy and procedures for identifying training needs and providing training of personnel?				
Are current job descriptions maintained for all personnel who manage, perform, or verify work affecting the quality of testing?				
Does management authorize specific personnel to: __perform particular types of sampling, __environmental test and/or calibration, __issue reports, __give opinions and interpretations, __operate particular types of equipment?				
Maintain records, with dates, of the relevant authorization(s), competence, educational and professional qualifications, training, skills, and experience for all technical and contracted personnel?				
Is there a defined minimum level of qualification, experience, and skills necessary for all positions in the lab?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Does the management maintain records to assure that all technical staff have demonstrated and documented initial and ongoing proficiency in the activities for which they are responsible?				
Does management ensure that training records kept up-to-date for all technical staff that include: ___Evidence that the employee has read, understands, and is using the latest version of the lab's in-house quality documentation, which relates to his/her job responsibilities; ___Training courses or workshops on specific equipment, analytical techniques, or lab procedures; ___Annual training course in data integrity procedures including the potential punishments & penalties for violations. ___Annual signature for each employee demonstrating they have read; acknowledge, and understand their personal & legal data integrity responsibilities including potential punishments & penalties for violations; and ___Documentation certifying that the employee has read, understands, and agrees to use the latest version of a test method used; and				
Does management ensure that the training records of each of the technical staff is updated by including documentation of continuing proficiency by at least one of the following: ___ cceptable performance of a blind sample; ___Another demonstration of capability; ___Successful analysis of a blind performance sample on a similar test method using the same technology; ___Analysis of at least 4 consecutive lab control samples with acceptable levels of precision and accuracy; or ___If one of the above can not be performed, the analysis of authentic samples that have been analyzed by another trained analyst with statistically indistinguishable results.				
Does the management assure supervision of all personnel employed by the laboratory?				
Does the management assure all sample acceptance criteria are verified and that samples are logged into the sample tracking system and properly labeled and stored?				
Does the management ensure the quality of all data reported by the laboratory?				
Does data integrity training include; ___Topics covered shall be documented in writing and provided to all trainees, ___organizational mission and its relationship to the critical need for honesty and full disclosure in all analytical reporting ___how and when to report data integrity issues,				

Relevant Aspect of Standards	Y	N	N/A	Comments
___record keeping ___employees are required to understand that any infractions of lab data integrity procedures will result in a detailed investigation that could lead to very serious consequences including immediate termination, or civil/criminal prosecution, ___specific examples of breaches of ethical behavior ___Discussion regarding all data integrity procedures, documentation, in-depth data monitoring. ___requirement for emphasis on the importance or proper written narration on the part of the analyst with respect the those cases where analytical data may be useful, but are in some way partially deficient?				
Quality System				
Establish and maintain a documented quality system appropriate to the type, range and volume of environmental testing activities it undertakes?				
Is the quality documentation available to, understood by, and implemented by all laboratory personnel?				
Is the laboratory's quality system policies and objectives defined in a quality manual?				
Does the quality manual and related quality documentation: ___state the laboratory's policies and procedures established in order to meet the requirements of Clients and certifications? ___include or make reference to the supporting procedures including technical procedures? ___outline the structure of the documentation used in the quality system? ___include the organization and management structure of the laboratory, its place in any parent organization, and relevant organizational charts? ___include procedures to ensure that all records are retained? ___include the relationship between management, technical operations, support services and the quality system? ___include job descriptions of key staff and reference to the job descriptions of other staff? ___include a quality policy statement with at least the following: ___Laboratory management's commitment to good professional practice and to the quality of its environmental testing in servicing its clients; ___management's statement of the laboratory's standard of service; ___objectives of the quality system? ___a requirement that all personnel familiarize themselves with the quality documentation and implement the policies and procedures in their work; ___The laboratory management's commitment to compliance with this standard.				

Relevant Aspect of Standards	Y	N	N/A	Comments
___ include procedures for control and maintenance of documentation through a document control system which ensures that all standard operating procedures, manuals, or documents clearly indicate the time period during which the procedure or document was in force? ___include procedures for achieving traceability of measurements? ___include a list of all methods under which the laboratory performs its accredited testing? ___include mechanisms for ensuring that the laboratory reviews all new work to ensure that it has the appropriate facilities and resources before commencing such work? ___include reference to the calibration and/or verification test procedures used? ___include procedures for handling submitted samples? ___include reference to the major equipment and reference measurement standards used as well as the facilities and services used by the laboratory in conducting tests? ___include reference to procedures for calibration, verification and maintenance of equipment? ___include reference to verification practices including inter-laboratory comparisons, proficiency testing programs, use of reference materials, and internal quality control schemes? ___include procedures to be followed for feedback and corrective action for failed quality control samples, or when departures from documented policies, procedures, or NELAC standards occur? ___management arrangements for exceptionally permitting departures from standard operating procedures, policies or standard specifications? ___include procedures for the resolution of complaints received from clients or other parties about the laboratory's activities? ___include processes/procedures for establishing that personnel are adequately experienced in the duties they are expected to carry out and/or receive any needed training? ___include procedures for audits and data review? ___define in detail the data integrity procedures, including training and documentation ___include reference to procedures for reporting analytical results? ___include a Table of Contents, and applicable lists of references and glossaries, and appendices?				
Have documented policies and procedures to ensure the protection of clients' confidential information and proprietary rights?				
Does management provide a mechanism for confidential reporting of data integrity issues within the lab?				
In instances of ethical concern, does the mechanism include a process whereby laboratory management are to be informed of any further detailed investigation?				
Document Control				

Relevant Aspect of Standards	Y	N	N/A	Comments
Establish and maintain procedures to control all documents that form part of its quality system, whether internally generated or from external sources?				
Are all documents issued to personnel in the laboratory as part of the quality system reviewed and approved for use by authorized personnel prior to issue?				
Have a master list or equivalent document control procedure which identifies the current version status and distribution of documents?				
Does the document control procedure ensure that; ___authorized editions of appropriate documents are available at all locations where operations essential to the effective functioning of the lab are performed, ___documents are periodically reviewed and, where necessary, revised to ensure continuing suitability and compliance with appropriate requirements, ___invalid or obsolete documents are promptly removed from all points of issue or use, or otherwise assured against unintended use, ___obsolete documents retained for either legal or knowledge preservation purposes are suitability marked?				
Are quality system documents generated by the laboratory uniquely identified by including: ___date of issue and/or revision identification, ___page numbering, ___the total number of pages or mark to signify the end of the document, ___issuing authority(ies)?				
Do the designated personnel have access to pertinent background information upon which to base their review and approval?				
Where practicable, is the altered or new text identified in the document or the appropriate attachments?				
Are procedures established to describe how changes in documents maintained in computerized systems are made and controlled?				
Client Contracts				
Establish and maintain procedures for review of requests, tenders and contracts?				
Do the policies and procedures for reviews leading to a contract for environmental testing ensure that; ___the requirements, including the methods to be used, are adequately defined, documented and understood; ___the laboratory has the capability and resources to meet the requirements;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___the appropriate environmental test method is selected and capable of meeting clients requirements?				
Inform the client if it indicates any potential conflict, deficiency, lack of appropriate accreditation status, or inability on the laboratory's part to complete the clients work?				
Maintain records of reviews, including any significant changes?				
Maintain records 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?				
Does the review cover any work that is subcontracted by the laboratory?				
Is the client informed of any deviation from the contract?				
If a contract needs to be amended after work has commenced, is the same contract review process repeated and any amendments communicated to all affected personnel?				
Does the laboratory report any suspension of accreditation, revocation or accreditation, or voluntary withdrawal of accreditation to the client?				
Does the lab afford clients or their representatives cooperation to clarify the client's request and to monitor the lab's performance in relation to the work performed, provided that the lab ensures confidentiality to other clients? (i.e. External Audits)				
Subcontracting				
Have records to indicate that it advise the client in writing of its intention to sub-contract any portion of the testing to another party?				
Where a laboratory sub-contracts any part of the testing covered under NELAP, do records indicate that this work is placed with a laboratory accredited under NELAP for the tests to be performed or with a laboratory that meets applicable statutory and regulatory requirements for performing the tests and submitting results of tests performed?				
Is non-NELAC work performed by a subcontracted laboratory clearly identified in the laboratory report?				
Accept responsibility for subcontractor's work, except in the case where the client or a regulatory authority specifies which subcontractor to be used?				
Maintain a register of all subcontractors that it uses for environmental tests and a record of the evidence (certificates of approval)?				
Purchasing				
Do documented policies and procedures exist for the selection and purchasing of services and supplies used that effect the quality of environmental testing operations of the laboratory?				
Do documented procedures exist for the purchase, reception and storage of consumable materials used				

Relevant Aspect of Standards	Y	N	N/A	Comments
for the technical operations of the laboratory?				
Ensure that purchased equipment and consumable materials are not used until they have been inspected, calibrated or otherwise verified as complying with any standard specifications relevant to the calibrations or tests concerned?				
Do the services and supplies used comply with specified requirements?				
Are records of actions taken to check compliance maintained?				
Are purchasing documents, containing data describing the services and supplies ordered, reviewed and approved for technical content prior to release?				
Evaluate suppliers of critical consumables, supplies and services which affect the quality of environmental testing?				
Maintain records of evaluations of all suppliers from whom it obtains support services or supplies required for tests and list those approved?				
Complaints				
Are records of the complaints and subsequent actions maintained?				
Non-conforming Work				
Have a policy and procedures that are implemented when any aspect of it's environmental testing work, or the result of this work, do not conform to its own procedures or agreed requirements of the client?				
Do the policy and procedures ensure that: ___the responsibilities and authorities for the management of nonconforming work are designated and actions are defined and taken when nonconforming work is identified; ___an evaluation of the nonconforming work is made; ___corrective actions are taken immediately, together with any decision about the acceptability of nonconforming work; ___where necessary, the client is notified and work is recalled; ___the responsibility for authorizing the resumption of work is defined.				
Implement corrective action procedures when the evaluation indicates that the nonconforming work could recur or that there is doubt about the compliance of the laboratory's operations with its own policies and procedures?				
Corrective Actions				
Established a corrective action policy and procedure?				
Designate appropriate authorities for implementing corrective action when nonconforming work or				

Relevant Aspect of Standards	Y	N	N/A	Comments
departures from policies & procedures in the quality system or technical operations have been identified?				
Does the corrective action procedure start with an investigation of root cause(s) of the problem?				
Identify potential corrective actions and select and implement the action(s) most likely to eliminate the problem and to prevent recurrence?				
Are corrective actions appropriate in degree to the magnitude and risk of the problem?				
Document and implement any required changes resulting from corrective action investigations?				
Monitor the results to ensure that the corrective actions taken have been effective?				
Ensure that appropriate areas of activity, identified or doubted as nonconforming or departure from policies and procedures, are promptly audited?				
Implement general procedures to be followed when there are departures from documented policies, procedures, and QC have occurred?				
Do the procedures to be followed when there is a departure from documented policies, procedures, and QC include but not limited to: ___Identify the individuals responsible for assessing each QC data type; ___Identify the individuals responsible for initiating and/or recommending corrective actions; ___Define how the analyst should treat the data set if the associated QC measurements are unacceptable; ___Specify how out-of-control situations and subsequent corrective actions are to be documented; and ___Specify procedures for management (including the QA officer) to review corrective action reports.				
If a QC measure is out of control and the data is to be reported, are data qualifiers reported with samples associated with failed QC measures?				
To the extent possible, are samples reported only if all quality control measures are acceptable?				
Preventive Action				
Have a pro-active process to identify opportunities for improvement?				
Are needed improvements and potential sources of non-conformances, either technical or concerning the quality system, identified?				
Develop, implement and monitor action plans where preventive action is required?				
Do procedures for preventive action include the initiation of such actions and application of controls to ensure that they are effective?				
Records				
Maintain a record system to suit its particular circumstances and comply with any applicable regulations?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Establish and maintain procedures for identification, collection, indexing, access, filing, storage, maintenance and disposal of quality and technical records?				
Do quality records include reports from internal audits and management reviews as well as records of corrective and preventive actions?				
Does the system produce unequivocal, accurate records, which document all laboratory activities?				
Retain on record all original observations, calculations and derived data, calibration records and a copy of the test report for a minimum of five years?				
Are all records legible?				
Does the record keeping system allow historical reconstruction of all laboratory activities that produced the resultant sample analytical data?				
Have a written SOP for how the laboratory will carry out legal chain of custody if the client specifies that a sample will be used for evidentiary purposes?				
Have procedures to prevent unauthorized access to or amendment of records stored electronically?				
Is the history of the sample readily understood through the documentation including inter-laboratory transfers of samples and/or extracts?				
Do the records include the identity of personnel involved in sampling, preparation, calibration or testing?				
Is all information relating to the laboratory facilities, equipment, analytical methods, and related laboratory activities, such as sample receipt, sample preparation, or data verification documented?				
Does the record keeping system facilitate the retrieval of all working files and archived records for inspection and verification purposes?				
Are all generated data, except those that are generated by automated data collection systems, recorded directly, promptly and legibly in permanent ink?				
Are entries to electronically maintained records changed so as to not erase or overwrite the files?				
Is the individual making the change to electronically maintained records identified?				
Do the records for each environmental test contain sufficient information to facilitate, if possible, identification of factors affecting the uncertainty and to enable the test to be repeated under conditions as close as possible to the original?				
Are entries in records not obliterated by methods such as erasures, overwritten files or markings?				
Are all corrections to record-keeping errors made by one line marked through the error and the individual making the correction signing (or initialing) and dating the correction?				
Are all records, certificates and reports held secure and in confidence to the client?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Are observations, data and calculations recorded at the time they are made?				
Are observations, data and calculations identifiable to the specific task?				
In the case of records stored electronically, are equivalent measures taken to avoid loss or change of original data?				
Are all records (including the hardware and software necessary for the historical reconstruction of electronic data) that are pertinent to a specified project retained for a minimum of five years from last entry unless otherwise designated for a longer period of time in another regulation?				
Do records that are stored or generated by computers have hard copy or write-protected backup copies?				
Have a record management system for control of laboratory notebooks; instrument logbooks; standards logbooks; and records for data reduction, validation storage and reporting?				
Is access to archived information documented with an access log?				
Is archived information protected against fire, theft, loss, environmental deterioration, and vermin and, in the case of electronic records, electronic or magnetic sources?				
Have a plan to ensure that the records are maintained or transferred according to the clients' instructions in the event that a laboratory transfers ownership or goes out of business?				
Retain records of the following procedures to which a sample is subjected while it is in the lab's possession: ___Sample preservation, appropriateness of containers, & compliance with holding time requirements ___Sample identification, receipt, acceptance or rejection, & log-in ___Sample storage & tracking including shipping receipts, transmittal forms, & assignments ___Documented procedures for receipt, retention, or safe disposal of test items that includes all provisions necessary to protect the integrity of the laboratory				
Retain : ___All original raw data, whether hard copy or electronic, for calibrations, sample analyses, & quality control measures ___A written description or reference to the specific test method used ___Copies of final reports ___Archived standard operating procedures ___Correspondence relating to its activities for a specific project ___All corrective action reports, audits, & audit response ___Proficiency test results & raw data ___Records of data review & cross checking.				

Relevant Aspect of Standards	Y	N	N/A	Comments
Do strip charts, tabular printouts, computer data files, analytical notebooks, and run logs include: ___Laboratory sample ID code ___Date of analysis and time of analysis ___Instrumentation identification and instrument operating conditions/parameters (or reference) ___Analysis type (method or technique) ___All calculations (automated and manual) ___Analyst's or operator's initials/signature ___Sample preparation including cleanup & separation protocols, ID codes, volumes, weights, instrument printouts, meter readings, calculations, & reagents used ___Sample analysis ___Standard & reagent origin, receipt, preparation, & use ___Calibration criteria, frequency, & acceptance criteria ___Data & statistical calculations, review, confirmation, interpretation, assessment, & reporting conventions ___Quality control protocols & assessment ___Electronic data security, Software documentation & , Software & hardware audits, Backups of automated data entries, Records of any changes to automated data entries ___Method performance criteria including expected quality control requirements				
Are the following administrative records maintained? ___Personnel qualifications, experience and training records ___Initial and continuing demonstration of proficiency for each analyst ___a log of names, initials and signatures for all individuals who are responsible for signing or initialing any laboratory record				
Managerial Reviews				
Have a procedure for the annual management review of the quality system and does it maintain records of review findings and actions?				
Is an annual review of the quality system completed by management to evaluate its continuing suitability and effectiveness and make any necessary changes or improvements?				
Does the annual review take into account: ___the suitability of policies and procedures; ___reports from managerial and supervisorial personnel; ___the outcome of recent internal audits; ___corrective and preventive actions;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___assessment by external bodies ; ___the results of interlaboratory comparisons or proficiency tests; ___any changes in the volume and type of work undertaken; ___feedback from clients; ___complaints; ___other relevant factors, such as quality control activities, resources and staff training?				
Data Integrity				
Are reviews conducted with respect to any evidence of inappropriate actions or vulnerabilities related to data integrity?				
Are discovery of potential issues handled in a confidential manner until such time as a follow-up evaluation, full investigation, or other appropriate actions have been completed and the issues clarified?				
Are all investigations that result in findings of inappropriate activity documented including any disciplinary actions involved, corrective actions taken, and all appropriate notifications of clients?				
Is documentation of data integrity investigations and actions taken maintained for five years?				
Are the data integrity procedures signed and dated by senior management?				
Are these procedures and the associated implementation records properly maintained and made available for assessor review?				
Are the data integrity procedures annually reviewed and updated by management?				
Do senior managers acknowledge their support of these procedures by: ___Upholding the spirit and intent of the organizations data integrity procedures, and; ___Effectively implementing the specific requirements of the procedures?				
Facilities				
Are tests stopped when the environmental conditions jeopardize the results?				
Are measures taken to prevent cross contamination?				
Are adequate measures taken to ensure good housekeeping and to ensure that any contamination does not adversely affect data quality?				
Test Methods, SOPs and Method Validation				
Use appropriate methods and procedures for all test methods and laboratory activities within its scope?				
Document instructions ___On the use and operation of all relevant equipment, ___On the handling and preparation of samples, where the absence of such instructions could jeopardize				

Relevant Aspect of Standards	Y	N	N/A	Comments
the calibrations or tests?				
Are all instructions, standards, manuals and reference data relevant to the work of the laboratory maintained up-to-date and readily available to the staff?				
Do deviations from test methods occur only if the deviation has been documented, technically justified, authorized, and accepted by the client?				
Maintain SOPs for all test methods and laboratory activities?				
Are copies of SOPs organized and assessable to all personnel?				
Does each SOP clearly indicate: ___Effective date of the SOP ___Revision number ___Signature(s) of approving authority				
Have an in-house method manual for each accredited analyte or test method that clearly describes the lab's method?				
In cases where modifications are made to published methods or where the reference test method is ambiguous or provides insufficient detail, are any modifications, changes, or clarifications clearly described?				
Each test method includes or references the following where applicable: ___Identification of the test method ___Applicable matrix or matrices ___Detection limit ___Scope and application ___Summary of the test method ___Definitions ___Interferences ___Safety ___Equipment and supplies ___Reagents and standards; ___Sample collection, preservation, shipment and storage; ___Quality control; ___Calibration and standardization; ___Procedure; ___Calculations; ___Method performance;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Pollution prevention; ___Data assessment and acceptance criteria for quality control measures; ___Corrective actions for out-of-control data; ___Contingencies for handling out-of-control or unacceptable data; ___Waste management; ___References; and ___Any tables, diagrams, flowcharts and validation data				
Use appropriate test methods and procedures, which meet the needs of the client, for all tests and related activities within its responsibility (including sample collection, handling, transport, storage, preparation, and analysis)?				
Ensure that it uses the latest valid edition of a standard source of methods?				
Use only the test method specified when the test method is mandated or requested?				
Inform the client when the method proposed by them is considered to be inappropriate or out of date?				
Is there a record of a satisfactory initial demonstration of method capability performed prior to the institution of any test method? (Not required for a test method that was in use by the lab prior to 7/99 and where there has been no significant changes)				
Have records on file to demonstrate that an initial demonstration of capability is not required for unchanged methods in use prior to 7/99?				
Complete a new demonstration of capability whenever there is a significant change in instrument type, personnel, or test method?				
Is the introduction of laboratory-developed methods a planned activity assigned to qualified personnel equipped with adequate resources?				
Are plans for laboratory developed methods updated as development proceeds and effective communication amongst all personnel involved ensured?				
When it is necessary to use non-standard methods, is their use subject to agreement with the client, including clear specification of client requirements and the purpose of the testing?				
Are all non-standard methods, laboratory-designed/developed methods, standard methods used outside their intended scope, and amplifications and modifications of standard methods validated to confirm they fit their intended use?				
Record the results of validations, the procedure used, and a statement as to whether the method is fit for the intended use?				
Is the range and accuracy of the values obtainable from validated methods, within the intended use,				

