APPENDIX B

Quality Assurance Project Plan (QAPP)

Draft
Quality Assurance Project Plan
Remedial Investigation Work Plan
Boeing Developmental Center
Tukwila, Washington

October 23, 2019

Prepared for

The Boeing Company
Seattle, Washington

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Quality Assurance Project Plan
Remedial Investigation Work Plan
Boeing Developmental Center
Tukwila, Washington

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LIST OF ABBREVIATIONS AND ACRONYMS

ANSI ..... American National Standards Institute
AOC ..... Area of Concern
ARI ..... Analytical Resources, Inc.
ASQC ..... American Society of Quality Control
Boeing ..... The Boeing Company
CLP ..... Contract Laboratory Program
COC ..... chain of custody
DQI ..... data quality indicator
DQO ..... data quality objective
Ecology ..... Washington State Department of Ecology
EDD ..... electronic data deliverable
EPA ..... US Environmental Protection Agency
EQuIS ..... Environmental Quality Information Systems
eV ..... electron volt
ft ..... feet, foot
HASP ..... health and safety plan
HAZWOPER ..... Hazardous Waste Operations and Emergency Response
LAI ..... Landau Associates, Inc.
LCS ..... laboratory control sample
LCSD ..... laboratory control sample duplicate
LDW ..... Lower Duwamish Waterway
MDL ..... method detection limit
MQO ..... measurement quality objective
MS ..... matrix spike
MSD ..... matrix spike duplicate
PAH ..... polycyclic aromatic hydrocarbon
PCB ..... polychlorinated biphenyl
PCOC ..... potential contaminant of concern
PID ..... photoionization detector
PQL ..... practical quantitation limit
QA ..... quality assurance
QAPP ..... quality assurance project plan
QC ..... quality control
RI ..... remedial investigation
RPD ..... relative percent difference
SAP ..... sampling and analysis plan
Site ..... Boeing Developmental Center
SL ..... screening level

SOPs ..... standard operating procedures
SWMU ..... Solid Waste Management Unit
TPH ..... total petroleum hydrocarbons
VOC ..... volatile organic compound
WAC ..... Washington Administrative Code

1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) establishes the quality assurance (QA) objectives for the remedial investigation (RI) being conducted at The Boeing Company (Boeing) Developmental Center (Site) located in Tukwila, Washington (Figures B-1 and B-2). This plan presents the quality control (QC) procedures developed to meet project QA objectives.

1.1 Distribution List

The following list identifies those individuals to receive an electronic copy of the approved QAPP, as well as any subsequent revised versions of the documentation:

- Byung Maeng—Project Manager for the Washington State Department of Ecology (Ecology) (bmae461@ecy.wa.gov)
- Lindsey Erickson—Project Manager for Boeing (lindsey.e.erickson@boeing.com)
- Ken Reid—Consultant (Landau Associates, Inc. [LAI]) Project Manager (kreid@landauinc.com)
- Danille Jorgensen—Consultant (LAI) Quality Assurance Officer (djorgensen@landauinc.com)
- Kelly Bottem—Project Coordinator for Analytical Resources, Inc. (ARI) (Kelly.bottem@arilabs.com).

1.2 Project Organization

Site RI activities will be implemented by Boeing; Lindsey Erickson is the project manager. LAI is responsible for preparing documents associated with the planned RI activities, implementing the activities, and reporting the RI results to Boeing. Ken Reid is the LAI RI project manager and will communicate directly with Lindsey Erickson, as necessary, during the course of RI activities. Mr. Reid will be responsible for implementing and executing the technical, QA, and administrative aspects of the RI and will manage LAI staff working on this project. Danille Jorgensen, the designated LAI Quality Assurance officer, is responsible for the overall management of the project-specific QA and QC requirements, including field and laboratory QC. LAI's staff managing field operations will report field progress and problems to Mr. Reid on a daily basis and will be responsible for managing subcontractors, as necessary, that support RI activities at the Site. Christine Kimmel is the designated Health and Safety Manager for field activities.

Specific QA responsibilities for this project are listed in Table B-1. The QA manager will be responsible for QA oversight during investigation activities including sampling events, analytical laboratory coordination, and direct implementation of this QAPP. The QA manager will be responsible for overseeing data validation and for confirming that the QA objectives of the project are met.