Relevant Aspect of Standards	Y	N	N/A	Comments
relevant to the clients needs?				
Have and implement a procedure to estimate the uncertainty of measurement?				
In cases where it is not possible to calculate the uncertainty of measurement in a rigorous metrological and statistically significant way, does the laboratory, at least, attempt to identify all the components of uncertainty and make a reasonable estimation? (reasonable means it is based on knowledge of the performance of the method , measurement scope, previous experience and validation data)				
Ensure that the form of reporting does not give a wrong impression of the uncertainty of measurement?				
Are all important uncertainty components taken into account using appropriate methods of analysis?				
Establish Standard Operating Procedures to ensure that the reported data is free from transcription and calculation errors?				
Establish Standard Operating Procedures to ensure that all quality control measures are reviewed, and evaluated before data is reported?				
Are calculations and data transfers subject to checks as established in the laboratory's SOP?				
Establish Standard Operating Procedures addressing manual calculations including manual integrations?				
Ensure that all requirements of the Chapter 5 are complied with where computers or automated equipment are used for the capture, processing, manipulation, recording, reporting, storage or retrieval of test data?				
When computers, automated equipment, or microprocessors are used for the acquisition, processing, recording, reporting, storage or retrieval of test or calibration data, does the laboratory ensure that computer software developed by the user is documented in sufficient detail and is suitably validated as being adequate for use?				
Are procedures established for protecting the integrity of data?				
Are procedures implemented for protecting the integrity of data?				
Do the procedures include, but are not be limited to: ___Integrity of data entry or capture ___Data storage ___Data transmission ___Data processing?				
Are computer and automated equipment maintained to ensure proper functioning and provided with the environmental and operating conditions necessary to maintain the integrity of calibration and test data?				
Establish and implement appropriate procedures for the maintenance of security of data including the				

Relevant Aspect of Standards	Y	N	N/A	Comments
prevention of unauthorized access to, and the unauthorized amendment of, computer records? (ex. Are access codes used?)				
Implement appropriate procedures for the maintenance of security of data including the prevention of unauthorized access to, and the unauthorized amendment of, computer records?				
Equipment and Reference Materials				
Furnish all items of equipment (including reference materials) required for the correct performance of tests for which accreditation is sought?				
Is equipment outside the permanent control of the laboratory handled so as to ensure the requirements of the NELAC standard are met?				
Is the equipment and the software used for testing, calibration and sampling capable of achieving the accuracy required and does it comply with specifications relevant to the tests concerned?				
Are calibration programs established for key quantities or values of the instruments where these properties have a significant effect of the results?				
Before being placed into service, is equipment (including that used for sampling) calibrated or checked to establish that it meets the laboratory's specification requirements and complies with the relevant standard specifications?				
Is all support equipment maintained in proper working order and records of all activities including service calls kept?				
Is all support equipment calibrated annually, using NIST traceable references when available, over the entire range in which the equipment is used?				
Are the results of support equipment calibration within the specifications required of the application for which it is used?				
Is support equipment that is not within the specifications required of the application: ___Removed from service until repaired				
Maintains records of established correction factors to correct measurements?				
Are all raw data records retained to document equipment performance?				
Prior to use on each working day, are balances, ovens, refrigerators, freezers, incubators and water baths checked with NIST traceable references (where available) in the expected use range?				
Is the acceptability for use continued use according to the needs of the analysis or application for which it is used?				
Are mechanical volumetric devices, including burettes, checked for accuracy on a quarterly basis?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Do glass microliter syringes come with a certificate attesting to established accuracy or is the accuracy initially demonstrated and documented by the laboratory?				
Is the temperature, cycle time, and pressure of each autoclave run for chemical tests documented by use of appropriate chemical indicators or temperature recorders and pressure gauges?				
Is equipment operated by authorized personnel?				
Is all equipment properly maintained, inspected and cleaned?				
Are maintenance procedures documented?				
Have procedures for safe handling, transport, storage, use and planned maintenance of measuring equipment to ensure proper functioning and to prevent contamination or deterioration?				
Is any item of the equipment which has been subjected to overloading or mishandling, or which gives suspect results, or has been shown by verification or otherwise to be defective, taken out of service, clearly identified and wherever possible stored at a specified place until it has been repaired and shown by calibration, verification or test to perform satisfactorily?				
Examine the effect of this defect or departure from specified limits on previous tests and/or calibrations and institute the “Control of Nonconforming Work” procedure?				
Are all items of equipment including reference materials labeled, marked or otherwise identified to indicate its calibration status, including the date when last calibrated and the date or expiration criteria when recalibration is due?				
Do records of major equipment and reference materials include the following: ___The name of the item of equipment ___The manufacturer's name, type identification, and serial number or other unique identification ___Checks that equipment comply with the specification ___Current location, where appropriate ___Copy of the manufacturer's instructions, where available ___Dates and results of calibrations & verifications and date of the next calibration and/or verification ___Details of maintenance carried out to date and planned for the future ___History of any damage, malfunction, modification or repair ___Date received and date placed in service ___Condition when received (e.g. new, used, reconditioned)				
If for any reason, equipment goes outside the direct control of the laboratory, does the laboratory ensure that the function and calibration status of the equipment is checked and shown to be satisfactory before equipment is returned to service?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Have procedures to ensure that copies of new correction factors are correctly applied/updated (e.g. in computer software)?				
Is test and calibration equipment, including both hardware and software, safeguarded from adjustments which would invalidate the test and/or calibration results?				
Measurement Traceability and Calibration				
Are all measuring operations and testing equipment having an effect on the accuracy or validity of tests calibrated and/or verified before being put into service and on a continuing basis?				
Have an established program for the calibration and verification of its measuring and test equipment including balances, thermometers and control standards?				
Ensure that the equipment used can provide the uncertainty of measurement needed (that contributes little to the total uncertainty of the test result)?				
Are measurements made by the lab traceable to national standards of measurement, where available?				
Provide satisfactory evidence of correlation of results in those cases where traceability to national standards of measurement is not applicable? (For example, participation in a suitable program of inter-laboratory comparisons, proficiency testing, or independent analysis.)				
Are reference standards of measurement held by the laboratory (such as Class S or equivalent weights or traceable thermometers) used for calibration only and for no other purpose, unless it is demonstrated that their performance as reference standards has not been invalidated?				
Are reference standards of measurement calibrated by a body that can provide, where possible, traceability to national or international standard reference materials?				
Is there a program of calibration and verification for reference standards?				
Are internal reference materials checked as far as technically and economically possible?				
Have defined procedures and schedules for carrying out checks of the calibration status of reference, primary, transfer or working standards and reference materials?				
Have procedures for safe handling, transport, storage, and use of reference standards and reference materials in order to protect their integrity, and prevent contamination and/or deterioration?				
Do documented procedures exist for the purchase, reception and storage of consumable materials used for the technical operations of the laboratory?				
Retain records for all standards, reagents, reference materials and media, including manufacturer/vendor, the manufacturers Certificate of Analysis or purity (if supplied), date of receipt, recommended storage conditions, and an expiration date after which the material shall not be used				

Relevant Aspect of Standards	Y	N	N/A	Comments
unless verified by the laboratory?				
Are original reagent containers labeled with the expiration date?				
Are detailed records maintained on standard and reference material preparation?				
Do the records of standard and reference material preparation indicate traceability to purchased stocks or neat compounds, reference to method of preparation, date of preparation, expiration date, and preparer's initials?				
Do all containers of prepared standards and reference materials bear a unique identifier and expiration date and can it be linked to the documentation of its preparation?				
Are procedures in place to ensure prepared reagents meet the requirements of the test method?				
Do all containers of prepared reagents bear an expiration date or is it documented elsewhere as indicated in the laboratory's quality manual or SOP?				
Sampling				
Does the sampling process address the factors to be controlled to ensure the validity of the test results?				
When sampling (as in obtaining sample aliquots from a submitted sample) is carried out as part of the test method, does the laboratory use documented procedures and appropriate techniques to obtain representative sub-samples?				
Are client required deviations, additions, or exclusions from the documented sampling procedure recorded in detail with the appropriate sampling data and included in all documents containing test results and communicated to appropriate personnel?				
Have procedures for recording relevant data and operations relating to sampling?				
Do sampling records include; ___the sampling procedure used, ___the identification of the sampler, ___environmental conditions (if relevant), ___diagrams or other equivalent means to identify the sampling location, ___if appropriate, the statistics the sampling procedure is based on?				
Sample Handling				
Have procedures for the transportation, receipt, handling, protection, storage, retention and/or disposal of samples, including provisions necessary to protect the integrity of the sample, and to protect the interests of the laboratory and the client?				
Have a documented system for uniquely identifying the items to be tested, to ensure that there can be no				

Relevant Aspect of Standards	Y	N	N/A	Comments
confusion regarding the identity of such items at any time?				
Does the system include identification for all samples, sub-samples and subsequent extracts and/or digestates?				
Assign a unique identification (ID) code to each sample container received in the laboratory?				
Does the sample code maintain an unequivocal link with the unique field ID code assigned each container?				
Is the laboratory ID code placed on the sample container as a durable label?				
Is the laboratory ID code entered into the laboratory records and does the link that associate the sample with related laboratory activities such as sample preparation or calibration?				
Have a written sample acceptance policy that clearly outlines the circumstances under which samples will be accepted or rejected?				
Is data from any sample which does not meet the policy criteria flagged in an unambiguous manner clearly defining the nature and substance of the variation?				
Is the sample acceptance policy made available to sample collecting personnel?				
Does the sample acceptance policy criteria include the following at a minimum? ___Proper, full, and complete documentation, which includes: ___sample identification, ___the location ___date and time of collection, ___collector's name, ___preservation type, ___sample type ___any special remarks concerning the sample. ___Proper sample labeling to include: ___unique identification ___a labeling system for the samples with requirements concerning the durability of the labels (water resistant) and the use of indelible ink. ___Use of appropriate sample containers. ___Adherence to specified holding times. ___Adequate sample volume to perform the necessary tests. ___Procedures to be used when samples show signs of damage or contamination.				
Upon receipt, is the condition of the sample recorded, including any abnormalities or departures from				

Relevant Aspect of Standards	Y	N	N/A	Comments
standard condition as prescribed in the relevant test method?				
Are all items specified in sample acceptance policy criteria checked?				
Are all samples, which require thermal preservation, considered acceptable if the arrival temperature is either within +/-2°C of the required temperature or in the method specified range?				
For samples with a specified temperature of 4 C, are samples maintained within a temperature of just above freezing to 6°C?				
In cases where samples are hand delivered to the laboratory immediately after collection and do not meet the temperature criteria considered acceptable, is there evidence that the chilling process has begun such as arrival on ice?				
Implement procedures for checking chemical preservation using readily available techniques, such as pH or temperature, prior to or during sample preparation or analysis?				
Are the results of all checks recorded?				
Where there is any doubt as to the item's suitability for testing, where the sample does not conform to the description provided, or where the test required is not fully specified, does the laboratory: ___consult with the client for further instruction before proceeding; and, ___establish whether the sample has received all necessary preparation, or whether the client requires preparation to be undertaken or arranged by the laboratory?				
If the sample does not meet the sample receipt acceptance criteria does the laboratory do any of the following: ___Retain correspondence and/or records of conversations concerning the final disposition of rejected ___Fully document any decision to proceed with the analysis of samples not meeting acceptance criteria ___Is the condition of these samples, at a minimum, noted on the chain of custody or transmittal form and laboratory receipt documents? ___Is the analysis data of these samples appropriately "qualified" on the final report?				
Utilize a permanent, sequential log, such as a logbook or electronic record, to document receipt of all sample containers?				
Is the following information recorded in the laboratory chronological log? ___Client/Project Name ___Date and time of laboratory receipt of sample ___Unique laboratory ID code ___Signature or initials of the person making the entries				
Is the following information unequivocally linked to the log in records, included as a part of the log, or if				

Relevant Aspect of Standards	Y	N	N/A	Comments
recorded/documented elsewhere is it a part of the laboratory's permanent records, easily retrievable upon request and readily available to individuals who will process the sample? ___Field ID code linked to laboratory ID code in the sample receipt log. ___Date and time of sample collection linked to the sample container and to the date and time received in the laboratory. ___Requested analyses (including applicable test method numbers) linked to the laboratory ID code. ___Any comments resulting from inspection for sample rejection linked to the laboratory ID code.				
Retain all documentation, such as memos or transmittal forms that are transmitted to the laboratory by the sample transmitter retained?				
Is a complete chain of custody record, if utilized, maintained?				
Have documented procedures to avoid deterioration or damage to the sample during storage, handling, preparation, and testing				
Follow any relevant instructions from the client in regards to the storage of a sample?				
Where items have to be stored or conditioned under specific environmental conditions, are these conditions maintained, monitored and recorded?				
Are samples stored according to the conditions specified by preservation protocols?				
Are samples stored away from all standards, reagents, food and other potentially contaminating sources in such a manner as to prevent cross contamination?				
Are samples, sample fractions, extracts, leachates or other sample preparation fractions stored according to the conditions specified by preservation protocols or according to the test method?				
Where a sample or portion of the sample is to be held secure (for example, for reasons of record, safety or value, or to enable check calibrations or tests to be performed later), does the laboratory have storage and security arrangements that protect the condition and integrity of the secured items or portions concerned?				
Have standard operating procedures for the disposal of samples, digestates, leachates and extracts or other sample preparation products?				
Assuring the Quality of Test Results				
Ensure the quality of results provided to clients by implementing checks to monitor the quality of the laboratory's analytical activities? For Example: ___Internal quality control procedures (using statistical techniques whenever possible); ___Participation in PT or other inter-laboratory comparisons; ___Reference material and/or in-house quality control using secondary reference materials;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Replicate testing; ___Re-testing of retained samples; and/or ___Correlation of results for different parameters of a sample.				
Have quality control procedures for monitoring the validity of environmental tests and calibrations undertaken?				
Are the resulting data recorded in such a way that trends are detectable and, where applicable, statistical techniques are applied to the reviewing of the results?				
Is the monitoring planned and reviewed?				
Are all quality control measures assessed and evaluated on an on-going basis, and quality control acceptance limits used to determine the usability of the data?				
Have procedures for the development of acceptance/rejection criteria where no method or regulatory criteria exist?				
Are the quality control protocols specified by the laboratory's method manual followed?				
Reports				
Report the results of each test, or series of tests carried out by the laboratory in a test report that reports the data accurately, clearly, unambiguously, and objectively?				
Does the test report contain all information necessary for the interpretation of the test results and all information required by the method used?				
Unless the laboratory is operated by a facility whose sole function is to provide data for the facility, does the report contain: ___A title ___Name/address of laboratory ___Location where analysis is carried out if different ___Phone number and name of contact person ___Unique identification of the test report and unique identification of each page, and the total number of pages. ___Name and address of client, where appropriate and project name if applicable ___Description and unambiguous identification of the tested sample including the client identification code ___where quality system requirements are not met, a statement of compliance/non compliance with requirements and/or specifications, including identification of results derived from samples that did not meet NELAC acceptance requirements such as improper container, holding time, or temperature.				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Date of receipt of sample, date and time of sample collection, date(s) of performance test, and time of sample preparation and/or analysis ___Identification of the test method used, ___Any deviations from, additions to or exclusions from the test method, and non-standard conditions that may have affected the quality of the results, and including the use of relevant data qualifiers and their meaning?				
Does the report contain: ___environmental test results with, where appropriate, the units of measurement, and any failures (such as failed quality control) identified and whether data are calculated on dry weight or wet weight, reporting units ___When required, a statement of the estimated uncertainty of the test result. ___A signature and title, or an equivalent electronic identification of the person(s) accepting responsibility for the content of the certificate or report (however produced), and date of issue, ___a statement to the effect that the results relate only to the samples , ___at the lab's discretion, a statement that the certificate or report shall not be reproduced except in full, without the written approval of the laboratory ___Clear identification of all data provided by outside sources, such as subcontracted laboratories, clients, etc. ___Clear indication of numerical results with values outside of quantitation limits.				
Are all applicable elements above readily available for review if not issued in a formal report by laboratory?				
Does management ensure that the appropriate report items are in the report to the regulatory authority if the report is prepared by another individual within the organization.				
When opinions and interpretations are included in the test report does the laboratory document the basis upon which the opinions and interpretations have been made?				
Are opinions and interpretations clearly marked in test reports?				
Where the certificate or report contains results of tests performed by sub-contractors, are these results clearly identified by subcontractor name or applicable accreditation number, and the subcontractor's report made available to the client on request?				
Is the format of the report designed to accommodate each type of test carried out and to minimize the possibility of misunderstanding or misuse?				
When it is necessary to issue a complete new test report, is this uniquely identified and does it contain a reference to the original that it replaces?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Are material amendments to a calibration certificate, test report or test certificate after issue made only in the form of a further document, or data transfer including the statement "Supplement to Test Report or Test Certificate, serial number . . . [or as otherwise identified]", or equivalent form of wording?				
Do amendments to the formal report meet all the relevant requirements of this standard?				
Notify clients 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 report or certificate?				
Have procedures that ensure, where clients require transmission of test results by telephone, fax, or email, that the requirements are met and that confidentiality is preserved?				
Do staff follow the documented procedures for the transmission of test results by telephone, fax or email?				
Certify that the test results meet all requirements of NELAC or provide reasons and/or justification if they do not?				
Report drinking water violations to the County Department of Health as required?				
Demonstration of Capability				
Is a demonstration of capability made prior to using any test method, and at any time there is a change in instrument type, personnel or test method?				
Are initial demonstrations and method certification documented through the use of the forms in the latest approved NELAC document?				
Retain all associated supporting data necessary to reproduce the analytical results summarized in the IDC certification statement?				
Is the QC sample used for the IDC, purchased from an outside source, or if not available, is the QC sample prepared by the laboratory independent of the instrument calibration?				
Is the concentrate of the QC sample diluted in a volume of clean matrix sufficient to prepare four aliquots at the required method volume to a concentration specified in the method, or, if unspecified, to a concentration of 1-4 times the limit of quantitation?				
Are four aliquots prepared and analyzed according to the method either concurrently or over a period of days?				
Is the average recovery and standard deviation for each parameter of interest calculated in the units used for reporting (such as mg/L)?				
When it is not possible to determine mean and standard deviations, such as for presence/absence and logarithmic values, does the laboratory assess performance against established and documented				

Relevant Aspect of Standards	Y	N	N/A	Comments
criteria?				
Does the average recovery and standard deviation meet the acceptance criteria for precision and accuracy of the method (if applicable) or in laboratory generated acceptance criteria (if there is no mandatory criteria)?				
Does the lab wait to begin the analysis of actual samples until all parameters of interest meet acceptance criteria?				
If one or more of the test parameters does not meet the acceptance criteria, is the problem corrected followed by repeated analysis of the four aliquots for all parameters or at least for those that failed to meet criteria?				
Is a copy of the initial demonstration of Capability Certificate (IDC) in the personnel records for each employee performing a test method?				
Determine the Limit of Detection (LOD) for the method for each target analyte of concern in the matrices approved?				
Do all sample-processing steps of the analytical method include the determination of the LOD?				
Is the validity of the LOD confirmed by qualitative identification of the analyte(s) in a QC sample in each approved matrix containing the analyte at no more than 2-3 X the LOD for single analyte tests and 1-4 X the LOD for multiple analyte tests?				
Is this verification performed on every instrument that is to be used for analysis of samples and reporting of data?				
Where an LOD study is not performed, does the laboratory not report a value below the Limit of Quantitation?				.
Determine the Limit of Quantitation (LOQ) for each analyte of concern according to a defined, documented procedure?				
Is the validity of the LOQ confirmed by successful analysis of a QC sample containing the analytes of concern in each in each approved matrix 1-2 times the claimed LOQ?				
When using standard methods, does the laboratory evaluate the precision and bias of a standard method for each analyte of concern for each quality system matrix according to the single-concentration four-replicate recovery study procedures in Appendix C.1 above (or alternate procedure documented in the quality manual when the analyte cannot be spiked into the sample matrix and QC samples are not commercially available)?				
When using Non-Standard methods for Laboratory-developed test methods or non-standard test methods that were not in use by the laboratory before July 2003, did the laboratory document procedure				

Relevant Aspect of Standards	Y	N	N/A	Comments
to evaluate precision and bias?				
Compare results of the precision and bias measurements with criteria established by the client, by criteria given in the reference method or criteria established by the laboratory?				
Do the precision & bias measurements evaluate the laboratory-developed or non-standard test method across the analytical calibration range of the method?				
Evaluate selectivity by following the checks established within the method?				
Chemical Testing and Air Testing Detailed Method Review				
Demonstrate that it meets all requirements contained in a mandated test method or by regulation, even if the requirement is more stringent than the corresponding NELAC standard? (If it is unclear which requirements are more stringent, the standard from the method of regulation shall be followed)				
Are the quality control protocols specified by the laboratory's method manual followed by all analysts?				
Are all essential quality control measures incorporated in the lab's method manual?				
Are all quality control measures assessed and evaluated on an on-going basis and is quality control acceptance criteria used to determine the validity of the data?				
Have procedures for developing acceptance/rejection criteria for each test where no method or regulatory criteria exist?				
Is the method blank processed along with and under the same conditions as the associated samples including all steps of the analytical procedure?				
Are procedures in place to determine if a method blank is contaminated?				
Are any affected samples associated with a contaminated blank reprocessed for analysis or are the results reported with appropriate data qualifying codes?				
Is a method blank performed; ___one per preparation batch, per matrix type; or ___in those instances for which there is no separate preparation method, is the batch defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples?				
Does the method blank consist of a matrix that is similar to the associated samples and is known to be free of the analytes of interest?				
Is each method blank critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Is the source of contamination investigated and measures taken to minimize or eliminate the problem and the affected samples reprocessed; or ___Is data appropriately qualified if: ___The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the test method or by regulation, AND is greater than 1/10 of the amount measured in any sample. ___The blank contamination affects the sample results as per the test method requirements or the individual project data quality objectives.				
When a blank is determined to be contaminated, does the laboratory investigate the cause and take measures to minimize or eliminate the problem?				
Evaluate samples associated with a contaminated blank as to the best corrective action for the samples (e.g. reprocessing or data qualifying codes) and is the corrective action documented ?				
Is the LCS used to evaluate the performance of the total analytical system including all preparation and analysis steps?				
Is an LCS (a sample matrix free of analytes of interest spiked with a verified known amount of analyte) performed at a frequency of: ___one per preparation batch per matrix type except for analytes for which spiking solutions are not available; or ___In those instances for which there is no separate preparation method, is the batch defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples??				
If the matrix spike is used as the LCS, is the acceptance criteria as stringent as the LCS?				
Are the components spiked those that are specified by the mandated test method or other regulatory requirement or as requested by the client?				
In the absence of specified spiking components does the laboratory spike per the following: ___For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, is the spike chosen so that it represents the chemistries and elution patterns of the components to be reported? ___For those test methods that have extremely long lists of analytes, is a representative number chosen as below? ___Are the analytes selected that representative of all analytes reported? ___Is the following criteria used for determining the minimum number of analytes to be spiked. ___Does the laboratory ensure that all targeted components are included in the spike mixture over a 2 year period?				