2.0 PROJECT BACKGROUND / DESCRIPTION

The Site is located at 9725 East Marginal Way South in Tukwila, Washington near Boeing Field and the Military Flight Center (now called the Military Delivery Center). The Site is bounded by the Lower Duwamish Waterway (LDW) on the west and south, and by East Marginal Way South on the east and the Museum of Flight and Slip 6 on the north. The Site is at an average elevation of approximately 20 feet (ft) above mean sea level. Surface topography at and in the vicinity of the Site is generally flat. The Site and surrounding area is paved.

The Site is an aircraft and aerospace research and development complex, primarily supporting projects for the US Department of Defense. The facility currently consists of more than 30 buildings on approximately 112 acres. It continues to be the primary research and development center for carbon fiber composite structures.

Various existing information evaluations, environmental investigations, and remedial actions have been conducted at the Site to characterize and evaluate the chemical quality and physical condition of soil, groundwater, air, and sediment, or to address specific releases. Descriptions of previous activities are provided in the text of the RI work plan.

2.1 Project Goals and Objectives

This QAPP has been prepared to cover work related to the RI. The specifics of the RI investigation are presented in the RI work plan published concurrently with this QAPP.

The purpose of this QAPP is to provide specific QA and QC procedures that will be used to support the evaluation and interpretation of data determined to be of acceptable quality and completeness. This QAPP has been prepared based on the requirements outlined in the US Environmental Protection Agency's (EPA's) Guidance for Quality Assurance Project Plans (EPA 2002), EPA's Requirements for Quality Assurance Project Plans (EPA 2001), and Ecology's Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies (Ecology 2004).

To the extent possible, the procedures included in this QAPP have been standardized to support effective evaluation of data resulting from sampling of the various media that has the potential to be evaluated at the Site. In the event that additional investigation activities are performed following the publication of this QAPP (i.e., additional activities not addressed in the RI work plan), work plan addenda will be prepared to document data quality objectives and sampling, and will include any revisions to screening levels (SLs), practical quantitation limits (PQLs), sampling procedures, and laboratories, as needed.

ARI in Tukwila, Washington is the laboratory to be used for planned RI activities. Analytical testing will be in accordance with the methodologies established by the EPA (EPA 1983, 1999) and Standard Methods for the Examination of Water and Wastewater, 20th edition (APHA 1998). The EPA

compendium of test methods (SW-846) provides for the analytical procedures to be used as well as the specific application of those procedures. Laboratory standard operating procedures (SOPs) are provided in Attachment B-1.

3.0 QUALITY ASSURANCE OBJECTIVES

This section presents the QA and QC objectives and processes including data quality objectives (DQOs), data quality indicators (DQIs), measurement quality objectives (MQOs), and QC procedures for field and laboratory work.

3.1 Data Quality Objectives

DQOs specify the environmental decisions that the data will support and the corresponding level of data quality required to ensure decisions are based on sound scientific data. The DQOs for this project are summarized below:

- Obtain data that are representative of Site conditions
- Characterize concentrations of potential contaminants of concern (PCOCs) in soil and groundwater, which may include volatile organic compounds (VOCs); gasoline-, diesel-, and oil-range total petroleum hydrocarbons (TPH); polycyclic aromatic hydrocarbons (PAHs); polychlorinated biphenyls (PCBs); total and/or dissolved metals (arsenic, barium, cadmium, chromium, copper, lead, mercury, and/or zinc)
- Obtain data that are comparable to applicable screening criteria

3.2 Data Quality Indicators

DQIs are used to establish DQOs and are discussed in detail below. A summary of DQIs and their associated MQOs are presented by sample matrix in Table B-2.

3.2.1 Precision

Precision is a measure of variability in the results of replicate measurements due to random error (Ecology 2004). Precision is best expressed in terms of the standard deviation or relative percent difference (RPD). QC sample types that can be used to evaluate precision include field and laboratory duplicates, matrix spike duplicates (MSDs), and laboratory control sample duplicates (LCSDs). The precision of duplicate measurements will be expressed as an RPD, which is calculated by dividing the absolute value of the difference of the two measurements by the average of the two measurements, and expressing it as a percentage. The formula for RPD calculation is shown below:

$$\mathrm{RPD} = \left[\frac{|\mathrm{D1} - \mathrm{D2}|}{[(\mathrm{D1} + \mathrm{D2}) \div 2]}\right] \times 100\%$$

Where:

D1 = first measurement value

D2 = second measurement value (duplicate).

3.2.2 Accuracy

Accuracy is a combination of precision and bias (described in Section 3.2.7), in that it represents the degree to which a measured value represents the known value (Ecology 2004). Accuracy is expressed as the percent recovery of spiked samples (matrix spike [MS], laboratory control sample [LCS], and surrogate spike). The general formula used to calculate percent recovery is shown below (for MS/MSD percent recovery, the result from the unspiked sample is taken into account in the formula):

$$\%R = \left[\frac{SSR}{C_s}\right] \times 100\%$$

Where:

%R = percent recovery

SSR = spiked sample result

C_s = concentration of the spike added.

3.2.3 Representativeness

Representativeness is an indicator of how accurately a result reflects the desired characteristic(s) of a defined population, accounting for both temporal and spatial variability (Ecology 2004). Representativeness qualitatively describes how well the analytical data characterize an area of concern. Representativeness is largely determined by the sampling design; analytical parameters for use in its evaluation include method-specified holding times and preservation requirements, and matrix heterogeneity. The sampling design for this project is discussed in the RI work plan.

3.2.4 Comparability

Comparability is the "degree of confidence with which one data set can be compared to another" (Ecology 2004). QC procedures and MQOs, as stated in this QAPP, will provide for measurements that are consistent and representative of the media and conditions measured.

3.2.5 Completeness

Completeness is a measure of "the amount of valid data obtained from a measurement system compared to the amount that could be expected to be obtained under normal conditions" (EPA 2009). Field completeness is calculated as the number of actual samples collected divided by the number of planned samples. Analytical completeness is calculated as the number of valid data points divided by the total number of data points requested. Data points are considered invalid if they are rejected during data validation. The data validation approach for this project is provided in Section 6.0. The requirements for field sampling and analytical completeness are 90 percent each.

3.2.6 Sensitivity

Sensitivity is the capability of a method or an instrument to discern the difference between very small amounts of a substance. For the purposes of this project, sensitivity is the lowest concentration that can be accurately detected by the analytical method, which is defined by the laboratory as the PQL. The analytical method will be considered sufficiently sensitive if the PQLs are below the specific SLs for the area under investigation. Proposed method and target PQLs are presented in Table B-3.

3.2.7 Bias

Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction. Bias of the laboratory results will be evaluated based on analysis of reference materials, method blanks, and MS samples, as described in Section 6.5.

4.0 SPECIAL TRAINING / CERTIFICATION

Personnel performing onsite investigation tasks will have completed formal 40-hour Hazardous Waste Operations and Emergency Response (HAZWOPER) health and safety training, in compliance with 29 Code of Federal Regulations 1910.120 and Chapter 296 of the Washington Administrative Code (WAC). Certificates of successful completion of training, which will be maintained in personnel health and safety files, will verify on-the-job training for those tasks staff are assigned to perform. At least one member of each field team and the designated site safety officer will be trained in cardiopulmonary resuscitation and first aid.

Borings will be completed and monitoring wells will be constructed by a licensed drilling contractor in the state of Washington, following Washington State well standards. Oversight of drilling and well installation activities will be performed by an environmental professional familiar with environmental sampling and construction of resource protection wells.

As indicated in Section 2.1, ARI in Tukwila, Washington is the laboratory to be used for planned RI activities. This laboratory is not in the Contract Laboratory Program (CLP), but is accredited through Ecology for the applicable methods and target analytes listed in this QAPP. All laboratories shall maintain current applicable state certification or US Department of Defense Environmental Laboratory Accreditation Program certification for the methods and target analytes listed in this QAPP while performing analyses for the project. Laboratories used for this project have a documented QA program that complies with standards promulgated by the American National Standards Institute/American Society of Quality Control (ANSI/ASQC 1994); ANSI's Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs (Johnson 1994); and the EPA's Requirements for Quality Assurance Project Plans (EPA 2001).

Excavation, trenching, and shoring (WAC 296-155-Part N) activities or work in confined spaces (WAC 296-62-Part M) are not anticipated in this scope of work; therefore, this QAPP does not address training in physical worker safety issues that may be associated with excavation or confined spaces.

5.0 DOCUMENTS AND RECORDS

This section describes the management requirements for production, distribution, and storage of documents and records associated with planned activities at the Site.