Relevant Aspect of Standards	Y	N	N/A	Comments
___For methods that include 1-10 targets, are all components spiked?; ___For methods that include 11-20 targets, are at least 10 or 80% spiked, whichever is greater; ___For methods with more than 20 targets, are at least 16 components spiked?				
Are the results of individual batch LCS calculated in percent recovery?				
Document the calculation for percent recovery?				
Is the individual LCS compared to the acceptance criteria: ___as published in the mandated test method; or ___where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits; or ___utilize client specified assessment criteria?				
Are samples analyzed along with a LCS determined to be out-of-control; ___considered suspect and the samples reprocessed and re-analyzed; or ___is the data reported with appropriate qualifying codes?				
Are the number of allowable marginal exceedences determined as follows: ☐ >90 analytes in LCS, no more than 5 analytes allowed in ME of the LCS control limit? ☐ 71-90 analytes in LCS, no more than 4 analytes allowed in ME of the LCS control limit? ☐ 51-70 analytes in LCS, no more than 3 analytes allowed in ME of the LCS control limit? ☐ 31-50 analytes in LCS, no more than 2 analytes allowed in ME of the LCS control limit? ☐ 11-30 analytes in LCS, no more than 1 analytes allowed in ME of the LCS control limit? ☐ <11 analytes in LCS, no analytes allowed in ME of the LCS control limit?				
Are the LCS marginal exceedences random?				
If the same analyte exceeds the LCS control limit repeatedly, it is an indication of a systemic problem. Is the source of the error located and corrective action taken?				
Have a written procedure to monitor the application of marginal exceedence allowance to the LCS to ensure random behavior?				
Document procedures for determining the effect of the sample matrix on method performance?				
Do these procedures relate to the analyses of matrix specific QC samples and are they designed as data indicators for a specific sample using the designated test method?				
Have procedures in place for tracking, managing, and handling matrix specific QC criteria including spiking appropriate components at appropriate concentrations, calculating recoveries and relative percent difference, evaluating and reporting results based on performance of the QC samples?				
Is the frequency of the analysis of matrix specific samples determined as part of a systematic planning				

Relevant Aspect of Standards	Y	N	N/A	Comments
process (e.g. Data Quality Objectives) or as specified by the required mandated test method?				
Are the components spiked those specified by the mandated test method, where applicable?				
Are any permit specified analytes, as specified by regulation or client requested analytes also included?				
If there are no specified components, does the laboratory spike per the following: ___For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, is the spike chosen which represents the chemistries and elution patterns of the components to be reported? ___For those test methods that have extremely long lists of analytes, are all analytes used, or are a representative number chosen using the following criteria: 1. For methods that include 1-10 targets, spike all components; 2.For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater; 3. For methods with more than 20 targets, spike at least 16 components.				
Include all targeted components in the spike mixture over a 2 year period?				
Is the matrix spike used to assess the precision and accuracy of analytical results in a given matrix and are they expressed as percent recovery (%R) and relative percent difference (RPD)?				
Document the calculation for relative percent difference?				
Are the results compared to the acceptance criteria in the mandated test method when published?				
Where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits?				
For matrix spike results outside established criteria, is corrective action documented or is the data reported with appropriate data qualifying codes?				
Are matrix duplicates defined as replicate aliquots of the same sample taken through the entire analytical procedure?				
Do the results from the analysis of matrix duplicates indicate the precision of the results for the specific sample using the selected method?				
Is the frequency of the analysis of matrix duplicates determined as part of a systematic planning process (e.g. Data Quality Objectives) or as specified by the mandated test method?				
Are matrix duplicates performed on replicate aliquots of actual sample?				
Are the results from matrix duplicates primarily designed to assess the precision of analytical results in a given matrix and are they expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences)?				
Document the calculation for relative percent difference or other statistical treatments?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Are the results compared to the method acceptance criteria as published in the mandated test method?				
Where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits?				
For matrix duplicates results outside established criteria, is corrective action documented or is the data reported with appropriate data qualifying codes?				
Are surrogate compounds added to all samples, standards, and blanks, whenever possible, for all organic chromatography methods?				
Are surrogate compounds chosen for being unlikely to occur as environmental contaminants and to represent the various chemistries of the target analytes in the method?				
Are the results of surrogate recoveries compared to the acceptance criteria published in the mandated test method?				
Where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits?				
Are surrogates outside the acceptance criteria evaluated for the effect indicated for the individual sample results?				
Is the appropriate corrective action guided by the data quality objectives or other site specific requirements?				
Are results reported from analyses with surrogate recoveries outside the acceptance criteria with appropriate data qualifiers?				
Are sample results quantitated from the initial instrument calibration and not from any continuing instrument calibration verification?				
Is the continuing instrument calibration verification used to confirm the continued validity of the initial calibration?				
Do the SOPs or the test method SOP reference the details of the initial calibration procedures, including calculations integrations, and acceptance criteria associated statistics?				
Are sufficient raw data records retained to permit reconstruction of the initial and continuing calibration including: ___Calibration date ___Test method ___Instrument ___Analysis date ___Each analyte name				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Concentration ___Response ___Calibration curve or response factor ___Analyst's initials or signature ___Unique equation or coefficient used to reduce instrument response to concentration.				
Are all initial calibration verification standards traceable to a national standard, when commercially available?				
Are all initial calibrations verified with a standard obtained from a second source manufacturer or lot if the lot can be demonstrated from the manufacturer as prepared independently from other lots?				
Is the criteria for the acceptance of an initial calibration established (correlation coefficient or relative percent difference) and appropriate to the calibration technique employed?				
Is the lowest calibration standard the lowest concentration for which quantitative data are to be reported. Any data reported below the lower limit of quantitation should be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or flags or explained in the case narrative.				
Is the highest calibration standard the highest concentration for which quantitative data are to be reported Any data reported above this highest standard should be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or flags or explained in the case narrative.				
If the results of samples are not bracketed by the initial calibration, are the results reported as having less certainty (defined qualifiers, flags, or explanation in the case narrative)?				
Is the lowest calibration standard of the initial calibration above the detection limit?				
For ICP and/or ICP-MS does the following occur; ___Prior to the analysis of samples the zero point/single point calibration must be analyzed and the linear range must be established by analyzing a series of standards, one of which must be at the lowest quantitation level, (results within the established linear range shall not require data qualifier flags) ___the zero point/single point calibration must be analyzed with each analytical batch, ___a standard corresponding to the limit of quantitation must be analyzed with each analytical batch and must meet established acceptance criteria, ___The linearity is verified at a frequency established by the method and/or the manufacturer.				
Are corrective actions performed if the results of the initial calibration are outside of established acceptance criteria?				
Is data associated with unacceptable initial instrument calibration not reported?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Have an SOP for determining the number of points for establishing the initial calibration?				
If a reference or mandated method does not specify the number of calibration standards, is the minimum number used 2, not including a blank or zero standard?				
When an initial calibration is not performed on the day of analysis, does the laboratory verify the validity of the initial calibration prior to the analysis of samples by analyzing a continuing instrument calibration verification sample?				
Are the details of the continuing instrument calibration procedure, calculations, and associated statistics included or referenced in the test method SOP?				
Is the calibration verified for each compound, element, or other discrete chemical species, except for multi-component analytes such as Aroclors, Total Petroleum Hydrocarbons, or Toxaphene where a representative chemical related substance or mixture can be used?				
Is a continuing instrument calibration verification performed: ___at the beginning and end of each analytical batch; (If an internal standard is used, only one continuing calibration verification must be analyzed per analytical batch) ___whenever it is expected that the analytical system may be out of calibration or might not meet verification acceptance criteria; ___if the time period for calibration or the most previous calibration verification has expired; or ___for analytical systems that contain a CCV requirement?				
Do the continuing calibration verification records explicitly connect the continuing verification data to the initial instrument calibration?				
Have established acceptance criteria of a continuing calibration verification analysis? (e.g. relative percent difference)				
Are routine corrective actions performed if the results of the continuing calibration verifications are outside of established acceptance criteria?				
If corrective action fails to produce an acceptable second consecutive(immediate) calibration verification, does the lab either perform a new initial calibration or analyze 2 consecutive acceptable calibration verifications before analyzing new samples?				
When sample data associated with a failed calibration verification is reported, does the laboratory qualify the data.				
If there was a high bias and there is a failed continuing calibration verification, is only data associated with samples that are non-detects reported? (Other affected samples are reanalyzed after a new curve has been established, evaluated, and accepted.)				

Relevant Aspect of Standards	Y	N	N/A	Comments
If there was a low bias and there is a failed continuing calibration verification, is only data associated with samples that have a result greater than the maximum regulatory limit/decision level reported? (Other affected samples are reanalyzed after a new curve has been established, evaluated, and accepted.)				
Utilize test methods that provide an LOD that is appropriate and relevant for the intended use of the data? (An LOD is not required for a test method when test results are not reported outside the calibration range.)				
Use an LOD that is determined by the protocol in the mandated test method or applicable regulation?				
If the protocol for determining LOD is not specified, does the selection made by the laboratory reflect instrument limitations and the intended application of the test method?				
Is the LOD initially determined in a matrix free of target analytes or interferences or in the matrix of interest?				
Are detection limits determined each time there is a significant change in the test method or instrument type?				
Are all procedures used to determine detection limits documented including the matrix type and is all supporting data retained?				
Does the laboratory have established procedures relate LOD with LOQ?				
Is the LOD verified annually for each quality system matrix, method and analyte?				
Are the test methods LOQ established and above the LOD?				
Is the LOQ verified annually for each quality matrix, method and analyte?				
Are procedures documented for data reduction, such as use of linear regression?				
Is the source of standards traceable to national standards or proven through inter-laboratory studies?				
In methods where the purity of reagents is not specified, is analytical reagent grade used?				
Use reagents of the purity or of greater purity than that specified in the method?				
Is the container labeling checked to verify that the purity of the reagents meets the requirements of the particular method?				
Document the checks to verify that the purity of the reagents meets the requirements of the particular test method?				
Is the quality of water sources monitored and documented to meet method specified requirements?				
Verify the concentration of titrants in accordance with written laboratory procedures?				
Evaluate selectivity by following the checks established within the method, which may include mass spectral tuning, second column confirmation, ICP interelement interference checks, chromatography				

Relevant Aspect of Standards	Y	N	N/A	Comments
retention time windows, sample blanks, spectrochemical absorption or fluorescence profiles, co-precipitation evaluations, and electrode response factors?				
Is confirmation performed for organic tests other than GC/MS or when recommended by the analytical method to verify the compound identification when positive results are detected on a sample from a location that has not been previously tested by the laboratory?				
If confirmation not performed, is it based on client written stipulation?				
Document all confirmations?				
Develop and document acceptance criteria for mass spectral tuning?				
Assure that the test instruments consistently operate within the specifications of the test methods and equipment manufacturer?				
Is glassware cleaned to meet the sensitivity of method?				
Are all cleaning and storage procedures that are not specified by the method documented in laboratory records and SOPs?				

Figure 2: SOP/Test Method Checklist
Name(s) of auditor(s): ___________________________________
Date: __________________
Name(s) of employee(s): ____________________________________
Analysis/Method: ________________________
SOP #: ________________________

PT Studies:	Notes:
☐ WP 1	____
☐ WP 2	____
☐ NELAC 1	____
☐ NELAC 2	____
☐ NELAC WS 1	____
☐ NELAC WS 2	____
☐ WS	____
☐ DRMQA	____

Corrective Action Follow-up:____
____
____
____
____

External Audit Follow-up: ____
____
____
____
____

Previous Internal Audit Follow-up: ____
____
____
____

General Checklist:	Complete?	Notes:
☐ Balance(s) Log Book	☐	_______________________
☐ Equipment Maintenance(s) Log Book	☐	_______________________
☐ Reagent(s) Log Book	☐	_______________________
☐ Standard(s) Log Book	☐	_______________________
☐ Nonconformance/Preventive Action	☐	_______________________
☐ Other Log Book____________	☐	_______________________
☐ MDL	☐	Date:__________________
☐ LOD	☐	Date:__________________
☐ LOQ	☐	Date:__________________
☐ Last Control Chart/Linear Range	☐	Date:__________________
☐ Retention Time Window Study	☐	Date:__________________
☐ Supplies Labeled	☐	_______________________

Data Chase:

Merit #: ________________ Run Date: ________________ Prep Date: _________________
QC Prep ID: ____________ QC Run ID: ______________ Calibration Date: _____________

Calibration Check:

Standard/Reagent	Lot #	Preparation Date	Expiration Date

Item	Limits	Agree w/ SOP?	Agree w/ Method?	Agree w/ Cert./Project?	Notes
# of Points		☐	☐	☐	
Second Source		☐	☐	☐	
Fit		☐	☐	☐	
R-value		☐	☐	☐	
ICV		☐	☐	☐	
CCV		☐	☐	☐	
		☐	☐	☐	
		☐	☐	☐	
		☐	☐	☐	

Preparation Check:

Standard/Reagent	Lot #	Preparation Date	Expiration Date

Bench Sheet Check:	Traceable?	Present?	Notes:
☐ Analysis Information	☐	☐	___________________________
☐ Batch Information	☐	☐	___________________________
☐ Reagent/Standard Information	☐	☐	___________________________
☐ Sample Information	☐	☐	___________________________
☐ Subsampling/Targeting		☐	___________________________
☐ Effective Date		☐	___________________________

☐ Clean/Legible Copy ☐ ____________________

Prep Batch Quality Control:

Item	Frequency

Analysis:

Raw Data Check:	Traceable?	Present?	Notes:
☐ Analysis Information	☐	☐	____________________
☐ Batch Information	☐	☐	____________________
☐ Reagent/Standard Information	☐	☐	____________________
☐ Sample Information	☐	☐	____________________
☐ Manual Integrations	☐	☐	____________________

Run Batch Quality Control:

Item	Frequency (1 per ?)	Limits	Acceptable?	Agree w/ SOP?	Agree w/ Method?	Agree w/ Cert./Project?
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐

☐ Associated Calibration/MDL are acceptable?

Data Review:

☐ Analyst
☐ Peer

Reagent traceability notes: ____
____
____
____

General notes: ____
____
____
____

SOP Check:

Section	Followed?	Agree w/ Method?	Notes:
Scope/Application	☐	☐	
Method #	☐	☐	
Matrix/Matrices	☐	☐	
Detection Limit	☐	☐	
Summary	☐	☐	
Interferences	☐	☐	
Apparatus & Materials	☐	☐	
Reagents/Standards	☐	☐	
Sample Collection, Preservation & Handling	☐	☐	
Procedure	☐	☐	
Calibration	☐	☐	
Calculations	☐	☐	
Quality Control	☐	☐	
Data Assessment	☐	☐	
Frequency	☐	☐	
Acceptance Criteria	☐	☐	
Corrective Actions	☐	☐	
Method Performance	☐	☐	
Maintenance & Troubleshooting	☐	☐	
Safety	☐	☐	
Waste Disposal & Pollution Prevention	☐	☐	
Definitions	☐	☐	
References	☐	☐	
Tables/Diagrams	☐	☐	
Documentation	☐	☐	
Benchsheet	☐	☐	
Amendments	☐	☐	

Method Specific Information: ____

____

____

____

____

____

Figure 3: Log-In/Sample Receiving Checklist
Name(s) of auditor(s): ____________________________________
Date: ___________________
Name(s) of employee(s): _____________________________________

Corrective Action Follow-up:____
____
____
____
____
____

External Audit Follow-up: ____
____
____
____
____
____

Previous Internal Audit Follow-up: ____
____
____
____
____
____

General Checklist:	Complete?	Notes:
☐ Nonconformance/Preventive Action	☐	________________________
☐ Supplies Labeled	☐	________________________
☐ Sample Acceptance Policy Available	☐	________________________

Data Chase:
Merit #: _______________ Log-in Date: _______________ COC #:_______________

Sample Receiving:	Complete?	Notes:
☐ Chain of Custody	☐	________________________
☐ Unique Identification (sample)	☐	________________________
☐ Unique Identification (container)	☐	________________________
☐ Durable Label Used	☐	________________________
☐ Sample Condition Checked	☐	________________________
☐ Temperature Checked	☐	________________________
☐ Chemical Preservation Checked	☐	________________________
☐ Data Flagged	☐	________________________
☐ Appropriate Storage Utilized	☐	________________________

Subcontracting:	Complete?	Notes:
☐ Client Notified	☐	____________________________
☐ Certified Laboratory Utilized	☐	____________________________
☐ Registry of Approved Subcontractors	☐	____________________________

Service to Client:	Complete?	Notes:
☐ Complaint(s) Recorded	☐	____________________________
☐ Maintain all Correspondence	☐	____________________________
☐ Confidentiality Protected	☐	____________________________

Records:	Complete?	Notes:
☐ Chain of Custody	☐	____________________________
☐ Field Sheet	☐	____________________________
☐ Sample Receiving Checklist	☐	____________________________
☐ Preservation Checklist	☐	____________________________

Reporting:	Complete?	Notes:
☐ Confidentiality Protected	☐	____________________________
☐ Explanation of Data Qualifiers	☐	____________________________
☐ Amendments clearly identified	☐	____________________________
☐ Subcontracting clearly identified	☐	____________________________
☐ Secondary reports labeled appropriately	☐	____________________________

General notes: ____
____
____
____
____

SOP Check:

Section	Followed?	Agree w/ Method?	Notes:
Scope/Application	☐	☐	
Method #	☐	☐	
Matrix/Matrices	☐	☐	
Detection Limit	☐	☐	
Summary	☐	☐	
Interferences	☐	☐	
Apparatus & Materials	☐	☐	
Reagents/Standards	☐	☐	
Sample Collection, Preservation & Handling	☐	☐	
Procedure	☐	☐	
Calibration	☐	☐	
Calculations	☐	☐	
Quality Control	☐	☐	
Data Assessment	☐	☐	
Frequency	☐	☐	
Acceptance Criteria	☐	☐	
Corrective Actions	☐	☐	
Method Performance	☐	☐	
Maintenance & Troubleshooting	☐	☐	
Safety	☐	☐	
Waste Disposal & Pollution Prevention	☐	☐	
Definitions	☐	☐	
References	☐	☐	
Tables/Diagrams	☐	☐	
Documentation	☐	☐	
Benchsheet	☐	☐	
Amendments	☐	☐	

Figure 4: Tentative procedure schedule

Procedure	Date
PT Studies	
WP PT Fall	August - October
WP PT Spring	March - May
WS PT Annual	January - April
DMRQA Annual	w/ Spring WP
NY NELAP Non-Potable Water & Solid	2 times year TBD by NY NELAP
NY NELAP Potable Water	2 times year TBD by NY NELAP
Staff Trainings	
Code of Ethics / Data Integrity	March - May
Chemical Hygiene training	March - May
Holding Times Training	March - May
Safety Training	March - May
Allowable deviation Training	March - May
Review of WP PT Fall	30 days after final report
Review of WP PT Spring	30 days after final report
Review of WS PT	30 days after final report
Review of NYNELAP PT Study	30 days after final report
Audits	
Internal Audit	March - May
Control Chart Evaluations	March - May
Quality Systems Review	March - May
QA/QC Manual Review	March - May
Log Book Reviews	March - May
Method Reviews	March - May
SOP QC Checks	March - May
Trend Analyses when applicable	March - May
QC Control Limits Review	March - May
Managerial Review	March - May (after Internal Audit)
SOP Review	March - May

APPENDIX C: LABORATORY REFERENCE DATA

Applied EcoSystems, Inc.
Environmental Management, Consulting & Field Services

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
Polychlorinated Biphenyls (PCBs) (GC)	608.3_PCB_PREC	608_Prep_PCB	Aroclor-1016	12674-11-2	0.100	0.0560	ug/L	50	140	30	50	140	36		
			Aroclor-1221	11104-28-2	0.100	0.0570	ug/L								
			Aroclor-1232	11141-16-5	0.100	0.0740	ug/L								
			Aroclor-1242	53469-21-9	0.100	0.0760	ug/L								
			Aroclor-1248	12672-29-6	0.100	0.0500	ug/L								
			Aroclor-1254	11097-69-1	0.100	0.0400	ug/L								
			Aroclor-1260	11096-82-5	0.100	0.0460	ug/L	8	140	30	8	140	38		
			DCB Decachlorobiphenyl	2051-24-3			ug/L							10	114
			Tetrachloro-m-xylene	877-09-8			ug/L							15	131
Semivolatile Organic Compounds (GC/MS)	625.1_PREC	625_Prep	Benzo[a]anthracene	56-55-3	10.0	0.171	ug/L	33	143	35	33	143	53		
			Benzo[a]pyrene	50-32-8	10.0	0.173	ug/L	17	163	35	17	163	72		
			Benzo[b]fluoranthene	205-99-2	10.0	0.154	ug/L	24	159	35	24	159	71		
			Benzo[g,h,i]perylene	191-24-2	10.0	0.178	ug/L	0	219	35	0	219	97		
			Acenaphthene	83-32-9	10.0	0.172	ug/L	47	145	35	47	145	48		
			Acenaphthylene	208-96-8	10.0	0.125	ug/L	33	145	35	33	145	74		
			Anthracene	120-12-7	10.0	0.135	ug/L	27	133	35	27	133	66		
			Benzo[k]fluoranthene	207-08-9	10.0	0.140	ug/L	11	162	35	11	162	63		
			Butyl benzyl phthalate	85-68-7	10.0	0.666	ug/L	0	152	35	0	152	60		
			Bis(2-chloroethoxy)methane	111-91-1	10.0	0.455	ug/L	33	184	35	33	184	54		
			Bis(2-chloroethyl)ether	111-44-4	10.0	0.402	ug/L	12	158	35	12	158	108		
			Bis(2-ethylhexyl) phthalate	117-81-7	10.0	2.22	ug/L	8	158	35	8	158	82		
			bis (2-chloroisopropyl) ether	108-60-1	10.0	0.551	ug/L	36	166	35	36	166	76		
			4-Bromophenyl phenyl ether	101-55-3	10.0	0.499	ug/L	53	127	35	53	127	43		
			2-Chloronaphthalene	91-58-7	10.0	0.483	ug/L	60	120	35	60	120	24		
			4-Chlorophenyl phenyl ether	7005-72-3	10.0	0.551	ug/L	25	158	35	25	158	61		
			Chrysene	218-01-9	10.0	0.186	ug/L	17	168	35	17	168	87		
			Dibenz(a,h)anthracene	53-70-3	10.0	0.151	ug/L	0	227	35	0	227	126		
			Di-n-butyl phthalate	84-74-2	10.0	1.80	ug/L	1	120	35	1	120	47		
			3,3'-Dichlorobenzidine	91-94-1	10.0	1.15	ug/L	0	262	35	0	262	108		
			Diethyl phthalate	84-66-2	10.0	3.82	ug/L	0	120	35	0	120	100		
			Dimethyl phthalate	131-11-3	10.0	0.515	ug/L	0	120	35	0	120	183		
			2,4-Dinitrotoluene	121-14-2	10.0	2.07	ug/L	39	139	35	39	139	42		
			2,6-Dinitrotoluene	606-20-2	10.0	2.13	ug/L	50	158	35	50	158	48		
			Di-n-octyl phthalate	117-84-0	10.0	0.821	ug/L	4	146	35	4	146	69		
			Fluoranthene	206-44-0	10.0	0.160	ug/L	26	137	35	26	137	66		
			Fluorene	86-73-7	10.0	0.169	ug/L	59	121	35	59	121	38		
			Hexachlorobenzene	118-74-1	10.0	0.161	ug/L	0	152	35	0	152	55		
			Hexachlorobutadiene	87-68-3	10.0	0.543	ug/L	24	120	35	24	120	62		
			Hexachloroethane	67-72-1	10.0	0.395	ug/L	40	120	35	40	120	52		
			Indeno[1,2,3-cd]pyrene	193-39-5	10.0	0.135	ug/L	0	171	35	0	171	99		
			Isophorone	78-59-1	10.0	0.324	ug/L	21	196	35	21	196	93		
			Naphthalene	91-20-3	10.0	0.109	ug/L	21	133	35	21	133	65		
			Nitrobenzene	98-95-3	10.0	0.514	ug/L	35	180	35	35	180	62		
			N-Nitrosodi-n-propylamine	621-64-7	10.0	0.253	ug/L	0	230	35	0	230	87		
			Phenanthrene	85-01-8	10.0	0.167	ug/L	54	120	35	54	120	39		
			Pyrene	129-00-0	10.0	0.175	ug/L	52	120	35	52	120	49		
			1,2,4-Trichlorobenzene	120-82-1	10.0	0.427	ug/L	44	142	35	44	142	50		
			4-Chloro-3-methylphenol	59-50-7	10.0	0.296	ug/L	22	147	35	22	147	73		
			2-Chlorophenol	95-57-8	10.0	0.273	ug/L	23	134	35	23	134	61		
			2,4-Dichlorophenol	120-83-2	10.0	0.262	ug/L	39	135	35	39	135	50		
			2,4-Dimethylphenol	105-67-9	10.0	0.518	ug/L	32	120	35	32	120	58		
			2,4-Dinitrophenol	51-28-5	50.0	6.21	ug/L	0	191	35	0	191	132		
			4,6-Dinitro-2-methylphenol	534-52-1	50.0	2.82	ug/L	0	181	35	0	181	203		
			2-Nitrophenol	88-75-5	10.0	0.564	ug/L	29	182	35	29	182	55		
			4-Nitrophenol	100-02-7	50.0	2.17	ug/L	0	132	35	0	132	131		
			Pentachlorophenol	87-86-5	10.0	3.10	ug/L	14	176	35	14	176	86		
			Phenol	108-95-2	10.0	0.128	ug/L	5	120	35	5	120	64		
			2,4,6-Trichlorophenol	88-06-2	10.0	1.80	ug/L	37	144	35	37	144	58		

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
			Benzidine	92-87-5	5.00	1.88	ug/L	5	120	35	5	120	35		
			Hexachlorocyclopentadiene	77-47-4	10.0	1.76	ug/L	19	120	35	10	120	35		
			N-Nitrosodimethylamine	62-75-9	1.00	0.219	ug/L	10	120	35	10	120	35		
			N-Nitrosodiphenylamine	86-30-6	10.0	0.440	ug/L	55	120	35	55	120	35		
			1,2-Diphenylhydrazine	122-66-7	1.00	0.433	ug/L	43	125	35	43	125	35		
			2-Fluorophenol	367-12-4			ug/L			35			35	10	120
			2,4,6-Tribromophenol	118-79-6			ug/L			35			35	28	120
			Nitrobenzene-d5	4165-60-0			ug/L			35			35	32	120
			Phenol-d5	4165-62-2			ug/L			35			35	10	120
			Terphenyl-d14	1718-51-0			ug/L			35			35	23	127
			2-Fluorobiphenyl (Surr)	321-60-8			ug/L			35			35	38	120
Volatile Organic Compounds (GC/MS)	624.1_LL_PREC	624_Prep	Benzene	71-43-2	1.00	0.130	ug/L	65	135	35	37	151	61		
			Ethylbenzene	100-41-4	1.00	0.110	ug/L	60	140	35	37	162	63		
			Toluene	108-88-3	1.00	0.140	ug/L	70	130	35	47	150	41		
			Vinyl chloride	75-01-4	1.00	0.200	ug/L	5	195	35	0	251	66		
			Xylenes, Total	1330-20-7	2.00	0.150	ug/L	80	120	35	67	120	25		
			Dichlorobromomethane	75-27-4	1.00	0.170	ug/L	65	135	35	35	155	56		
			Bromoform	75-25-2	1.00	0.760	ug/L	70	130	35	45	169	42		
			Bromomethane	74-83-9	1.00	0.420	ug/L	15	185	35	0	242	61		
			Carbon tetrachloride	56-23-5	1.00	0.260	ug/L	70	130	35	70	140	41		
			Chlorobenzene	108-90-7	1.00	0.140	ug/L	65	135	35	37	160	53		
			Chlorodibromomethane	124-48-1	1.00	0.390	ug/L	70	135	35	53	149	50		
			Chloroethane	75-00-3	1.00	0.830	ug/L	40	160	35	14	230	78		
			2-Chloroethyl vinyl ether	110-75-8	10.0	0.260	ug/L	0	225	35	0	305	71		
			Chloroform	67-66-3	1.00	0.130	ug/L	70	135	35	51	138	54		
			Chloromethane	74-87-3	1.00	0.200	ug/L	0	205	35	0	273	60		
			1,2-Dichlorobenzene	95-50-1	1.00	0.150	ug/L	65	135	35	18	190	57		
			1,3-Dichlorobenzene	541-73-1	1.00	0.150	ug/L	70	130	35	59	156	43		
			1,4-Dichlorobenzene	106-46-7	1.00	0.160	ug/L	65	135	35	18	190	57		
			1,1-Dichloroethane	75-34-3	1.00	0.170	ug/L	70	130	35	59	155	40		
			1,1-Dichloroethene	75-35-4	1.00	0.190	ug/L	50	150	35	0	234	32		
			1,2-Dichloroethane	107-06-2	1.00	0.210	ug/L	70	130	35	49	155	49		
			trans-1,2-Dichloroethene	156-60-5	0.500	0.190	ug/L	70	130	35	54	156	45		
			1,2-Dichloropropane	78-87-5	1.00	0.150	ug/L	35	165	35	0	210	55		
			cis-1,3-Dichloropropene	10061-01-5	1.00	0.610	ug/L	25	127	35	0	227	58		
			trans-1,3-Dichloropropene	10061-02-6	1.00	0.670	ug/L	50	150	35	17	183	86		
			Methylene Chloride	75-09-2	5.00	2.62	ug/L	60	140	35	0	221	28		
			1,1,2,2-Tetrachloroethane	79-34-5	1.00	0.130	ug/L	60	140	35	46	157	61		
			Tetrachloroethene	127-18-4	1.00	0.150	ug/L	70	130	35	64	148	39		
			1,1,1-Trichloroethane	71-55-6	1.00	0.240	ug/L	70	130	35	52	162	36		
			1,1,2-Trichloroethane	79-00-5	1.00	0.0900	ug/L	70	130	35	52	150	45		
			Trichloroethene	79-01-6	1.00	0.100	ug/L	65	135	35	70	157	48		
			m-Xylene & p-Xylene	179601-23-1	2.00	0.0800	ug/L								
			o-Xylene	95-47-6	1.00	0.0900	ug/L								
			Acrolein	107-02-8	20.0	2.07	ug/L	60	140	35	40	160	60		
			Acrylonitrile	107-13-1	20.0	1.13	ug/L	60	140	35	40	160	60		
			1,3-Dichloropropene, Total	542-75-6	2.00	1.29	ug/L	61	128	35	45	124	28		
			4-Bromofluorobenzene (Surr)	460-00-4			ug/L			35				79	120
			1,2-Dichloroethane-d4 (Surr)	17060-07-0			ug/L			35				70	121
			Toluene-d8 (Surr)	2037-26-5			ug/L			35				70	123
Organochlorine Pesticides in Water	608.3_Pest_PREC	608_CLLE_Prep	Aldrin	309-00-2	0.0500	0.00240	ug/L	42	140	35	42	140	35		
			alpha-BHC	319-84-6	0.0500	0.00200	ug/L	37	140	35	37	140	36		
			beta-BHC	319-85-7	0.0500	0.00460	ug/L	17	147	35	17	147	44		
			delta-BHC	319-86-8	0.0500	0.00430	ug/L	19	140	35	19	140	52		
			gamma-BHC (Lindane)	58-89-9	0.0500	0.00250	ug/L	32	140	35	32	140	39		
			Chlordane (technical)	12789-03-6	0.500	0.0465	ug/L								
			4,4'-DDD	72-54-8	0.0500	0.00530	ug/L	31	141	35	31	141	39		

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
			4,4'-DDE	72-55-9	0.0500	0.00430	ug/L	30	145	35	30	145	35		
			4,4'-DDT	50-29-3	0.0500	0.00480	ug/L	25	160	35	25	160	42		
			Dieldrin	60-57-1	0.0500	0.00230	ug/L	36	146	35	36	146	49		
			Endosulfan I	959-98-8	0.0500	0.00370	ug/L	45	153	35	45	153	28		
			Endosulfan II	33213-65-9	0.0500	0.00230	ug/L	0	202	35	10	202	53		
			Endosulfan sulfate	1031-07-8	0.0500	0.00370	ug/L	26	144	35	26	144	38		
			Endrin	72-20-8	0.0500	0.00250	ug/L	30	147	35	30	147	48		
			Endrin aldehyde	7421-93-4	0.0500	0.00460	ug/L	47	120	35	47	120	35		
			Heptachlor	76-44-8	0.0500	0.00330	ug/L	34	140	35	34	140	43		
			Heptachlor epoxide	1024-57-3	0.0500	0.00260	ug/L	37	142	35	37	142	26		
			Toxaphene	8001-35-2	2.00	0.0581	ug/L								
			Chlordane (technical) Peak 1	STL00379	0.500	0.0465	ug/L								
			Chlordane (technical) Peak 2	STL00380	0.500	0.0465	ug/L								
			Chlordane (technical) Peak 3	STL00084	0.500	0.0465	ug/L								
			Chlordane (technical) Peak 4	STL00065	0.500	0.0465	ug/L								
			Toxaphene Peak 1	STL00100	2.00	0.0581	ug/L								
			Toxaphene Peak 2	STL00109	2.00	0.0581	ug/L								
			Toxaphene Peak 3	STL00220	2.00	0.0581	ug/L								
			Toxaphene Peak 4	STL00083	2.00	0.0581	ug/L								
			Toxaphene Peak 5	STL00051	2.00	0.0581	ug/L								
			DCB Decachlorobiphenyl	2051-24-3			ug/L			35			35	10	120
			Tetrachloro-m-xylene	877-09-8			ug/L			35			35	33	120
Mercury (CVAA)	245.1	245.1_Prep	Mercury	7439-97-6	0.000200	0.000130	mg/L	85	115	20	70	130	20		
Metals (ICP)	200.7	200.7_P_TR	Chromium	7440-47-3	0.0500	0.000625	mg/L	85	115	20	75	125	20		
			Nickel	7440-02-0	0.0100	0.00220	mg/L	85	115	20	75	125	20		
			Lead	7439-92-1	0.0500	0.00277	mg/L	85	115	20	75	125	20		
			Zinc	7440-66-6	0.0200	0.00967	mg/L	85	115	20	75	125	20		
Solids, Total Suspended (TSS)	2540D		Total Suspended Solids	STL00161	4.00	2.22	mg/L	64	120	20					
Chromium, Trivalent	3500_CR3_B		Chromium, trivalent	16065-83-1	calc		mg/L								
Chromium, Hexavalent	3500_CR_B		Chromium, hexavalent	18540-29-9	0.00500	0.00300	mg/L	80	123	20	31	151	20		
Dioxin Screen (GC/MS SIM)	625DioxinScreen	3510C	2,3,7,8-TCDD	1746-01-6			NONE								
HEM and SGT-HEM	1664A_NP		HEM	STL00181	5.00	1.02	mg/L	78	114	11	78	114	18		
Anions, Ion Chromatography	9056A_28D		Sulfate	14808-79-8	1.00	0.348	mg/L	90	110	20	80	120	15		
Sulfide, Acid soluble and Insoluble (Titrimetri	9034_Calc	9030B	Sulfide	18496-25-8	3.00	1.41	mg/L	70	120	20	32	130	30		
Hardness, Total (mg/l as CaC03)	2340C		Hardness as calcium carbonate	STL00009	5.00	2.39	mg/L	90	110	20	80	120	10		
Alkalinity	2320B		Alkalinity	STL00171	5.00	2.60	mg/L	86	123	20	10	190	35		
Volatile Organic Compounds (GC/MS)	8260B	5030B	Acetone	67-64-1	10.0	5.41	ug/L	21	162	35	10	168	35		
			Benzene	71-43-2	1.00	0.130	ug/L	80	123	35	71	122	22		
			Bromodichloromethane	75-27-4	1.00	0.170	ug/L	77	125	35	64	125	27		
			Bromoform	75-25-2	1.00	0.760	ug/L	49	141	35	44	129	28		
			Bromomethane	74-83-9	1.00	0.420	ug/L	41	175	35	19	187	35		
			2-Butanone (MEK)	78-93-3	10.0	1.16	ug/L	39	163	35	37	156	35		
			Carbon disulfide	75-15-0	5.00	0.280	ug/L	60	138	35	43	144	33		
			Carbon tetrachloride	56-23-5	1.00	0.260	ug/L	63	140	35	41	143	30		
			Chlorobenzene	108-90-7	1.00	0.140	ug/L	80	121	35	70	123	23		
			Chloroethane	75-00-3	1.00	0.830	ug/L	33	173	35	11	189	35		
			Chloroform	67-66-3	1.00	0.130	ug/L	79	127	35	68	130	23		
			Chloromethane	74-87-3	1.00	0.200	ug/L	54	143	35	31	154	35		

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
			1,1-Dichloroethane	75-34-3	1.00	0.170	ug/L	75	133	35	63	136	23		
			1,2-Dichloroethane	107-06-2	1.00	0.210	ug/L	71	135	35	65	135	24		
			1,1-Dichloroethene	75-35-4	1.00	0.190	ug/L	65	139	35	53	140	35		
			1,2-Dichloropropane	78-87-5	1.00	0.150	ug/L	78	133	35	70	132	26		
			cis-1,3-Dichloropropene	10061-01-5	1.00	0.610	ug/L	64	132	35	48	127	30		
			trans-1,3-Dichloropropene	10061-02-6	1.00	0.670	ug/L	55	128	35	40	125	27		
			Ethylbenzene	100-41-4	1.00	0.110	ug/L	80	120	35	66	120	24		
			2-Hexanone	591-78-6	10.0	0.540	ug/L	43	148	35	42	150	35		
			Methylene Chloride	75-09-2	5.00	2.62	ug/L	70	134	35	61	130	29		
			4-Methyl-2-pentanone (MIBK)	108-10-1	10.0	0.420	ug/L	49	143	35	44	143	35		
			Styrene	100-42-5	1.00	0.100	ug/L	79	120	35	68	120	26		
			1,1,2,2-Tetrachloroethane	79-34-5	1.00	0.130	ug/L	65	139	35	60	137	31		
			Tetrachloroethene	127-18-4	1.00	0.150	ug/L	74	130	35	51	136	23		
			Toluene	108-88-3	1.00	0.140	ug/L	78	129	35	62	132	23		
			Trichloroethene	79-01-6	1.00	0.100	ug/L	76	125	35	55	131	23		
			Vinyl chloride	75-01-4	1.00	0.200	ug/L	58	143	35	43	154	29		
			Xylenes, Total	1330-20-7	2.00	0.150	ug/L	80	120	35	67	120	25		
			1,1,1-Trichloroethane	71-55-6	1.00	0.240	ug/L	69	134	35	51	138	27		
			1,1,2-Trichloroethane	79-00-5	1.00	0.0900	ug/L	78	133	35	76	132	25		
			Cyclohexane	110-82-7	1.00	0.240	ug/L	58	145	35	42	135	35		
			1,2-Dibromo-3-Chloropropane	96-12-8	1.00	0.910	ug/L	46	132	35	38	124	35		
			1,2-Dibromoethane	106-93-4	1.00	0.120	ug/L	77	123	35	71	123	27		
			Dichlorodifluoromethane	75-71-8	1.00	0.350	ug/L	29	148	35	28	136	35		
			cis-1,2-Dichloroethene	156-59-2	1.00	0.160	ug/L	76	128	35	64	130	21		
			trans-1,2-Dichloroethene	156-60-5	1.00	0.190	ug/L	78	133	35	68	133	24		
			Isopropylbenzene	98-82-8	1.00	0.0900	ug/L	74	120	35	59	120	31		
			Methyl acetate	79-20-9	10.0	1.72	ug/L	52	145	35	41	142	35		
			Methyl tert-butyl ether	1634-04-4	1.00	0.0700	ug/L	51	133	35	41	136	29		
			1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	1.00	0.410	ug/L	50	156	35	31	156	35		
			1,2,4-Trichlorobenzene	120-82-1	1.00	0.260	ug/L	42	133	35	30	126	35		
			1,2-Dichlorobenzene	95-50-1	1.00	0.150	ug/L	78	120	35	64	120	30		
			1,3-Dichlorobenzene	541-73-1	1.00	0.150	ug/L	78	120	35	62	120	31		
			1,4-Dichlorobenzene	106-46-7	1.00	0.160	ug/L	78	120	35	63	120	28		
			Trichlorofluoromethane	75-69-4	1.00	0.450	ug/L	51	164	35	37	174	35		
			Dibromochloromethane	124-48-1	1.00	0.390	ug/L	70	132	35	60	129	26		
			Methylcyclohexane	108-87-2	1.00	0.330	ug/L	60	125	35	37	123	35		
			m-Xylene & p-Xylene	179601-23-1	2.00	0.0800	ug/L								
			o-Xylene	95-47-6	1.00	0.0900	ug/L								
			1,2-Dichloroethane-d4 (Surr)	17060-07-0	1.00		ug/L			35				70	121
			4-Bromofluorobenzene (Surr)	460-00-4	1.00		ug/L			35				59	120
			Toluene-d8 (Surr)	2037-26-5	1.00		ug/L			35				70	123
			Dibromofluoromethane (Surr)	1868-53-7	1.00		ug/L			35				75	128

APPENDIX D: FIELD ANALYTICAL AND SAPLING STANDARD OPERATING PROCEDURES

Applied EcoSystems, Inc.

Environmental Management, Consulting & Field Services

LOW FLOW GROUNDWATER SAMPLING

Standard Operating Procedure

Applied EcoSystems

Needed Equipment (including, but not limited to): HASP, Tools to open wells, Interface Probe, Low Flow Water Quality Meter, Low Flow Peristaltic Pump, Sample Bottles, MasterFlex (silicone) tubing, polyethylene tubing, bailer (just in case), Buckets, COOLER with ice, *Low Flow Sampling Logs* (one per well plus extra), distilled water.