5.1 Document Distribution

Prior to beginning field activities, field staff will receive and have an opportunity to review project-related documents pertinent to the field activities, including work plans, sampling and analysis plans (SAPs), and health and safety plans (HASPs), as appropriate to the planned activities. Project managers/coordinators will meet with field staff prior to field activities to review the relevant plans accordingly. The HASP will be reviewed in the field on the first day of activities, with each field person documenting their attendance to the HASP review on a sign-in sheet. The HASP will be reviewed again every few days or when a new field person begins working on field activities. The SAP, HASP, and work plans for each phase of the project will be finalized prior to commencement of field activities, and only the finalized versions will be distributed to field staff. Changes to procedures and plans after finalization will be documented as addenda and distributed along with the original finalized versions.

5.2 Field Documentation

Field equipment will have reference and related manuals stored in with the equipment. In addition, equipment that requires calibration will be accompanied by a calibration logbook. Field staff will record the calibration process in the logbook every time a calibration is performed.

A complete record of field activities will be maintained for the duration of the field phase of the work. Documentation will include the following:

- Daily recordkeeping by field personnel of field activities
- Recordkeeping of samples collected for analysis (field sampling forms)
- Use of sample labels and tracking forms for samples collected for analysis.

The field logs will provide a description of sampling activities completed, sampling personnel, daily weather conditions, and a record of modifications to the procedures and plans identified in the work plan or related documentation. The field logs are intended to provide sufficient data and observations to enable project staff to reconstruct events that occurred during the sampling period.

Field logs will be supplemented by sample collection forms, boring logs, and groundwater well logs completed by field staff, as applicable. The information that will be recorded in these forms is specified in the RI SAP.

Additional records associated with drilling will include driller's daily reports and well-related documentation when a well is installed.

Sample possession and handling will also be documented with chain-of-custody (COC) forms so that it is traceable from the time of sample processing in the field, to delivery to the laboratory, and to the ultimate data analysis. Sample handling and COC procedures are described in Section 6.3.

The following example field forms are provided in Attachment B-2:

- Chain-of-Custody
- Field Report
- Groundwater Low-Flow Sample Collection Form
- Log of Exploration
- Soil/Sediment Sample Collection Form
- Survey Field Notes Form
- As-Built Well Completion Form
- Well Development Record Form
- Seep Reconnaissance Survey Form.

5.3 Analytical Data Records

Laboratory analytical data reports will be provided in electronic format by the laboratory. These reports will be included as appendices in documents where data are reported, and will be kept along with all other documents in the project files. Data will be provided in a Level II laboratory report format. Data package elements are listed in Section 6.7.

5.4 Storage

Documents and records associated with the project (i.e., final documents, billing, and invoice records) and the documents described in Sections 5.2 and 5.3 will be stored in electronic form in project files on LAI's servers for the duration of the project and 10 years subsequent from the date of completion of work, as per the requirements in the associated Agreed Order (No. DE 16275).

6.0 DATA GENERATION AND ACQUISITION

This section provides an overview of the data collecting and handling processes that will ensure data quality that meets project standards. More details about these processes are included in the RI SAP.

6.1 Sampling Process Design

A sampling design that achieves the DQOs described in Section 3.0 has been prepared and is detailed in the RI SAP.

6.2 Sampling Methods and Containers

Samples will be collected using methods that are standard in environmental remediation. A detailed description of the sampling methods for each medium is provided in the RI SAP. Methods for sampling, decontamination, and well installation are provided in the RI work plan and Sampling and Analysis Plan, published concurrently with this QAPP.

Sampling containers will be provided by the laboratory. Extra containers will be requested to ensure that clean containers are available to replace any broken or misused containers during sampling events. The laboratory will provide kits (e.g., plunger for EPA Method 5035 soil sampling) to collect samples for analyses that require special methods to fill the sample container.

6.3 Sample Handling and Custody

Soil and water samples submitted to the analytical laboratory will be collected in the appropriate sample containers and preserved as specified in Table B-4. The storage temperatures and maximum holding times for physical/chemical analyses are also provided in Table B-4.

The transportation and handling of samples will be accomplished in a manner that not only protects the integrity of the sample, but also prevents any detrimental effects due to release of samples. Samples will be logged on a COC form (Attachment B-2) and will be kept in coolers on ice until delivery to the analytical laboratory. The COC will accompany each shipment of samples to the laboratory. A sample is in custody if at least one of the following is true:

- It is in someone's physical possession.
- It is in someone's view.
- It is secured in a locked container or otherwise sealed so that tampering will be evident.
- It is kept in a secured area, restricted to authorized personnel only.