Health and Safety

- Review HASP
- Complete Tailgate Safety Meeting Form

Depth to Water Gauging

- Gauge all wells per Gauging and Sampling Order
- Gauging the depth to water (DTW) and depth to NAPL (DTNAPL) and Depth to Bottom (DTB) with an Interface probe. Record in Field book. Note, If no NAPL is detected, record as “ND” **NOT 0.00!**

Low-Flow Groundwater Sampling

- Attached new/unused MasterFlex Tubing to peristaltic head
- Insert new/unused ¼-inch polyethylene tubing to well. Set inlet to approximately the center of the screen
- Attach ¼-inch tubing to the inlet side of the MasterFlex tubing.
- Cut approximately one to two additional feet of ¼-inch tubing to the outlet of side of the MasterFlex.
- Attach outlet tubing to water quality meter
- Start pump at lowest setting that will allow water flow. Adjust flow to minimize drawdown. Gauge periodically and record on *Low Flow Groundwater Sampling Log*
- Record pH, ORP, DO, Conductivity, Turbidity, Temperature, and Depth to water at least every three minutes.
- Continue pumping until one of the following occurs;
    - All parameters stabilized for the last three readings. Monitoring parameters must fall within these limits;

pH	± 0.1 units *(for values greater than 5 NTU; if three Turbidity values are less than 5 NTU, consider the values as stabilized)*
Temperature	± 3%
Specific Conductance	± 3%
Oxygen Reduction Potential (ORP)	± 10 mV
Dissolved Oxygen	± 10% *(for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized)*
Turbidity	± 10%
Water Level drawdown	< 0.3 feet

    - The well goes dry
    - Purging has continued for 30 minutes
- Once purge water has stabilized, **remove water quality meter**. Do not change the rate of purging.
- PUT ON NEW CLEAN GLOVES BEFORE HANDLING CONTAINER.
- Collect water samples in laboratory supplied containers.
- Complete Chain-of-Custody (COC) **as samples are collected.**
- IN ADDITION TO WELL SAMPLE COLLECT THE FOLLOWING **QA/QC SAMPLES**;
    - One **Field Blank** per day **AT THE BEGINNING OF THE DAY** (pour distilled water into one set of laboratory supplied containers). Analyzed for same parameters as well samples.
    - One **Duplicate** for each 10 well samples collected (minimum of one duplicate) collected from the most impacted and/or last well sampled. Analyzed for same parameters as well samples.
    - One **Equipment Blank** per day **AT THE END OF THE DAY IN THE FIELD** (pump distilled water through clean new sample tubing into laboratory supplied containers). Analyzed for same parameters as well samples.
    - One **Trip Blank** per sampling event (NOT per day) should be supplied by the laboratory. Analyzed for VOCs only. Trip Blank stays in cooler and with samples until samples are delivered to the laboratory.

- Discard used tubing and make sure well is secure.
- DECON thoroughly between wells with PFAS free water.

Sample Event Wrap-up:
Make sure all well lids are secure, LOCK GATES and
No trash (used disposable gloves, etc..) from sample event remains on site.

LOW FLOW GROUNDWATER SAMPLING (PFAS)

Standard Operating Procedure

Applied EcoSystems

Needed Equipment (including, but not limited to): HASP, Tools to open wells, Interface Probe, Low Flow Water Quality Meter, Low Flow Peristaltic Pump, Sample Bottles, MasterFlex (silicone) tubing, HDPE tubing, Buckets, COOLER with ice, *Low Flow Sampling Logs*, PFAS free water.

Health and Safety

- Review HASP
- Complete Tailgate Safety Meeting Form

Depth to Water Gauging

- Gauge all wells per the Gauging and Sampling Order (least impacted to most impacted per previous sampling or screening results)
- Gauging the depth to water (DTW) and depth to NAPL (DTNAPL) and Depth to Bottom (DTB) with an Interface probe. Record in Field book. Note, If no NAPL is detected, record as "ND" **NOT 0.00!**

Low-Flow Groundwater Sampling

- Attached new/unused MasterFlex Tubing to peristaltic head
- Insert new/unused ¼-inch **HDPE** tubing to well. Set inlet to approximately the center of the screen
- Attach ¼-inch tubing to the inlet side of the MasterFlex tubing.
- Cut approximately one to two additional feet of ¼-inch tubing to the outlet of side of the MasterFlex.
- Attach outlet tubing to water quality meter
- Start pump at lowest setting that will allow water flow. Adjust flow to minimize drawdown. Gauge periodically and record on *Low Flow Groundwater Sampling Log*
- Record pH, ORP, DO, Conductivity, Turbidity, Temperature, and Depth to water at least every three to five minutes.
- Continue pumping until one of the following occurs;
  - All parameters stabilized for the last three readings. Monitoring parameters must fall within these limits;

pH	± 0.1 units *(for values greater than 5 NTU; if three Turbidity values are less than 5 NTU, consider the values as stabilized)*
Temperature	± 3%
Specific Conductance	± 3%
Oxygen Reduction Potential (ORP)	± 10 mV
Dissolved Oxygen	± 10% *(for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized)*
Turbidity	± 10%
Water Level drawdown	< 0.3 feet

  - The well goes dry
  - Purging has continued for 30 minutes
- Once purge water has stabilized, **remove water quality meter**. Do not change the rate of purging.
- PUT ON NEW CLEAN GLOVES BEFORE HANDLING PFAS CONTAINER.
  - One field technician will touch ONLY the laboratory supplied sampling container.
  - The second field technician will handle all other tasks associated with collection of the sample.
- Collect water samples in laboratory supplied containers. Do not touch the lab containers with tubing.
- ONLY fill PFAS container to BETWEEN 5 and 6 ml mark.
- Complete Chain-of-Custody (COC) **as samples are collected.**
- IN ADDITION TO WELL SAMPLE COLLECT THE FOLLOWING **QA/QC SAMPLES**;
  - One **Field Blank** per day **AT THE BEGINNING OF THE DAY** (pour PFAS-Free water (5-6 ml) into one set of laboratory supplied containers). Analyzed for same parameters as well samples.

  - One **Duplicate** for each 10 well samples collected (minimum of one duplicate) collected from the most impacted and/or last well sampled. Analyzed for same parameters as well samples.
  - One **Equipment Blank** per day **AT THE END OF THE DAY IN THE FIELD** (pump PFAS-Free water through clean new sample tubing into laboratory supplied containers). Analyzed for same parameters as well samples.
  - One **Trip Blank** per sampling event (NOT per day) should be supplied by the laboratory. Trip Blank stays in cooler and with samples until samples are delivered to the laboratory.
- Discard used tubing and make sure well is secure.
- DECON water quality meter thoroughly between wells with PFAS free water.

Sample Event Wrap-up:

Make sure all well lids are secure, LOCK GATES and
No trash (used disposable gloves, etc..) from sample event remains on site.

GENERAL SOIL SAMPLING PROCEDURES

Standard Operating Procedure

Applied EcoSystems

Note: Soil sampling is site and task specific. Further training and information should be given to you prior to your arrival on site. The procedure below begins with soil collection for laboratory analysis and does not take into account any site or task specific information (depths, intervals, locations, etc.).

Equipment Needed

- PID and isobutylene calibration gas
- Sampling Material (nitrile gloves, digital scale, soil samplers, sampling jars)
- Plastic freezer baggies, garbage bags
- Black Sharpie Marker
- Measuring Tape
- 2 Coolers (minimum)
- Ice
- Small trowel
- Buckets
- Non-Hazardous Drum Labels
- Decon equipment (buckets, brushes, alconox, paper towel)

Procedure

1) Put on a clean pair of Nitrile gloves.
2) Describe soil lithology in field book or boring log form.
3) Collect and then split soil sample into two samples (one for laboratory analysis sample-place in ice filled cooler and one for field screening sample).
4) Place field screening sample into a clean plastic freezer bag, label bag with appropriate Soil Sample #.
5) Place laboratory analysis sample into a clean plastic freezer bag, label bag with appropriate Soil Sample #, and place it in ice-filled. Make sure the sample bag has no air in it.
6) Measure headspace.
    - Let soil sit for a few minutes to allow vapors to gather.
    - Field screen soil with a calibrated PID. Record readings into field book.
    - Discard soil into approved location.
7) Use laboratory analysis sample in cooler for soil sampling collection.
    - Gather sampling material (scale, soil samplers, sampling jars)
    - Fill all sampling jars with the appropriate amount of soil (use scale and soil sampler for VOAs)
    - Preserve sample per laboratory/analytical method requirements.
    - Label all containers with appropriate information.
    - Place all sampling jars into a plastic freezer bag and place them into the cooler.
8) Repeat the above steps (1-6) for each soil sample.
9) Fill out COC completely before leaving site.

SOIL BORING INSTALLATION

Standard Operating Procedure

Applied EcoSystems

SOIL BORING PROCEDURES

Prior to on-site activities, MISS DIG is notified for utility locating/marking. In addition, a private contractor is utilized to mark on-site utilities. A site walk is conducted with the utility locating contractor, in which the soil boring locations are marked. Locations of utility meters, cleanouts, shut off boxes, surface cover saw cuts, etc. are also noted to aid in identifying the locations of underground utilities. The locations of underground utilities identified by MISS DIG and the utility locating contractor are marked using color-coded spray paint on the ground surface in paved areas and color-coded flags on metal stakes in unpaved areas. The soil borings are then relocated, if necessary, to clear underground and overhead utilities.

A geoprobe is utilized to collect the soil samples, which is operated by a private contractor under the supervision of an Applied EcoSystems (Æ) professional. All sampling completed by Æ follows standard sampling procedures established in ASTM Method D 1903-97 and U.S. EPA Method 5035. If needed, a decontaminated, steel hand auger is utilized to advance the first five feet of the boring to clear possible utilities. In some cases, a vacuum excavation machine (air knife) is utilized in conjunction with the hand auger.

A) Soil Boring Hole Clearing Procedures

1) Soil Boring Clearing Procedure – Hand Auger

In cases where a hand auger is used to clear a boring, the soil boring clearing procedure involves breaking the surface cover and using a decontaminated hand auger to advance the boring to a depth of one foot below grade. The hand auger is then decontaminated, and is then advanced in the open bore hole deep enough to collect a sufficient volume of soil for screening and sampling purposes (approximately 3 inches). Once the soil sample was collected, the hand auger is used to clear the boring for another one foot of depth, is again decontaminated, and then is used to collect another soil sample. This procedure is repeated to a depth of 5 feet below grade.

2. Soil Boring Clearing Procedure – Air Knife

In cases where an air knife is used to clear a boring, the soil boring clearing procedure involves breaking the surface cover and using the air knife to clear the boring to a depth of one foot below grade. Once the borehole is cleared to one foot below grade, a decontaminated hand auger is used to collect a soil sample. The hand auger is advanced deep enough to collect a sufficient volume of soil for screening and sampling purposes (approximately 3 inches). Once the soil sample is collected, the air knife is used to clear the boring for another one foot of depth and the hand auger is decontaminated, and then used to collect another soil sample. This procedure is repeated to a depth of 5 feet below grade.

B. Soil Boring Sampling Procedure – Tractor Mounted Push Probe

A tractor-mounted hydraulic probe, equipped with a 5-foot long, 2.2” OD steel macro-core and 2-foot long, 1.5” OD steel large bore is used to drill the soil borings below the 5-foot depth. A macro-core (MC) sampler is decontaminated using a non-phosphate detergent followed by a tap water rinse. A new (1¾” OD) acrylic sleeve is then inserted into the macro-core and secured. The macro-core is then driven into the soil to a depth of 5 feet (MC) below the base of the borehole and retrieved. The sample retrieval process is repeated for the next 5-foot interval using a new acrylic sleeve and following decontamination procedures.

After the sleeve is removed from the macro-core, an Æ geologist visually inspects the un-cut, see-through acrylic tube for evidence of saturation and staining. The sleeve is then cut longitudinally and visually inspected for lithology variations and staining/odor. The core is then cut into sampling and screening intervals (usually 1-foot long). One soil sample is collected for methanol preservation, and this sample is labeled and placed in a cooler containing ice. A second sample consisting of a small amount of soil is collected from the same area of the sleeve and placed in a re-sealable plastic bag for headspace readings. This procedure is repeated again for the next core section and continued to the total depth of the boring.

The selection of the soil samples at each core interval is based on olfactory and visual criteria, such as odor and/or staining or lithology differences. If no impact is detected, a soil sample is collected from the deepest unsaturated soil location or from both sides of a lithology interface. Soil samples for VOC analysis are preserved using methanol, as specified under U.S. EPA SW-846 Method 5035 and MDEQ protocol. Furthermore, soil samples are also collected from the same core section, if a lithology change was observed.

Once all the soil samples are collected from each core section of the boring hole, headspace of all the bagged samples are screened for volatile organic compounds (VOCs) utilizing a photoionization detector (PID). The result of this field screening is recorded on bore logs. The unsaturated soil sample indicating the highest PID reading, as well as a soil sample from the bottom of the boring, is submitted for chemical analysis. The remaining methanol preserved samples that were collected and not laboratory analyzed are sent to the selected laboratory for proper disposal. All soil samples are collected in laboratory-provided containers, which are labeled and placed in a cooler containing ice.

C) MONITOR WELL INSTALLATION PROCEDURES

Hollow Stem Auger

Following the collection of the soil samples with the geoprobe, the boreholes are over-drilled using 4¼-inch inside diameter hollow-stem augers for installation of the monitor wells. The monitor wells are constructed of 2-inch Schedule 40 PVC material (larger diameter well would require a different drilling method). The well screens are five feet in length and are constructed from 0.010-inch (No. 10 slot), 2-inch Schedule 40 PVC material or stainless steel.

The well screen and casing are inserted into the hollow stem auger, and the sand filter medium is backfilled as the auger is progressively withdrawn. A layer of hydrated bentonite pellets is placed above the filter medium to about one foot below grade. A locking 2-inch expandable well cover (well cap) is fitted onto the top of each PVC riser. The monitor wells are finished off with an 8-inch flush-mounted steel protective manhole embedded in a concrete surface seal or with an above grade steel guard pipe. After the wells are installed, they are developed by removing water from the wells using a submersible pump with a dedicated length of polyethylene tubing for each well or a disposable bailer. The development water removed is placed into a steel 55-gallon drum that is stored on site, pending waste characterization for disposal at a later date.

Direct Push Well installation

Alternatively, if the geology of the site permits, monitoring wells can be installed using advancing a 3.5-inch steel casing with a disposable bottom plug to the target screen depth. The well casing is then inserted into the casing and the bottom plug is knocked out. The well is then installed in the same manner as described above.

D) MONITOR WELL SURVEYING PROCEDURES

Before conducting groundwater monitoring, newly installed monitor wells are surveyed relative to an on-site benchmark to obtain top-of-casing (TOC) elevations. The benchmark used is a fixed point on the site surface that is assigned an arbitrary elevation of 100.00 feet, unless a known elevation is available. Using a surveyor’s level and graduated rod, vertical measurements are obtained for the benchmark and the TOC for each of the monitor wells and the ground elevation next to the well. Surveying measurements are obtained from the north side of the well casing. The vertical measurements obtained for the well casings are converted to elevations based on the vertical measurement obtained for the benchmark.

APPENDIX E: FIELD AUDIT CHECKLIST

Applied EcoSystems, Inc.
Environmental Management, Consulting & Field Services

Appendix E Field Audit Checklist

Briefing with Project Manager

Signature of Auditor: ______________________ Date of Audit: ____________________

Project Manager: ______________________ Project No: ____________________

Project Location: ____

Type of Investigation: ____

Yes No N/A 1. Was a project plan prepared? If yes, what items are addressed in the plan?

____

____

____

Yes No N/A 2. Were additional instructions given to project participants (i.e., changes in the project plan)? If yes, describe these changes.

____

____

____

Yes No N/A 3. Is there a written list of sampling locations and descriptions? If yes, describe where documents are.

____

____

____

Yes No N/A 4. Is there a map of sampling locations? If yes, where is the map?

____

____

____

Yes No N/A 5. Are the number, frequency, and types of field measurements and observations taken as specified in the project plan or as directed by the project manager? If yes, where are they recorded?

____

____

____

Appendix E Field Audit Checklist

Briefing with Project Manager

Signature of Auditor: __________ Date of Audit: __________

Project Manager: __________ Project No: __________

Project Location: __________

Type of Investigation: __________

Yes No N/A 6. Are samples collected in the types of containers specified for each type of analysis? If no, what kind of sample containers are used?

Yes No N/A 7. Are samples preserved as required? If no or N/A, explain.

Yes No N/A 8. Are the number, frequency, and types of samples collected as specified in the project plan or as directed by the project manager? If no, explain why not.

Yes No N/A 9. Are samples packed for preservation when required (i.e., packed in ice, etc.)? If no or N/A, explain why.

Yes No N/A 10. Is sample custody maintained? How?

Appendix E **Field Audit Checklist**

Briefing with Project Manager

Signature of Auditor: ____________________ Date of Audit: ________________

Project Manager: ____________________ Project No: ________________

Project Location: ____

Type of Investigation: ____

Yes No N/A 11. Are samples identified with sample tags? If no, how are samples identified?

____

____

____

Yes No N/A 12. Are sample tags completed (e.g., station no., location, date, time. analyses, signatures on samples, type, preservatives. etc.)? If yes, describe types of information recorded.

____

____

____

Yes No N/A 13. Are samples collected listed on a chain of custody record? If yes, describe the type of chain of custody record used and what information is recorded.

____

____

____

Yes No N/A 14. If used, are sample tag numbers recorded on chain of custody documents?

____

____

____

Yes No N/A 15. Does information on sample tags and chain of custody records match?

____

____

____

Appendix E Field Audit Checklist

Briefing with Project Manager

Signature of Auditor: ____________________ Date of Audit: ____________________

Project Manager: ____________________ Project No: ____________________

Project Location: ____

Type of Investigation: ____

Yes No N/A 16. Does the chain of custody record indicate the method of sample shipment?

Yes No N/A 17. Is the chain of custody record included with the samples in the shipping container?

Yes No N/A 18. If used, do the sample traffic reports agree with the sample tags?

Yes No N/A 19. If used, are blank samples identified?

Yes No N/A 20. If collected, are duplicate samples identified on sample tags and chain of custody records?

Appendix E Field Audit Checklist

Briefing with Project Manager

Signature of Auditor: ______________ Date of Audit: ______________

Project Manager: ______________ Project No: ______________

Project Location: ______________

Type of Investigation: ______________

Yes No N/A 21. If used, are spiked samples identified?

Yes No N/A 22. Were Sampling forms filled out property and completely? If no, what were this issues?

Yes No N/A 23. Are photographs documented in logbooks (e.g., time, date, description of subject, photographe,r etc.)?

Yes No N/A 24. If film from a self-developing camera is used, are photos matched with logbook documentation?

Yes No N/A 25. Are sample tag numbers recorded? If yes, describe where they are recorded.

Field Audit Checklist

Briefing with Project Manager

Signature of Auditor: ______________________ Date of Audit: ____________________

Project Manager: ______________________ Project No: ____________________

Project Location: ____

Type of Investigation: ____

Yes No N/A 26. Are calibration of pH meters, conductivity meters, etc., documented? If yes, describe where this is documented.

Yes No N/A 27. Are amendments to the project plan documented? If yes, describe where the amendments are documented.

Yes No N/A 28. Was a debriefing held with project manager and/or other participants?

Yes No N/A 29. Were any recommendations made to the project participants during the debriefing? If yes, list recommendations.

APPENDIX F: LABORATORY AUDIT CHECKLIST

Applied EcoSystems, Inc.
Environmental Management, Consulting & Field Services

Relevant Aspect of Standards	Y	N	N/A	Comments
PT Studies				
Are all PT samples are handled (i.e., managed, analyzed, and reported) in the same manner as real environmental samples utilizing the same staff, methods as used for routine analysis of that analyte, procedures, equipment, facilities, and frequency of analysis?				
Satisfactorily analyze at least one proficiency test sample per analyte per year for every accredited Potable Water Method?				
Perform proficiency testing two times per year per analyte per matrix per program from a NELAC approved provider?				
Personnel				
Has managerial staff with the authority and resources needed to discharge their duties?				
Have processes to ensure its personnel are free from any commercial, financial and other undue pressures, which might adversely affect the quality of the work?				
Organized in such a way that confidence in its independence of judgment and integrity is maintained at all times?				
Specify and document the responsibility, authority, and interrelation of all personnel who manage, perform or verify work affecting the quality of calibrations and tests in job descriptions for all positions.				
Does the documentation clearly described the lines of responsibility in the laboratory and shall be proportioned such that adequate supervision is maintained?				
Is supervision provided by persons familiar with the calibration or test methods and procedures, and the objective of the calibration or test and the assessment of the results.				
Does the Technical Director document the certification of the personnel performing all tests for which the laboratory is accredited have the appropriate educational and/or technical backgrounds?				
Do the technical director have overall responsibility for the technical operation of the environmental testing laboratory?				
Quality assurance officer: ___ensure that the quality system is implemented and followed at all times? ___have direct access to the highest level of management at which decisions are taken on laboratory policy or resources, and to the technical director? ___serve as the focal point for QA/QC?				

Relevant Aspect of Standards	Y	N	N/A	Comments
___responsible for the oversight and/or review of quality control data? ___functions independent from laboratory operations where QA oversight is provided? ___evaluate data objectively and perform assessments without outside (e.g., managerial) influence? ___have documented training and/or experience in QA/QC procedures? ___have a general knowledge of the analytical methods for which data review is performed?				
Are deputies nominated in the case of absence of the technical director or QA officer?				
Are records maintained to indicate that it has sufficient personnel, having the necessary education, training, technical knowledge and experience for their assigned functions?				
Are personnel responsible for complying with all quality assurance/quality control requirements that pertain to their organizational/technical function?				
Does each technical staff member have a combination of experience and education to adequately demonstrate: __a specific knowledge of their particular function; and __a general knowledge of laboratory operations, analytical methods, QA/QC procedures and records management?				
Does management ensure that staff who are undergoing training are provided with appropriate supervision?				
Does management formulate goals with respect to the education, training and skills for laboratory personnel?				
Have a policy and procedures for identifying training needs and providing training of personnel?				
Are current job descriptions maintained for all personnel who manage, perform, or verify work affecting the quality of testing?				
Does management authorize specific personnel to: __perform particular types of sampling, __environmental test and/or calibration, __issue reports, __give opinions and interpretations, __operate particular types of equipment?				
Maintain records, with dates, of the relevant authorization(s), competence, educational and professional qualifications, training, skills, and experience for all technical and contracted personnel?				
Is there a defined minimum level of qualification, experience, and skills necessary for all positions in the lab?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Does the management maintain records to assure that all technical staff have demonstrated and documented initial and ongoing proficiency in the activities for which they are responsible?				
Does management ensure that training records kept up-to-date for all technical staff that include: ___Evidence that the employee has read, understands, and is using the latest version of the lab's in-house quality documentation, which relates to his/her job responsibilities; ___Training courses or workshops on specific equipment, analytical techniques, or lab procedures; ___Annual training course in data integrity procedures including the potential punishments & penalties for violations. ___Annual signature for each employee demonstrating they have read; acknowledge, and understand their personal & legal data integrity responsibilities including potential punishments & penalties for violations; and ___Documentation certifying that the employee has read, understands, and agrees to use the latest version of a test method used; and				
Does management ensure that the training records of each of the technical staff is updated by including documentation of continuing proficiency by at least one of the following: ___ cceptable performance of a blind sample; ___Another demonstration of capability; ___Successful analysis of a blind performance sample on a similar test method using the same technology; ___Analysis of at least 4 consecutive lab control samples with acceptable levels of precision and accuracy; or ___If one of the above can not be performed, the analysis of authentic samples that have been analyzed by another trained analyst with statistically indistinguishable results.				
Does the management assure supervision of all personnel employed by the laboratory?				
Does the management assure all sample acceptance criteria are verified and that samples are logged into the sample tracking system and properly labeled and stored?				
Does the management ensure the quality of all data reported by the laboratory?				
Does data integrity training include; ___Topics covered shall be documented in writing and provided to all trainees, ___organizational mission and its relationship to the critical need for honesty and full disclosure in all analytical reporting ___how and when to report data integrity issues,				

Relevant Aspect of Standards	Y	N	N/A	Comments
___record keeping ___employees are required to understand that any infractions of lab data integrity procedures will result in a detailed investigation that could lead to very serious consequences including immediate termination, or civil/criminal prosecution, ___specific examples of breaches of ethical behavior ___Discussion regarding all data integrity procedures, documentation, in-depth data monitoring. ___requirement for emphasis on the importance or proper written narration on the part of the analyst with respect the those cases where analytical data may be useful, but are in some way partially deficient?				
Quality System				
Establish and maintain a documented quality system appropriate to the type, range and volume of environmental testing activities it undertakes?				
Is the quality documentation available to, understood by, and implemented by all laboratory personnel?				
Is the laboratory's quality system policies and objectives defined in a quality manual?				
Does the quality manual and related quality documentation: ___state the laboratory's policies and procedures established in order to meet the requirements of Clients and certifications? ___include or make reference to the supporting procedures including technical procedures? ___outline the structure of the documentation used in the quality system? ___include the organization and management structure of the laboratory, its place in any parent organization, and relevant organizational charts? ___include procedures to ensure that all records are retained**?** ___include the relationship between management, technical operations, support services and the quality system? ___include job descriptions of key staff and reference to the job descriptions of other staff? ___include a quality policy statement with at least the following: ___Laboratory management's commitment to good professional practice and to the quality of its environmental testing in servicing its clients; ___management's statement of the laboratory's standard of service; ___objectives of the quality system? ___a requirement that all personnel familiarize themselves with the quality documentation and implement the policies and procedures in their work; ___The laboratory management's commitment to compliance with this standard.				

Relevant Aspect of Standards	Y	N	N/A	Comments
___ include procedures for control and maintenance of documentation through a document control system which ensures that all standard operating procedures, manuals, or documents clearly indicate the time period during which the procedure or document was in force? ___include procedures for achieving traceability of measurements? ___include a list of all methods under which the laboratory performs its accredited testing? ___include mechanisms for ensuring that the laboratory reviews all new work to ensure that it has the appropriate facilities and resources before commencing such work? ___include reference to the calibration and/or verification test procedures used? ___include procedures for handling submitted samples? ___include reference to the major equipment and reference measurement standards used as well as the facilities and services used by the laboratory in conducting tests? ___include reference to procedures for calibration, verification and maintenance of equipment? ___include reference to verification practices including inter-laboratory comparisons, proficiency testing programs, use of reference materials, and internal quality control schemes? ___include procedures to be followed for feedback and corrective action for failed quality control samples, or when departures from documented policies, procedures, or NELAC standards occur? ___management arrangements for exceptionally permitting departures from standard operating procedures, policies or standard specifications? ___include procedures for the resolution of complaints received from clients or other parties about the laboratory's activities? ___include processes/procedures for establishing that personnel are adequately experienced in the duties they are expected to carry out and/or receive any needed training? ___include procedures for audits and data review? ___define in detail the data integrity procedures, including training and documentation ___include reference to procedures for reporting analytical results? ___include a Table of Contents, and applicable lists of references and glossaries, and appendices?				
Have documented policies and procedures to ensure the protection of clients' confidential information and proprietary rights?				
Does management provide a mechanism for confidential reporting of data integrity issues within the lab?				
In instances of ethical concern, does the mechanism include a process whereby laboratory management are to be informed of any further detailed investigation?				
Document Control				

Relevant Aspect of Standards	Y	N	N/A	Comments
Establish and maintain procedures to control <u>all</u> documents that form part of its quality system, whether internally generated or from external sources?				
Are all documents issued to personnel in the laboratory as part of the quality system reviewed and approved for use by authorized personnel prior to issue?				
Have a master list or equivalent document control procedure which identifies the current version status and distribution of documents?				
Does the document control procedure ensure that; ___authorized editions of appropriate documents are available at all locations where operations essential to the effective functioning of the lab are performed, ___documents are periodically reviewed and, where necessary, revised to ensure continuing suitability and compliance with appropriate requirements, ___invalid or obsolete documents are promptly removed from all points of issue or use, or otherwise assured against unintended use, ___obsolete documents retained for either legal or knowledge preservation purposes are suitability marked?				
Are quality system documents generated by the laboratory uniquely identified by including: ___date of issue and/or revision identification, ___page numbering, ___the total number of pages or mark to signify the end of the document, ___issuing authority(ies)?				
Do the designated personnel have access to pertinent background information upon which to base their review and approval?				
Where practicable, is the altered or new text identified in the document or the appropriate attachments?				
Are procedures established to describe how changes in documents maintained in computerized systems are made and controlled?				
Client Contracts				
Establish and maintain procedures for review of requests, tenders and contracts?				
Do the policies and procedures for reviews leading to a contract for environmental testing ensure that; ___the requirements, including the methods to be used, are adequately defined, documented and understood; ___the laboratory has the capability and resources to meet the requirements;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___the appropriate environmental test method is selected and capable of meeting clients requirements?				
Inform the client if it indicates any potential conflict, deficiency, lack of appropriate accreditation status, or inability on the laboratory's part to complete the clients work?				
Maintain records of reviews, including any significant changes?				
Maintain records 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?				
Does the review cover any work that is subcontracted by the laboratory?				
Is the client informed of any deviation from the contract?				
If a contract needs to be amended after work has commenced, is the same contract review process repeated and any amendments communicated to all affected personnel?				
Does the laboratory report any suspension of accreditation, revocation or accreditation, or voluntary withdrawal of accreditation to the client?				
Does the lab afford clients or their representatives cooperation to clarify the client's request and to monitor the lab's performance in relation to the work performed, provided that the lab ensures confidentiality to other clients? (i.e. External Audits)				
Subcontracting				
Have records to indicate that it advise the client in writing of its intention to sub-contract any portion of the testing to another party?				
Where a laboratory sub-contracts any part of the testing covered under NELAP, do records indicate that this work is placed with a laboratory accredited under NELAP for the tests to be performed or with a laboratory that meets applicable statutory and regulatory requirements for performing the tests and submitting results of tests performed?				
Is non-NELAC work performed by a subcontracted laboratory clearly identified in the laboratory report?				
Accept responsibility for subcontractor's work, except in the case where the client or a regulatory authority specifies which subcontractor to be used?				
Maintain a register of all subcontractors that it uses for environmental tests and a record of the evidence (certificates of approval)?				
Purchasing				
Do documented policies and procedures exist for the selection and purchasing of services and supplies used that effect the quality of environmental testing operations of the laboratory?				
Do documented procedures exist for the purchase, reception and storage of consumable materials used				

Relevant Aspect of Standards	Y	N	N/A	Comments
for the technical operations of the laboratory?				
Ensure that purchased equipment and consumable materials are not used until they have been inspected, calibrated or otherwise verified as complying with any standard specifications relevant to the calibrations or tests concerned?				
Do the services and supplies used comply with specified requirements?				
Are records of actions taken to check compliance maintained?				
Are purchasing documents, containing data describing the services and supplies ordered, reviewed and approved for technical content prior to release?				
Evaluate suppliers of critical consumables, supplies and services which affect the quality of environmental testing?				
Maintain records of evaluations of all suppliers from whom it obtains support services or supplies required for tests and list those approved?				
Complaints				
Are records of the complaints and subsequent actions maintained?				
Non-conforming Work				
Have a policy and procedures that are implemented when any aspect of it's environmental testing work, or the result of this work, do not conform to its own procedures or agreed requirements of the client?				
Do the policy and procedures ensure that: ___the responsibilities and authorities for the management of nonconforming work are designated and actions are defined and taken when nonconforming work is identified; ___an evaluation of the nonconforming work is made; ___corrective actions are taken immediately, together with any decision about the acceptability of nonconforming work; ___where necessary, the client is notified and work is recalled; ___the responsibility for authorizing the resumption of work is defined.				
Implement corrective action procedures when the evaluation indicates that the nonconforming work could recur or that there is doubt about the compliance of the laboratory's operations with its own policies and procedures?				
Corrective Actions				
Established a corrective action policy and procedure?				
Designate appropriate authorities for implementing corrective action when nonconforming work or				

Relevant Aspect of Standards	Y	N	N/A	Comments
departures from policies & procedures in the quality system or technical operations have been identified?				
Does the corrective action procedure start with an investigation of root cause(s) of the problem?				
Identify potential corrective actions and select and implement the action(s) most likely to eliminate the problem and to prevent recurrence?				
Are corrective actions appropriate in degree to the magnitude and risk of the problem?				
Document and implement any required changes resulting from corrective action investigations?				
Monitor the results to ensure that the corrective actions taken have been effective?				
Ensure that appropriate areas of activity, identified or doubted as nonconforming or departure from policies and procedures, are promptly audited?				
Implement general procedures to be followed when there are departures from documented policies, procedures, and QC have occurred?				
Do the procedures to be followed when there is a departure from documented policies, procedures, and QC include but not limited to: ___Identify the individuals responsible for assessing each QC data type; ___Identify the individuals responsible for initiating and/or recommending corrective actions; ___Define how the analyst should treat the data set if the associated QC measurements are unacceptable; ___Specify how out-of-control situations and subsequent corrective actions are to be documented; and ___Specify procedures for management (including the QA officer) to review corrective action reports.				
If a QC measure is out of control and the data is to be reported, are data qualifiers reported with samples associated with failed QC measures?				
To the extent possible, are samples reported only if all quality control measures are acceptable?				
Preventive Action				
Have a pro-active process to identify opportunities for improvement?				
Are needed improvements and potential sources of non-conformances, either technical or concerning the quality system, identified?				
Develop, implement and monitor action plans where preventive action is required?				
Do procedures for preventive action include the initiation of such actions and application of controls to ensure that they are effective?				
Records				
Maintain a record system to suit its particular circumstances and comply with any applicable regulations?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Establish and maintain procedures for identification, collection, indexing, access, filing, storage, maintenance and disposal of quality and technical records?				
Do quality records include reports from internal audits and management reviews as well as records of corrective and preventive actions?				
Does the system produce unequivocal, accurate records, which document all laboratory activities?				
Retain on record all original observations, calculations and derived data, calibration records and a copy of the test report for a minimum of five years?				
Are all records legible?				
Does the record keeping system allow historical reconstruction of all laboratory activities that produced the resultant sample analytical data?				
Have a written SOP for how the laboratory will carry out legal chain of custody if the client specifies that a sample will be used for evidentiary purposes?				
Have procedures to prevent unauthorized access to or amendment of records stored electronically?				
Is the history of the sample readily understood through the documentation including inter-laboratory transfers of samples and/or extracts?				
Do the records include the identity of personnel involved in sampling, preparation, calibration or testing?				
Is all information relating to the laboratory facilities, equipment, analytical methods, and related laboratory activities, such as sample receipt, sample preparation, or data verification documented?				
Does the record keeping system facilitate the retrieval of all working files and archived records for inspection and verification purposes?				
Are all generated data, except those that are generated by automated data collection systems, recorded directly, promptly and legibly in permanent ink?				
Are entries to electronically maintained records changed so as to not erase or overwrite the files?				
Is the individual making the change to electronically maintained records identified?				
Do the records for each environmental test contain sufficient information to facilitate, if possible, identification of factors affecting the uncertainty and to enable the test to be repeated under conditions as close as possible to the original?				
Are entries in records not obliterated by methods such as erasures, overwritten files or markings?				
Are all corrections to record-keeping errors made by one line marked through the error and the individual making the correction signing (or initialing) and dating the correction?				
Are all records, certificates and reports held secure and in confidence to the client?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Are observations, data and calculations recorded at the time they are made?				
Are observations, data and calculations identifiable to the specific task?				
In the case of records stored electronically, are equivalent measures taken to avoid loss or change of original data?				
Are all records (including the hardware and software necessary for the historical reconstruction of electronic data) that are pertinent to a specified project retained for a minimum of five years from last entry unless otherwise designated for a longer period of time in another regulation?				
Do records that are stored or generated by computers have hard copy or write-protected backup copies?				
Have a record management system for control of laboratory notebooks; instrument logbooks; standards logbooks; and records for data reduction, validation storage and reporting?				
Is access to archived information documented with an access log?				
Is archived information protected against fire, theft, loss, environmental deterioration, and vermin and, in the case of electronic records, electronic or magnetic sources?				
Have a plan to ensure that the records are maintained or transferred according to the clients' instructions in the event that a laboratory transfers ownership or goes out of business?				
Retain records of the following procedures to which a sample is subjected while it is in the lab's possession: ___Sample preservation, appropriateness of containers, & compliance with holding time requirements ___Sample identification, receipt, acceptance or rejection, & log-in ___Sample storage & tracking including shipping receipts, transmittal forms, & assignments ___Documented procedures for receipt, retention, or safe disposal of test items that includes all provisions necessary to protect the integrity of the laboratory				
Retain : ___All original raw data, whether hard copy or electronic, for calibrations, sample analyses, & quality control measures ___A written description or reference to the specific test method used ___Copies of final reports ___Archived standard operating procedures ___Correspondence relating to its activities for a specific project ___All corrective action reports, audits, & audit response ___Proficiency test results & raw data ___Records of data review & cross checking.				

Relevant Aspect of Standards	Y	N	N/A	Comments
Do strip charts, tabular printouts, computer data files, analytical notebooks, and run logs include: ___Laboratory sample ID code ___Date of analysis and time of analysis ___Instrumentation identification and instrument operating conditions/parameters (or reference) ___Analysis type (method or technique) ___All calculations (automated and manual) ___Analyst's or operator's initials/signature ___Sample preparation including cleanup & separation protocols, ID codes, volumes, weights, instrument printouts, meter readings, calculations, & reagents used ___Sample analysis ___Standard & reagent origin, receipt, preparation, & use ___Calibration criteria, frequency, & acceptance criteria ___Data & statistical calculations, review, confirmation, interpretation, assessment, & reporting conventions ___Quality control protocols & assessment ___Electronic data security, Software documentation & , Software & hardware audits, Backups of automated data entries, Records of any changes to automated data entries ___Method performance criteria including expected quality control requirements				
Are the following administrative records maintained? ___Personnel qualifications, experience and training records ___Initial and continuing demonstration of proficiency for each analyst ___a log of names, initials and signatures for all individuals who are responsible for signing or initialing any laboratory record				
Managerial Reviews				
Have a procedure for the annual management review of the quality system and does it maintain records of review findings and actions?				
Is an annual review of the quality system completed by management to evaluate its continuing suitability and effectiveness and make any necessary changes or improvements?				
Does the annual review take into account: ___the suitability of policies and procedures; ___reports from managerial and supervisorial personnel; ___the outcome of recent internal audits; ___corrective and preventive actions;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___assessment by external bodies ; ___the results of interlaboratory comparisons or proficiency tests; ___any changes in the volume and type of work undertaken; ___feedback from clients; ___complaints; ___other relevant factors, such as quality control activities, resources and staff training?				
Data Integrity				
Are reviews conducted with respect to any evidence of inappropriate actions or vulnerabilities related to data integrity?				
Are discovery of potential issues handled in a confidential manner until such time as a follow-up evaluation, full investigation, or other appropriate actions have been completed and the issues clarified?				
Are all investigations that result in findings of inappropriate activity documented including any disciplinary actions involved, corrective actions taken, and all appropriate notifications of clients?				
Is documentation of data integrity investigations and actions taken maintained for five years?				
Are the data integrity procedures signed and dated by senior management?				
Are these procedures and the associated implementation records properly maintained and made available for assessor review?				
Are the data integrity procedures annually reviewed and updated by management?				
Do senior managers acknowledge their support of these procedures by: ___Upholding the spirit and intent of the organizations data integrity procedures, and; ___Effectively implementing the specific requirements of the procedures?				
Facilities				
Are tests stopped when the environmental conditions jeopardize the results?				
Are measures taken to prevent cross contamination?				
Are adequate measures taken to ensure good housekeeping and to ensure that any contamination does not adversely affect data quality?				
Test Methods, SOPs and Method Validation				
Use appropriate methods and procedures for all test methods and laboratory activities within its scope?				
Document instructions ___On the use and operation of all relevant equipment, ___On the handling and preparation of samples, where the absence of such instructions could jeopardize				

Relevant Aspect of Standards	Y	N	N/A	Comments
the calibrations or tests?				
Are all instructions, standards, manuals and reference data relevant to the work of the laboratory maintained up-to-date and readily available to the staff?				
Do deviations from test methods occur only if the deviation has been documented, technically justified, authorized, and accepted by the client?				
Maintain SOPs for all test methods and laboratory activities?				
Are copies of SOPs organized and assessable to all personnel?				
Does each SOP clearly indicate: ___Effective date of the SOP ___Revision number ___Signature(s) of approving authority				
Have an in-house method manual for each accredited analyte or test method that clearly describes the lab's method?				
In cases where modifications are made to published methods or where the reference test method is ambiguous or provides insufficient detail, are any modifications, changes, or clarifications clearly described?				
Each test method includes or references the following where applicable: ___Identification of the test method ___Applicable matrix or matrices ___Detection limit ___Scope and application ___Summary of the test method ___Definitions ___Interferences ___Safety ___Equipment and supplies ___Reagents and standards; ___Sample collection, preservation, shipment and storage; ___Quality control; ___Calibration and standardization; ___Procedure; ___Calculations; ___Method performance;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Pollution prevention; ___Data assessment and acceptance criteria for quality control measures; ___Corrective actions for out-of-control data; ___Contingencies for handling out-of-control or unacceptable data; ___Waste management; ___References; and ___Any tables, diagrams, flowcharts and validation data				
Use appropriate test methods and procedures, which meet the needs of the client, for all tests and related activities within its responsibility (including sample collection, handling, transport, storage, preparation, and analysis)?				
Ensure that it uses the latest valid edition of a standard source of methods?				
Use only the test method specified when the test method is mandated or requested?				
Inform the client when the method proposed by them is considered to be inappropriate or out of date?				
Is there a record of a satisfactory initial demonstration of method capability performed prior to the institution of any test method? (Not required for a test method that was in use by the lab prior to 7/99 and where there has been no significant changes)				
Have records on file to demonstrate that an initial demonstration of capability is not required for unchanged methods in use prior to 7/99?				
Complete a new demonstration of capability whenever there is a significant change in instrument type, personnel, or test method?				
Is the introduction of laboratory-developed methods a planned activity assigned to qualified personnel equipped with adequate resources?				
Are plans for laboratory developed methods updated as development proceeds and effective communication amongst all personnel involved ensured?				
When it is necessary to use non-standard methods, is their use subject to agreement with the client, including clear specification of client requirements and the purpose of the testing?				
Are all non-standard methods, laboratory-designed/developed methods, standard methods used outside their intended scope, and amplifications and modifications of standard methods validated to confirm they fit their intended use?				
Record the results of validations, the procedure used, and a statement as to whether the method is fit for the intended use?				
Is the range and accuracy of the values obtainable from validated methods, within the intended use,				