Sample control and COC protocols in the field and during transport to the laboratory will be conducted in general conformance with the procedures described below:

- As few persons as possible will handle samples.

- Sample bottles will be obtained new or pre-cleaned from the laboratory performing the analyses.
- The sample collector will be personally responsible for the completion of the COC record and the care and custody of samples collected until they are transferred to another person or dispatched properly under COC rules.
- The onsite team leader will oversee implementation of the field custody procedures during the field work and, in the event of non-compliance, will determine if corrective action is required.
- The coolers in which the samples are shipped will be accompanied by the COC record identifying their contents. The original record and laboratory copy will accompany the shipment (sealed inside the shipping container). The other copy will be distributed as appropriate to LAI's QA officer or designee. The QA officer for this project is Danille Jorgensen.
- Shipping containers will be sealed with custody seals for shipment to the laboratory. The method of shipment, name of courier, and other pertinent information will be entered in the "remarks" section of the COC record.
- If sent by mail, the package will be registered with return receipt requested. If sent by common carrier, a bill of lading will be used. Freight bills, postal services receipts, and bills of lading will be retained as part of the permanent documentation.

When samples are transferred, the individuals relinquishing and receiving the samples will sign the COC form and record the date and time of transfer. The sample collector will sign the form in the first signature space. The only exception to this is the shipment of samples via commercial carriers. Because sample containers are sealed with the COC record inside prior to delivery to the carrier, the custody signature will be that of the individual taking possession of the samples from the carrier at its final destination. Each person taking custody will observe whether the shipping container is correctly sealed and in the same condition as noted by the previous custodian; deviations will be noted on the appropriate section of the COC record.

A designated sample custodian at the laboratory will accept custody of the shipped samples, verify the integrity of the custody seals, and certify that the sample identification numbers match those on the COC record. The custodian will then enter sample identification number data into a bound logbook, which is arranged by a project code and station number. If containers arrive with broken custody seals, the laboratory will note this on the COC record and immediately notify the sampler who will, in turn, notify the QA manager and the LAI project manager.

6.4 Analytical Methods

Laboratory methods and target PQLs for all potential analyses of soil and water are summarized in Table B-3. Samples collected and analyzed as part of the RI will be reported to the PQL, and in those instances when the PQL is greater than the SL, the SL will be raised to the PQL.

For all groundwater analyses except dissolved metals, suspended material in the sample may be allowed to settle prior to analysis of the supernatant. For the dissolved metals analyses, the samples will be filtered in the field to remove any suspended material.

Sample containers, preservation, and holding times are provided in Table B-4.

6.5 Quality Control

Field and analytical laboratory control samples will be collected and analyzed to evaluate data precision, accuracy, representativeness, comparability, completeness, bias, and sensitivity of the analytical results for this investigation. The quality control samples and the frequency at which they will be collected and/or analyzed by matrix and analysis is summarized in Table B-2. The evaluation of these quality control samples is further discussed in Section 8.

6.6 Instrument/Equipment/Consumables

To ensure that field measurement is accomplished accurately, field equipment undergoes routine maintenance and calibration as described below.

6.6.1 Testing, Inspection, and Maintenance

LAI performs routine inspections and preventive maintenance (parts replacement and cleaning) for all pieces of field equipment in our supply and equipment room. Maintenance activities are conducted by our field technicians, who are specifically trained in the use, operation, and maintenance of the equipment. All field equipment used during this project, which may include water level indicators, photoionization detectors (PIDs), and water field parameter meters (e.g., pH), will be cleaned and decontaminated prior to use. Each piece of equipment will be inspected and tested to ensure proper working function and facilitate replacement or repair of broken or non-operational components. Extra batteries will be included in the equipment cases or in field vehicles for replacing dead batteries during field work. Extra disposables will be packed for equipment requiring disposables for use, such as ferrous iron kits.

Field equipment is maintained by the field equipment manager. Field staff continually notify the field equipment manager when equipment maintenance is needed. This system ensures the equipment is maintained and working for the next field project. Equipment will be repaired or replaced, as needed.

Meters used to make field measurements will be further inspected and tested during calibration, as described in the next section.