Relevant Aspect of Standards	Y	N	N/A	Comments
relevant to the clients needs?				
Have and implement a procedure to estimate the uncertainty of measurement?				
In cases where it is not possible to calculate the uncertainty of measurement in a rigorous metrological and statistically significant way, does the laboratory, at least, attempt to identify all the components of uncertainty and make a reasonable estimation? (reasonable means it is based on knowledge of the performance of the method , measurement scope, previous experience and validation data)				
Ensure that the form of reporting does not give a wrong impression of the uncertainty of measurement?				
Are all important uncertainty components taken into account using appropriate methods of analysis?				
Establish Standard Operating Procedures to ensure that the reported data is free from transcription and calculation errors?				
Establish Standard Operating Procedures to ensure that all quality control measures are reviewed, and evaluated before data is reported?				
Are calculations and data transfers subject to checks as established in the laboratory's SOP?				
Establish Standard Operating Procedures addressing manual calculations including manual integrations?				
Ensure that all requirements of the Chapter 5 are complied with where computers or automated equipment are used for the capture, processing, manipulation, recording, reporting, storage or retrieval of test data?				
When computers, automated equipment, or microprocessors are used for the acquisition, processing, recording, reporting, storage or retrieval of test or calibration data, does the laboratory ensure that computer software developed by the user is documented in sufficient detail and is suitably validated as being adequate for use?				
Are procedures established for protecting the integrity of data?				
Are procedures implemented for protecting the integrity of data?				
Do the procedures include, but are not be limited to: ___Integrity of data entry or capture ___Data storage ___Data transmission ___Data processing?				
Are computer and automated equipment maintained to ensure proper functioning and provided with the environmental and operating conditions necessary to maintain the integrity of calibration and test data?				
Establish and implement appropriate procedures for the maintenance of security of data including the				

Relevant Aspect of Standards	Y	N	N/A	Comments
prevention of unauthorized access to, and the unauthorized amendment of, computer records? (ex. Are access codes used?)				
Implement appropriate procedures for the maintenance of security of data including the prevention of unauthorized access to, and the unauthorized amendment of, computer records?				
Equipment and Reference Materials				
Furnish all items of equipment (including reference materials) required for the correct performance of tests for which accreditation is sought?				
Is equipment outside the permanent control of the laboratory handled so as to ensure the requirements of the NELAC standard are met?				
Is the equipment and the software used for testing, calibration and sampling capable of achieving the accuracy required and does it comply with specifications relevant to the tests concerned?				
Are calibration programs established for key quantities or values of the instruments where these properties have a significant effect of the results?				
Before being placed into service, is equipment (including that used for sampling) calibrated or checked to establish that it meets the laboratory's specification requirements and complies with the relevant standard specifications?				
Is all support equipment maintained in proper working order and records of all activities including service calls kept?				
Is all support equipment calibrated annually, using NIST traceable references when available, over the entire range in which the equipment is used?				
Are the results of support equipment calibration within the specifications required of the application for which it is used?				
Is support equipment that is not within the specifications required of the application: ___Removed from service until repaired				
Maintains records of established correction factors to correct measurements?				
Are all raw data records retained to document equipment performance?				
Prior to use on each working day, are balances, ovens, refrigerators, freezers, incubators and water baths checked with NIST traceable references (where available) in the expected use range?				
Is the acceptability for use continued use according to the needs of the analysis or application for which it is used?				
Are mechanical volumetric devices, including burettes, checked for accuracy on a quarterly basis?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Do glass microliter syringes come with a certificate attesting to established accuracy or is the accuracy initially demonstrated and documented by the laboratory?				
Is the temperature, cycle time, and pressure of each autoclave run for chemical tests documented by use of appropriate chemical indicators or temperature recorders and pressure gauges?				
Is equipment operated by authorized personnel?				
Is all equipment properly maintained, inspected and cleaned?				
Are maintenance procedures documented?				
Have procedures for safe handling, transport, storage, use and planned maintenance of measuring equipment to ensure proper functioning and to prevent contamination or deterioration?				
Is any item of the equipment which has been subjected to overloading or mishandling, or which gives suspect results, or has been shown by verification or otherwise to be defective, taken out of service, clearly identified and wherever possible stored at a specified place until it has been repaired and shown by calibration, verification or test to perform satisfactorily?				
Examine the effect of this defect or departure from specified limits on previous tests and/or calibrations and institute the "Control of Nonconforming Work" procedure?				
Are all items of equipment including reference materials labeled, marked or otherwise identified to indicate its calibration status, including the date when last calibrated and the date or expiration criteria when recalibration is due?				
Do records of major equipment and reference materials include the following: ___The name of the item of equipment ___The manufacturer's name, type identification, and serial number or other unique identification ___Checks that equipment comply with the specification ___Current location, where appropriate ___Copy of the manufacturer's instructions, where available ___Dates and results of calibrations & verifications and date of the next calibration and/or verification ___Details of maintenance carried out to date and planned for the future ___History of any damage, malfunction, modification or repair ___Date received and date placed in service ___Condition when received (e.g. new, used, reconditioned)				
If for any reason, equipment goes outside the direct control of the laboratory, does the laboratory ensure that the function and calibration status of the equipment is checked and shown to be satisfactory before equipment is returned to service?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Have procedures to ensure that copies of new correction factors are correctly applied/updated (e.g. in computer software)?				
Is test and calibration equipment, including both hardware and software, safeguarded from adjustments which would invalidate the test and/or calibration results?				
Measurement Traceability and Calibration				
Are all measuring operations and testing equipment having an effect on the accuracy or validity of tests calibrated and/or verified before being put into service and on a continuing basis?				
Have an established program for the calibration and verification of its measuring and test equipment including balances, thermometers and control standards?				
Ensure that the equipment used can provide the uncertainty of measurement needed (that contributes little to the total uncertainty of the test result)?				
Are measurements made by the lab traceable to national standards of measurement, where available?				
Provide satisfactory evidence of correlation of results in those cases where traceability to national standards of measurement is not applicable? (For example, participation in a suitable program of inter-laboratory comparisons, proficiency testing, or independent analysis.)				
Are reference standards of measurement held by the laboratory (such as Class S or equivalent weights or traceable thermometers) used for calibration only and for no other purpose, unless it is demonstrated that their performance as reference standards has not been invalidated?				
Are reference standards of measurement calibrated by a body that can provide, where possible, traceability to national or international standard reference materials?				
Is there a program of calibration and verification for reference standards?				
Are internal reference materials checked as far as technically and economically possible?				
Have defined procedures and schedules for carrying out checks of the calibration status of reference, primary, transfer or working standards and reference materials?				
Have procedures for safe handling, transport, storage, and use of reference standards and reference materials in order to protect their integrity, and prevent contamination and/or deterioration?				
Do documented procedures exist for the purchase, reception and storage of consumable materials used for the technical operations of the laboratory?				
Retain records for all standards, reagents, reference materials and media, including manufacturer/vendor, the manufacturers Certificate of Analysis or purity (if supplied), date of receipt, recommended storage conditions, and an expiration date after which the material shall not be used				

Relevant Aspect of Standards	Y	N	N/A	Comments
unless verified by the laboratory?				
Are original reagent containers labeled with the expiration date?				
Are detailed records maintained on standard and reference material preparation?				
Do the records of standard and reference material preparation indicate traceability to purchased stocks or neat compounds, reference to method of preparation, date of preparation, expiration date, and preparer's initials?				
Do all containers of prepared standards and reference materials bear a unique identifier and expiration date and can it be linked to the documentation of its preparation?				
Are procedures in place to ensure prepared reagents meet the requirements of the test method?				
Do all containers of prepared reagents bear an expiration date or is it documented elsewhere as indicated in the laboratory's quality manual or SOP?				
Sampling				
Does the sampling process address the factors to be controlled to ensure the validity of the test results?				
When sampling (as in obtaining sample aliquots from a submitted sample) is carried out as part of the test method, does the laboratory use documented procedures and appropriate techniques to obtain representative sub-samples?				
Are client required deviations, additions, or exclusions from the documented sampling procedure recorded in detail with the appropriate sampling data and included in all documents containing test results and communicated to appropriate personnel?				
Have procedures for recording relevant data and operations relating to sampling?				
Do sampling records include; ___the sampling procedure used, ___the identification of the sampler, ___environmental conditions (if relevant), ___diagrams or other equivalent means to identify the sampling location, ___if appropriate, the statistics the sampling procedure is based on?				
Sample Handling				
Have procedures for the transportation, receipt, handling, protection, storage, retention and/or disposal of samples, including provisions necessary to protect the integrity of the sample, and to protect the interests of the laboratory and the client?				
Have a documented system for uniquely identifying the items to be tested, to ensure that there can be no				

Relevant Aspect of Standards	Y	N	N/A	Comments
confusion regarding the identity of such items at any time?				
Does the system include identification for all samples, sub-samples and subsequent extracts and/or digestates?				
Assign a unique identification (ID) code to each sample container received in the laboratory?				
Does the sample code maintain an unequivocal link with the unique field ID code assigned each container?				
Is the laboratory ID code placed on the sample container as a durable label?				
Is the laboratory ID code entered into the laboratory records and does the link that associate the sample with related laboratory activities such as sample preparation or calibration?				
Have a written sample acceptance policy that clearly outlines the circumstances under which samples will be accepted or rejected?				
Is data from any sample which does not meet the policy criteria flagged in an unambiguous manner clearly defining the nature and substance of the variation?				
Is the sample acceptance policy made available to sample collecting personnel?				
Does the sample acceptance policy criteria include the following at a minimum? ___Proper, full, and complete documentation, which includes: ___sample identification, ___the location ___date and time of collection, ___collector's name, ___preservation type, ___sample type ___any special remarks concerning the sample. ___Proper sample labeling to include: ___unique identification ___a labeling system for the samples with requirements concerning the durability of the labels (water resistant) and the use of indelible ink. ___Use of appropriate sample containers. ___Adherence to specified holding times. ___Adequate sample volume to perform the necessary tests. ___Procedures to be used when samples show signs of damage or contamination.				
Upon receipt, is the condition of the sample recorded, including any abnormalities or departures from				

Relevant Aspect of Standards	Y	N	N/A	Comments
standard condition as prescribed in the relevant test method?				
Are all items specified in sample acceptance policy criteria checked?				
Are all samples, which require thermal preservation, considered acceptable if the arrival temperature is either within +/-2°C of the required temperature or in the method specified range?				
For samples with a specified temperature of 4 C, are samples maintained within a temperature of just above freezing to 6°C?				
In cases where samples are hand delivered to the laboratory immediately after collection and do not meet the temperature criteria considered acceptable, is there evidence that the chilling process has begun such as arrival on ice?				
Implement procedures for checking chemical preservation using readily available techniques, such as pH or temperature, prior to or during sample preparation or analysis?				
Are the results of all checks recorded?				
Where there is any doubt as to the item's suitability for testing, where the sample does not conform to the description provided, or where the test required is not fully specified, does the laboratory: ___consult with the client for further instruction before proceeding; and, ___establish whether the sample has received all necessary preparation, or whether the client requires preparation to be undertaken or arranged by the laboratory?				
If the sample does not meet the sample receipt acceptance criteria does the laboratory do any of the following: ___Retain correspondence and/or records of conversations concerning the final disposition of rejected ___Fully document any decision to proceed with the analysis of samples not meeting acceptance criteria ___Is the condition of these samples, at a minimum, noted on the chain of custody or transmittal form and laboratory receipt documents? ___Is the analysis data of these samples appropriately "qualified" on the final report?				
Utilize a permanent, sequential log, such as a logbook or electronic record, to document receipt of all sample containers?				
Is the following information recorded in the laboratory chronological log? ___Client/Project Name ___Date and time of laboratory receipt of sample ___Unique laboratory ID code ___Signature or initials of the person making the entries				
Is the following information unequivocally linked to the log in records, included as a part of the log, or if				

Relevant Aspect of Standards	Y	N	N/A	Comments
recorded/documented elsewhere is it a part of the laboratory's permanent records, easily retrievable upon request and readily available to individuals who will process the sample? ___Field ID code linked to laboratory ID code in the sample receipt log. ___Date and time of sample collection linked to the sample container and to the date and time received in the laboratory. ___Requested analyses (including applicable test method numbers) linked to the laboratory ID code. ___Any comments resulting from inspection for sample rejection linked to the laboratory ID code.				
Retain all documentation, such as memos or transmittal forms that are transmitted to the laboratory by the sample transmitter retained?				
Is a complete chain of custody record, if utilized, maintained?				
Have documented procedures to avoid deterioration or damage to the sample during storage, handling, preparation, and testing				
Follow any relevant instructions from the client in regards to the storage of a sample?				
Where items have to be stored or conditioned under specific environmental conditions, are these conditions maintained, monitored and recorded?				
Are samples stored according to the conditions specified by preservation protocols?				
Are samples stored away from all standards, reagents, food and other potentially contaminating sources in such a manner as to prevent cross contamination?				
Are samples, sample fractions, extracts, leachates or other sample preparation fractions stored according to the conditions specified by preservation protocols or according to the test method?				
Where a sample or portion of the sample is to be held secure (for example, for reasons of record, safety or value, or to enable check calibrations or tests to be performed later), does the laboratory have storage and security arrangements that protect the condition and integrity of the secured items or portions concerned?				
Have standard operating procedures for the disposal of samples, digestates, leachates and extracts or other sample preparation products?				
Assuring the Quality of Test Results				
Ensure the quality of results provided to clients by implementing checks to monitor the quality of the laboratory's analytical activities? For Example: ___Internal quality control procedures (using statistical techniques whenever possible); ___Participation in PT or other inter-laboratory comparisons; ___Reference material and/or in-house quality control using secondary reference materials;				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Replicate testing; ___Re-testing of retained samples; and/or ___Correlation of results for different parameters of a sample.				
Have quality control procedures for monitoring the validity of environmental tests and calibrations undertaken?				
Are the resulting data recorded in such a way that trends are detectable and, where applicable, statistical techniques are applied to the reviewing of the results?				
Is the monitoring planned and reviewed?				
Are all quality control measures assessed and evaluated on an on-going basis, and quality control acceptance limits used to determine the usability of the data?				
Have procedures for the development of acceptance/rejection criteria where no method or regulatory criteria exist?				
Are the quality control protocols specified by the laboratory's method manual followed?				
Reports				
Report the results of each test, or series of tests carried out by the laboratory in a test report that reports the data accurately, clearly, unambiguously, and objectively?				
Does the test report contain all information necessary for the interpretation of the test results and all information required by the method used?				
Unless the laboratory is operated by a facility whose sole function is to provide data for the facility, does the report contain: ___A title ___Name/address of laboratory ___Location where analysis is carried out if different ___Phone number and name of contact person ___Unique identification of the test report and unique identification of each page, and the total number of pages. ___Name and address of client, where appropriate and project name if applicable ___Description and unambiguous identification of the tested sample including the client identification code ___where quality system requirements are not met, a statement of compliance/non compliance with requirements and/or specifications, including identification of results derived from samples that did not meet NELAC acceptance requirements such as improper container, holding time, or temperature.				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Date of receipt of sample, date and time of sample collection, date(s) of performance test, and time of sample preparation and/or analysis ___Identification of the test method used, ___Any deviations from, additions to or exclusions from the test method, and non-standard conditions that may have affected the quality of the results, and including the use of relevant data qualifiers and their meaning?				
Does the report contain: ___environmental test results with, where appropriate, the units of measurement, and any failures (such as failed quality control) identified and whether data are calculated on dry weight or wet weight, reporting units ___When required, a statement of the estimated uncertainty of the test result. ___A signature and title, or an equivalent electronic identification of the person(s) accepting responsibility for the content of the certificate or report (however produced), and date of issue, ___a statement to the effect that the results relate only to the samples , ___at the lab's discretion, a statement that the certificate or report shall not be reproduced except in full, without the written approval of the laboratory ___Clear identification of all data provided by outside sources, such as subcontracted laboratories, clients, etc. ___Clear indication of numerical results with values outside of quantitation limits.				
Are all applicable elements above readily available for review if not issued in a formal report by laboratory?				
Does management ensure that the appropriate report items are in the report to the regulatory authority if the report is prepared by another individual within the organization.				
When opinions and interpretations are included in the test report does the laboratory document the basis upon which the opinions and interpretations have been made?				
Are opinions and interpretations clearly marked in test reports?				
Where the certificate or report contains results of tests performed by sub-contractors, are these results clearly identified by subcontractor name or applicable accreditation number, and the subcontractor's report made available to the client on request?				
Is the format of the report designed to accommodate each type of test carried out and to minimize the possibility of misunderstanding or misuse?				
When it is necessary to issue a complete new test report, is this uniquely identified and does it contain a reference to the original that it replaces?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Are material amendments to a calibration certificate, test report or test certificate after issue made only in the form of a further document, or data transfer including the statement "Supplement to Test Report or Test Certificate, serial number . . . [or as otherwise identified]", or equivalent form of wording?				
Do amendments to the formal report meet all the relevant requirements of this standard?				
Notify clients 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 report or certificate?				
Have procedures that ensure, where clients require transmission of test results by telephone, fax, or email, that the requirements are met and that confidentiality is preserved?				
Do staff follow the documented procedures for the transmission of test results by telephone, fax or email?				
Certify that the test results meet all requirements of NELAC or provide reasons and/or justification if they do not?				
Report drinking water violations to the County Department of Health as required?				
Demonstration of Capability				
Is a demonstration of capability made prior to using any test method, and at any time there is a change in instrument type, personnel or test method?				
Are initial demonstrations and method certification documented through the use of the forms in the latest approved NELAC document?				
Retain all associated supporting data necessary to reproduce the analytical results summarized in the IDC certification statement?				
Is the QC sample used for the IDC, purchased from an outside source, or if not available, is the QC sample prepared by the laboratory independent of the instrument calibration?				
Is the concentrate of the QC sample diluted in a volume of clean matrix sufficient to prepare four aliquots at the required method volume to a concentration specified in the method, or, if unspecified, to a concentration of 1-4 times the limit of quantitation?				
Are four aliquots prepared and analyzed according to the method either concurrently or over a period of days?				
Is the average recovery and standard deviation for each parameter of interest calculated in the units used for reporting (such as mg/L)?				
When it is not possible to determine mean and standard deviations, such as for presence/absence and logarithmic values, does the laboratory assess performance against established and documented				

Relevant Aspect of Standards	Y	N	N/A	Comments
criteria?				
Does the average recovery and standard deviation meet the acceptance criteria for precision and accuracy of the method (if applicable) or in laboratory generated acceptance criteria (if there is no mandatory criteria)?				
Does the lab wait to begin the analysis of actual samples until all parameters of interest meet acceptance criteria?				
If one or more of the test parameters does not meet the acceptance criteria, is the problem corrected followed by repeated analysis of the four aliquots for all parameters or at least for those that failed to meet criteria?				
Is a copy of the initial demonstration of Capability Certificate (IDC) in the personnel records for each employee performing a test method?				
Determine the Limit of Detection (LOD) for the method for each target analyte of concern in the matrices approved?				
Do all sample-processing steps of the analytical method include the determination of the LOD?				
Is the validity of the LOD confirmed by qualitative identification of the analyte(s) in a QC sample in each approved matrix containing the analyte at no more than 2-3 X the LOD for single analyte tests and 1-4 X the LOD for multiple analyte tests?				
Is this verification performed on every instrument that is to be used for analysis of samples and reporting of data?				
Where an LOD study is not performed, does the laboratory not report a value below the Limit of Quantitation?				
Determine the Limit of Quantitation (LOQ) for each analyte of concern according to a defined, documented procedure?				
Is the validity of the LOQ confirmed by successful analysis of a QC sample containing the analytes of concern in each in each approved matrix 1-2 times the claimed LOQ?				
When using standard methods, does the laboratory evaluate the precision and bias of a standard method for each analyte of concern for each quality system matrix according to the single-concentration four-replicate recovery study procedures in Appendix C.1 above (or alternate procedure documented in the quality manual when the analyte cannot be spiked into the sample matrix and QC samples are not commercially available)?				
When using Non-Standard methods for Laboratory-developed test methods or non-standard test methods that were not in use by the laboratory before July 2003, did the laboratory document procedure				

Relevant Aspect of Standards	Y	N	N/A	Comments
to evaluate precision and bias?				
Compare results of the precision and bias measurements with criteria established by the client, by criteria given in the reference method or criteria established by the laboratory?				
Do the precision & bias measurements evaluate the laboratory-developed or non-standard test method across the analytical calibration range of the method?				
Evaluate selectivity by following the checks established within the method?				
Chemical Testing and Air Testing Detailed Method Review				
Demonstrate that it meets all requirements contained in a mandated test method or by regulation, even if the requirement is more stringent than the corresponding NELAC standard? (If it is unclear which requirements are more stringent, the standard from the method of regulation shall be followed)				
Are the quality control protocols specified by the laboratory's method manual followed by all analysts?				
Are all essential quality control measures incorporated in the lab's method manual?				
Are all quality control measures assessed and evaluated on an on-going basis and is quality control acceptance criteria used to determine the validity of the data?				
Have procedures for developing acceptance/rejection criteria for each test where no method or regulatory criteria exist?				
Is the method blank processed along with and under the same conditions as the associated samples including all steps of the analytical procedure?				
Are procedures in place to determine if a method blank is contaminated?				
Are any affected samples associated with a contaminated blank reprocessed for analysis or are the results reported with appropriate data qualifying codes?				
Is a method blank performed; ___one per preparation batch, per matrix type; or ___in those instances for which there is no separate preparation method, is the batch defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples?				
Does the method blank consist of a matrix that is similar to the associated samples and is known to be free of the analytes of interest?				
Is each method blank critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Is the source of contamination investigated and measures taken to minimize or eliminate the problem and the affected samples reprocessed; or ___Is data appropriately qualified if: ___The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the test method or by regulation, AND is greater than 1/10 of the amount measured in any sample. ___The blank contamination affects the sample results as per the test method requirements or the individual project data quality objectives.				
When a blank is determined to be contaminated, does the laboratory investigate the cause and take measures to minimize or eliminate the problem?				
Evaluate samples associated with a contaminated blank as to the best corrective action for the samples (e.g. reprocessing or data qualifying codes) and is the corrective action documented ?				
Is the LCS used to evaluate the performance of the total analytical system including all preparation and analysis steps?				
Is an LCS (a sample matrix free of analytes of interest spiked with a verified known amount of analyte) performed at a frequency of: ___one per preparation batch per matrix type except for analytes for which spiking solutions are not available; or ___In those instances for which there is no separate preparation method, is the batch defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples??				
If the matrix spike is used as the LCS, is the acceptance criteria as stringent as the LCS?				
Are the components spiked those that are specified by the mandated test method or other regulatory requirement or as requested by the client?				
In the absence of specified spiking components does the laboratory spike per the following: ___For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, is the spike chosen so that it represents the chemistries and elution patterns of the components to be reported? ___For those test methods that have extremely long lists of analytes, is a representative number chosen as below? ___Are the analytes selected that representative of all analytes reported? ___Is the following criteria used for determining the minimum number of analytes to be spiked. ___Does the laboratory ensure that all targeted components are included in the spike mixture over a 2 year period?				