6.6.2 Calibration and Frequency

All field equipment is calibrated according to the manufacturers' guidelines and recommendations. If a PID is used during this project, it will be calibrated on a daily basis according to the manufacturer's specifications. The PID preferred by LAI field personnel uses a 10.2-eV (electron volt) probe and is

calibrated using a manufacturer-supplied standard gas (isobutylene, equivalent to 34 parts per million benzene). Similarly, water field parameter meters will be calibrated at the start of each sampling day with laboratory-prepared calibration standards within the range of the anticipated measurement. An instrument will also be recalibrated at any time an anomalous reading suggests instrument imprecision or inaccuracy.

6.6.3 Inspection/Acceptance of Supplies and Consumables

Supplies are ordered and maintained by the field equipment manager. Disposables and consumables include nitrile gloves, Ziploc® bags for sample ice, field test kits, and polyethylene tubing.

6.7 Data Management

All laboratory analytical results, including QC data, will be submitted electronically. Electronic formats will include a PDF file of the laboratory report, and electronic data deliverable (EDD) files that will be uploaded directly to an Environmental Quality Information Systems (EQuIS) database; the data management team will supply the required format for the EDDs. EQuIS EDDs will be provided by the laboratory in the EFWEDD format (also known as EQuIS 4-File), using LAI valid values. After validation of the data, any applicable qualifiers will be added to the database.

Field data (groundwater field parameter data and water levels measurements) will be entered into cumulative Excel® spreadsheets and/or the EQuIS database. Data will be verified to determine all entered data are correct and without omissions and errors.

Field notes, including field reports, sampling forms, survey forms, test pit logs, boring logs, and well construction diagrams, will be maintained in the project files. Survey notes will be reduced to provide coordinates and elevations that will be uploaded to the database.

Level II laboratory reports will include the following:

- Case narrative, including adherence to prescribed protocols, non-conformity events, corrective measures, and/or data deficiencies (including initial and continuing instrument calibrations, and explanations for any missed target PQLs)
- Sample analytical results
- Surrogate recoveries
- Matrix spike/matrix spike duplicate results
- Blank spike/blank spike duplicate results
- Laboratory duplicates
- Blank results
- Sample custody (including signed COC records, and laboratory sample receipt forms)
- Analytical responsibility.

7.0 ASSESSMENT AND OVERSIGHT

This section describes assessment and oversight.

7.1 Assessment and Response Actions

Assessments during implementation of the project will include daily communication and updates during field work and data quality review by the LAI project manager and field staff. Response actions to assessed issues will be coordinated between the LAI project manager, field staff, the project manager for Boeing, and involved subcontractors, as appropriate. Data management assessment activities are discussed in greater detail in Section 8.2.4.

If any project non-conformance is considered significant or requires special expertise, corrective action(s) may include the following:

- Reanalyzing the samples, if holding times can be met
- Resampling and analyzing
- Evaluating and amending sampling and analytical procedures
- Accepting data and acknowledging the level of uncertainty or inaccuracy by flagging the data.

8.0 DATA VALIDATION AND USABILITY

This section describes data validation and usability.

8.1 Data Review, Verification, and Validation

All RI data will be verified and validated to determine that the results are acceptable and meet the quality objectives described in Section 3.

Validation of the data will be performed by a data validator with guidance from applicable portions of the National Functional Guidelines for Organic Data Review (EPA 2016b) and the National Functional Guidelines for Inorganic Data Review (EPA 2016a).

All data generated as part of the RI will undergo a Level IIA verification and validation.

EPA Level IIA-equivalent verification and validation elements are presented in Table B-5 and will include the following:

- Verification that the laboratory data package contains all necessary documentation (including COC records; identification of samples received by the laboratory; date and time of receipt of the samples at the laboratory; sample conditions upon receipt at the laboratory; date and time of sample analysis; and, if applicable, date of extraction, definition of laboratory data qualifiers, all sample-related QC data, and QC acceptance criteria)
- Verification that all requested analyses, special cleanups, and special handling methods were conducted
- Verification that QC samples were analyzed per the method and frequency specified in the QAPP
- Evaluation of sample holding times
- Evaluation of QC data compared to acceptance criteria, including field QC samples (field duplicates, trip blanks, and/or equipment blanks) and laboratory QC samples (method blanks, surrogate recoveries, laboratory duplicate and/or replicate results, and LCS results)
- Verification that PQLs for target analytes are at or below the target PQLs specified in the QAPP.