Relevant Aspect of Standards	Y	N	N/A	Comments
___For methods that include 1-10 targets, are all components spiked?; ___For methods that include 11-20 targets, are at least 10 or 80% spiked, whichever is greater; ___For methods with more than 20 targets, are at least 16 components spiked?				
Are the results of individual batch LCS calculated in percent recovery?				
Document the calculation for percent recovery?				
Is the individual LCS compared to the acceptance criteria: ___as published in the mandated test method; or ___where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits; or ___utilize client specified assessment criteria?				
Are samples analyzed along with a LCS determined to be out-of-control; ___considered suspect and the samples reprocessed and re-analyzed; or ___is the data reported with appropriate qualifying codes?				
Are the number of allowable marginal exceedences determined as follows: ☐ >90 analytes in LCS, no more than 5 analytes allowed in ME of the LCS control limit? ☐ 71-90 analytes in LCS, no more than 4 analytes allowed in ME of the LCS control limit? ☐ 51-70 analytes in LCS, no more than 3 analytes allowed in ME of the LCS control limit? ☐ 31-50 analytes in LCS, no more than 2 analytes allowed in ME of the LCS control limit? ☐ 11-30 analytes in LCS, no more than 1 analytes allowed in ME of the LCS control limit? ☐ <11 analytes in LCS, no analytes allowed in ME of the LCS control limit?				
Are the LCS marginal exceedences random?				
If the same analyte exceeds the LCS control limit repeatedly, it is an indication of a systemic problem. Is the source of the error located and corrective action taken?				
Have a written procedure to monitor the application of marginal exceedence allowance to the LCS to ensure random behavior?				
Document procedures for determining the effect of the sample matrix on method performance?				
Do these procedures relate to the analyses of matrix specific QC samples and are they designed as data indicators for a specific sample using the designated test method?				
Have procedures in place for tracking, managing, and handling matrix specific QC criteria including spiking appropriate components at appropriate concentrations, calculating recoveries and relative percent difference, evaluating and reporting results based on performance of the QC samples?				
Is the frequency of the analysis of matrix specific samples determined as part of a systematic planning				

Relevant Aspect of Standards	Y	N	N/A	Comments
process (e.g. Data Quality Objectives) or as specified by the required mandated test method?				
Are the components spiked those specified by the mandated test method, where applicable?				
Are any permit specified analytes, as specified by regulation or client requested analytes also included?				
If there are no specified components, does the laboratory spike per the following: ___For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, is the spike chosen which represents the chemistries and elution patterns of the components to be reported? ___For those test methods that have extremely long lists of analytes, are all analytes used, or are a representative number chosen using the following criteria: 1. For methods that include 1-10 targets, spike all components; 2.For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater; 3. For methods with more than 20 targets, spike at least 16 components.				
Include all targeted components in the spike mixture over a 2 year period?				
Is the matrix spike used to assess the precision and accuracy of analytical results in a given matrix and are they expressed as percent recovery (%R) and relative percent difference (RPD)?				
Document the calculation for relative percent difference?				
Are the results compared to the acceptance criteria in the mandated test method when published?				
Where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits?				
For matrix spike results outside established criteria, is corrective action documented or is the data reported with appropriate data qualifying codes?				
Are matrix duplicates defined as replicate aliquots of the same sample taken through the entire analytical procedure?				
Do the results from the analysis of matrix duplicates indicate the precision of the results for the specific sample using the selected method?				
Is the frequency of the analysis of matrix duplicates determined as part of a systematic planning process (e.g. Data Quality Objectives) or as specified by the mandated test method?				
Are matrix duplicates performed on replicate aliquots of actual sample?				
Are the results from matrix duplicates primarily designed to assess the precision of analytical results in a given matrix and are they expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences)?				
Document the calculation for relative percent difference or other statistical treatments?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Are the results compared to the method acceptance criteria as published in the mandated test method?				
Where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits?				
For matrix duplicates results outside established criteria, is corrective action documented or is the data reported with appropriate data qualifying codes?				
Are surrogate compounds added to all samples, standards, and blanks, whenever possible, for all organic chromatography methods?				
Are surrogate compounds chosen for being unlikely to occur as environmental contaminants and to represent the various chemistries of the target analytes in the method?				
Are the results of surrogate recoveries compared to the acceptance criteria published in the mandated test method?				
Where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits?				
Are surrogates outside the acceptance criteria evaluated for the effect indicated for the individual sample results?				
Is the appropriate corrective action guided by the data quality objectives or other site specific requirements?				
Are results reported from analyses with surrogate recoveries outside the acceptance criteria with appropriate data qualifiers?				
Are sample results quantitated from the initial instrument calibration and not from any continuing instrument calibration verification?				
Is the continuing instrument calibration verification used to confirm the continued validity of the initial calibration?				
Do the SOPs or the test method SOP reference the details of the initial calibration procedures, including calculations integrations, and acceptance criteria associated statistics?				
Are sufficient raw data records retained to permit reconstruction of the initial and continuing calibration including: ___Calibration date ___Test method ___Instrument ___Analysis date ___Each analyte name				

Relevant Aspect of Standards	Y	N	N/A	Comments
___Concentration ___Response ___Calibration curve or response factor ___Analyst's initials or signature ___Unique equation or coefficient used to reduce instrument response to concentration.				
Are all initial calibration verification standards traceable to a national standard, when commercially available?				
Are all initial calibrations verified with a standard obtained from a second source manufacturer or lot if the lot can be demonstrated from the manufacturer as prepared independently from other lots?				
Is the criteria for the acceptance of an initial calibration established (correlation coefficient or relative percent difference) and appropriate to the calibration technique employed?				
Is the lowest calibration standard the lowest concentration for which quantitative data are to be reported. Any data reported below the lower limit of quantitation should be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or flags or explained in the case narrative.				
Is the highest calibration standard the highest concentration for which quantitative data are to be reported Any data reported above this highest standard should be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or flags or explained in the case narrative.				
If the results of samples are not bracketed by the initial calibration, are the results reported as having less certainty (defined qualifiers, flags, or explanation in the case narrative)?				
Is the lowest calibration standard of the initial calibration above the detection limit?				
For ICP and/or ICP-MS does the following occur; ___Prior to the analysis of samples the zero point/single point calibration must be analyzed and the linear range must be established by analyzing a series of standards, one of which must be at the lowest quantitation level, (results within the established linear range shall not require data qualifier flags) ___the zero point/single point calibration must be analyzed with each analytical batch, ___a standard corresponding to the limit of quantitation must be analyzed with each analytical batch and must meet established acceptance criteria, ___The linearity is verified at a frequency established by the method and/or the manufacturer.				
Are corrective actions performed if the results of the initial calibration are outside of established acceptance criteria?				
Is data associated with unacceptable initial instrument calibration not reported?				

Relevant Aspect of Standards	Y	N	N/A	Comments
Have an SOP for determining the number of points for establishing the initial calibration?				
If a reference or mandated method does not specify the number of calibration standards, is the minimum number used 2, not including a blank or zero standard?				
When an initial calibration is not performed on the day of analysis, does the laboratory verify the validity of the initial calibration prior to the analysis of samples by analyzing a continuing instrument calibration verification sample?				
Are the details of the continuing instrument calibration procedure, calculations, and associated statistics included or referenced in the test method SOP?				
Is the calibration verified for each compound, element, or other discrete chemical species, except for multi-component analytes such as Aroclors, Total Petroleum Hydrocarbons, or Toxaphene where a representative chemical related substance or mixture can be used?				
Is a continuing instrument calibration verification performed: ___at the beginning and end of each analytical batch; (If an internal standard is used, only one continuing calibration verification must be analyzed per analytical batch) ___whenever it is expected that the analytical system may be out of calibration or might not meet verification acceptance criteria; ___if the time period for calibration or the most previous calibration verification has expired; or ___for analytical systems that contain a CCV requirement?				
Do the continuing calibration verification records explicitly connect the continuing verification data to the initial instrument calibration?				
Have established acceptance criteria of a continuing calibration verification analysis? (e.g. relative percent difference)				
Are routine corrective actions performed if the results of the continuing calibration verifications are outside of established acceptance criteria?				
If corrective action fails to produce an acceptable second consecutive(immediate) calibration verification, does the lab either perform a new initial calibration or analyze 2 consecutive acceptable calibration verifications before analyzing new samples?				
When sample data associated with a failed calibration verification is reported, does the laboratory qualify the data.				
If there was a high bias and there is a failed continuing calibration verification, is only data associated with samples that are non-detects reported? (Other affected samples are reanalyzed after a new curve has been established, evaluated, and accepted.)				

Relevant Aspect of Standards	Y	N	N/A	Comments
If there was a low bias and there is a failed continuing calibration verification, is only data associated with samples that have a result greater than the maximum regulatory limit/decision level reported? (Other affected samples are reanalyzed after a new curve has been established, evaluated, and accepted.)				
Utilize test methods that provide an LOD that is appropriate and relevant for the intended use of the data? (An LOD is not required for a test method when test results are not reported outside the calibration range.)				
Use an LOD that is determined by the protocol in the mandated test method or applicable regulation?				
If the protocol for determining LOD is not specified, does the selection made by the laboratory reflect instrument limitations and the intended application of the test method?				
Is the LOD initially determined in a matrix free of target analytes or interferences or in the matrix of interest?				
Are detection limits determined each time there is a significant change in the test method or instrument type?				
Are all procedures used to determine detection limits documented including the matrix type and is all supporting data retained?				
Does the laboratory have established procedures relate LOD with LOQ?				
Is the LOD verified annually for each quality system matrix, method and analyte?				
Are the test methods LOQ established and above the LOD?				
Is the LOQ verified annually for each quality matrix, method and analyte?				
Are procedures documented for data reduction, such as use of linear regression?				
Is the source of standards traceable to national standards or proven through inter-laboratory studies?				
In methods where the purity of reagents is not specified, is analytical reagent grade used?				
Use reagents of the purity or of greater purity than that specified in the method?				
Is the container labeling checked to verify that the purity of the reagents meets the requirements of the particular method?				
Document the checks to verify that the purity of the reagents meets the requirements of the particular test method?				
Is the quality of water sources monitored and documented to meet method specified requirements?				
Verify the concentration of titrants in accordance with written laboratory procedures?				
Evaluate selectivity by following the checks established within the method, which may include mass spectral tuning, second column confirmation, ICP interelement interference checks, chromatography				

Relevant Aspect of Standards	Y	N	N/A	Comments
retention time windows, sample blanks, spectrochemical absorption or fluorescence profiles, co-precipitation evaluations, and electrode response factors?				
Is confirmation performed for organic tests other than GC/MS or when recommended by the analytical method to verify the compound identification when positive results are detected on a sample from a location that has not been previously tested by the laboratory?				
If confirmation not performed, is it based on client written stipulation?				
Document all confirmations?				
Develop and document acceptance criteria for mass spectral tuning?				
Assure that the test instruments consistently operate within the specifications of the test methods and equipment manufacturer?				
Is glassware cleaned to meet the sensitivity of method?				
Are all cleaning and storage procedures that are not specified by the method documented in laboratory records and SOPs?				

Figure 2: SOP/Test Method Checklist
Name(s) of auditor(s): ____________________________________
Date: ___________________
Name(s) of employee(s): _____________________________________
Analysis/Method: _________________________
SOP #: _________________________

PT Studies:	Notes:
☐ WP 1	____
☐ WP 2	____
☐ NELAC 1	____
☐ NELAC 2	____
☐ NELAC WS 1	____
☐ NELAC WS 2	____
☐ WS	____
☐ DRMQA	____

Corrective Action Follow-up:____
____
____
____
____

External Audit Follow-up: ____
____
____
____
____

Previous Internal Audit Follow-up: ____
____
____
____

General Checklist:	Complete?	Notes:
☐ Balance(s) Log Book	☐	_______________________
☐ Equipment Maintenance(s) Log Book	☐	_______________________
☐ Reagent(s) Log Book	☐	_______________________
☐ Standard(s) Log Book	☐	_______________________
☐ Nonconformance/Preventive Action	☐	_______________________
☐ Other Log Book____________	☐	_______________________
☐ MDL	☐	Date:___________________
☐ LOD	☐	Date:___________________
☐ LOQ	☐	Date:___________________
☐ Last Control Chart/Linear Range	☐	Date:___________________
☐ Retention Time Window Study	☐	Date:___________________
☐ Supplies Labeled	☐	_______________________

Data Chase:

Merit #: ________________ Run Date: ________________ Prep Date: _________________
QC Prep ID: ____________ QC Run ID: ______________ Calibration Date: _____________

Calibration Check:

Standard/Reagent	Lot #	Preparation Date	Expiration Date

Item	Limits	Agree w/ SOP?	Agree w/ Method?	Agree w/ Cert./Project?	Notes
# of Points		☐	☐	☐	
Second Source		☐	☐	☐	
Fit		☐	☐	☐	
R-value		☐	☐	☐	
ICV		☐	☐	☐	
CCV		☐	☐	☐	
		☐	☐	☐	
		☐	☐	☐	
		☐	☐	☐	

Preparation Check:

Standard/Reagent	Lot #	Preparation Date	Expiration Date

Bench Sheet Check:	Traceable?	Present?	Notes:
☐ Analysis Information	☐	☐	__________________________
☐ Batch Information	☐	☐	__________________________
☐ Reagent/Standard Information	☐	☐	__________________________
☐ Sample Information	☐	☐	__________________________
☐ Subsampling/Targeting		☐	__________________________
☐ Effective Date		☐	__________________________

☐ Clean/Legible Copy ☐ ______________________

Prep Batch Quality Control:

Item	Frequency

Analysis:

Raw Data Check:	Traceable?	Present?	Notes:
☐ Analysis Information	☐	☐	______________________
☐ Batch Information	☐	☐	______________________
☐ Reagent/Standard Information	☐	☐	______________________
☐ Sample Information	☐	☐	______________________
☐ Manual Integrations	☐	☐	______________________

Run Batch Quality Control:

Item	Frequency (1 per ?)	Limits	Acceptable?	Agree w/ SOP?	Agree w/ Method?	Agree w/ Cert./Project?
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐
			☐	☐	☐	☐

☐ Associated Calibration/MDL are acceptable?

Data Review:

☐ Analyst

☐ Peer

Reagent traceability notes: ____
____
____
____

General notes: ____
____
____
____

SOP Check:

Section	Followed?	Agree w/ Method?	Notes:
Scope/Application	☐	☐	
Method #	☐	☐	
Matrix/Matrices	☐	☐	
Detection Limit	☐	☐	
Summary	☐	☐	
Interferences	☐	☐	
Apparatus & Materials	☐	☐	
Reagents/Standards	☐	☐	
Sample Collection, Preservation & Handling	☐	☐	
Procedure	☐	☐	
Calibration	☐	☐	
Calculations	☐	☐	
Quality Control	☐	☐	
Data Assessment	☐	☐	
Frequency	☐	☐	
Acceptance Criteria	☐	☐	
Corrective Actions	☐	☐	
Method Performance	☐	☐	
Maintenance & Troubleshooting	☐	☐	
Safety	☐	☐	
Waste Disposal & Pollution Prevention	☐	☐	
Definitions	☐	☐	
References	☐	☐	
Tables/Diagrams	☐	☐	
Documentation	☐	☐	
Benchsheet	☐	☐	
Amendments	☐	☐	

Method Specific Information: ____

____

____

____

____

____

Figure 3: Log-In/Sample Receiving Checklist
Name(s) of auditor(s): ____________________________________
Date: ___________________
Name(s) of employee(s): _____________________________________

Corrective Action Follow-up:____
____
____
____
____
____

External Audit Follow-up: ____
____
____
____
____
____

Previous Internal Audit Follow-up: ____
____
____
____
____
____

General Checklist:	Complete?	Notes:
☐ Nonconformance/Preventive Action	☐	________________________
☐ Supplies Labeled	☐	________________________
☐ Sample Acceptance Policy Available	☐	________________________

Data Chase:
Merit #: _______________ Log-in Date: _______________ COC #:_______________

Sample Receiving:	Complete?	Notes:
☐ Chain of Custody	☐	________________________
☐ Unique Identification (sample)	☐	________________________
☐ Unique Identification (container)	☐	________________________
☐ Durable Label Used	☐	________________________
☐ Sample Condition Checked	☐	________________________
☐ Temperature Checked	☐	________________________
☐ Chemical Preservation Checked	☐	________________________
☐ Data Flagged	☐	________________________
☐ Appropriate Storage Utilized	☐	________________________

Subcontracting:	Complete?	Notes:
☐ Client Notified	☐	____________________________
☐ Certified Laboratory Utilized	☐	____________________________
☐ Registry of Approved Subcontractors	☐	____________________________

Service to Client:	Complete?	Notes:
☐ Complaint(s) Recorded	☐	____________________________
☐ Maintain all Correspondence	☐	____________________________
☐ Confidentiality Protected	☐	____________________________

Records:	Complete?	Notes:
☐ Chain of Custody	☐	____________________________
☐ Field Sheet	☐	____________________________
☐ Sample Receiving Checklist	☐	____________________________
☐ Preservation Checklist	☐	____________________________

Reporting:	Complete?	Notes:
☐ Confidentiality Protected	☐	____________________________
☐ Explanation of Data Qualifiers	☐	____________________________
☐ Amendments clearly identified	☐	____________________________
☐ Subcontracting clearly identified	☐	____________________________
☐ Secondary reports labeled appropriately	☐	____________________________

General notes: ____
____
____
____
____

SOP Check:

Section	Followed?	Agree w/ Method?	Notes:
Scope/Application	☐	☐	
Method #	☐	☐	
Matrix/Matrices	☐	☐	
Detection Limit	☐	☐	
Summary	☐	☐	
Interferences	☐	☐	
Apparatus & Materials	☐	☐	
Reagents/Standards	☐	☐	
Sample Collection, Preservation & Handling	☐	☐	
Procedure	☐	☐	
Calibration	☐	☐	
Calculations	☐	☐	
Quality Control	☐	☐	
Data Assessment	☐	☐	
Frequency	☐	☐	
Acceptance Criteria	☐	☐	
Corrective Actions	☐	☐	
Method Performance	☐	☐	
Maintenance & Troubleshooting	☐	☐	
Safety	☐	☐	
Waste Disposal & Pollution Prevention	☐	☐	
Definitions	☐	☐	
References	☐	☐	
Tables/Diagrams	☐	☐	
Documentation	☐	☐	
Benchsheet	☐	☐	
Amendments	☐	☐	

Figure 4: Tentative procedure schedule

Procedure	Date
PT Studies	
WP PT Fall	August - October
WP PT Spring	March - May
WS PT Annual	January - April
DMRQA Annual	w/ Spring WP
NY NELAP Non-Potable Water & Solid	2 times year TBD by NY NELAP
NY NELAP Potable Water	2 times year TBD by NY NELAP
Staff Trainings	
Code of Ethics / Data Integrity	March - May
Chemical Hygiene training	March - May
Holding Times Training	March - May
Safety Training	March - May
Allowable deviation Training	March - May
Review of WP PT Fall	30 days after final report
Review of WP PT Spring	30 days after final report
Review of WS PT	30 days after final report
Review of NYNELAP PT Study	30 days after final report
Audits	
Internal Audit	March - May
Control Chart Evaluations	March - May
Quality Systems Review	March - May
QA/QC Manual Review	March - May
Log Book Reviews	March - May
Method Reviews	March - May
SOP QC Checks	March - May
Trend Analyses when applicable	March - May
QC Control Limits Review	March - May
Managerial Review	March - May (after Internal Audit)
SOP Review	March - May