In the event that a portion of the data is outside the DQO limits or the EPA guidance (EPA 2016a, b), or sample collection and/or documentation practices are deficient, corrective action(s) will be initiated. Corrective action, as described in Section 7.1, may include any of the following:

- Rejection of the data and resampling
- Qualification of the data
- Modified field and/or laboratory procedures.

8.2 Verification and Validation Methods

The processes that will be used to verify and validate data are described in the sections below.

8.2.1 Data Verification Methods

This section describes data verification methods.

8.2.1.1 Chain of Custody

COC forms will be reviewed by field personnel upon completion of sampling, who will verify information against the packed sample coolers they represent. A copy of the COC form will be retained in the electronic project files, and the original and remaining copies will be taped inside the cooler for delivery to the analytical laboratory.

8.2.1.2 Corrective Actions

The corrective action process may be initiated by any project team member. The process consists of identifying a problem, acting to eliminate the problem, documenting the corrective action, monitoring the effectiveness of the corrective action, and verifying that the problem has been sufficiently addressed. The LAI field lead will be responsible for correcting and resolving situations in the field that may result in non-compliance with the QAPP. Corrective measures identified by the field lead will be immediately documented in the field notes. Examples of corrective actions for field measurements may include: repetition of a measurement to check the error, check for proper adjustments for ambient conditions, check of batteries, recalibration, replacement of instruments, revisions to COCs forms, and (if necessary) stop work. Laboratory project managers are responsible for ensuring that corrective action processes as identified in their quality systems manuals, SOPs, and this QAPP are followed. The laboratory project manager is responsible for notifying the LAI QA manager of any non-conformance. If a corrective action is initiated at the laboratory, it shall be narrated in the laboratory data package. Technical staff will be responsible for reporting any QA non-conformance or suspected deficiencies they identify to the LAI project manager, who will in turn notify the LAI QA manager. The LAI QA manager is responsible for assessing the suspected deficiency or non-conformance and its potential to impact data quality.

If corrective actions are required, a copy of the documented corrective action taken will be maintained in the electronic project files. At the completion of the sampling event, the LAI QA officer and the LAI project manager will ensure all appropriate corrective actions have been taken and that the corrective action reports have been included in the electronic project files; if corrective actions have not been taken, the project manager will ensure action is taken.

8.2.1.3 Field Notes

Field notes will be reviewed internally and placed in the electronic project files.

8.2.1.4 Analytical Data Packages

All laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal.

All laboratory data packages, with the exception of waste characterization samples, will be verified by a data validator who is not associated with the collection or analysis of samples, interpretation of sample data, or with any decision-making process within the scope of the investigation.

The data validator will conduct an EPA Level IIA-equivalent validation and verification, which will be performed with guidance from applicable portions of the National Functional Guidelines for Organic Data Review (EPA 2016b) and the National Functional Guidelines for Inorganic Data Review (EPA 2016a). Additional information regarding the data validation process is provided in the following sections.

8.2.2 Data Validation Methods

Validation of the analytical data will include the criteria listed below. Validation procedures will be followed to ensure data are evaluated properly, completely, and consistently for use in meeting DQOs.

The data validator (unless noted otherwise) will complete the following:

- Data deliverables: Ensure all required verified information on sampling and analysis has been made available as part of data validation (see Section 8.2.1; this also includes associated planning documents [i.e., work plan, SAP, or QAPP]).
- Analytes: Ensure the required list of analytes was reported as specified in the planning documents.
- COC: Review the COC form for traceability of the data from sample collection through to data reporting.
- Holding times: Ensure samples were analyzed within specified holding times (i.e., method, procedure, or planning document). If holding times were not met, confirm the laboratory has documented any deviations and made appropriate notifications to the project team, and that approval to proceed was received prior to analysis.
- Sample handling: Ensure sample handling, receipt, and storage procedures were followed, with any deviations documented.
- Sampling methods and procedures: Establish that required sampling methods were used and any deviations documented. Ensure the sampling procedures and field measurements met performance criteria and any deviations were documented.
- Field transcription: Authenticate transcription accuracy of field data (i.e., from field forms to report tables).

- Analytical methods and procedures: Establish that required analytical methods were used, with any deviations documented. Ensure QC samples met performance criteria, with any deviations documented.
- Data qualifiers: Determine laboratory data qualifiers were defined and applied as specified (i.e., method, procedure, or planning document).
- Laboratory transcription: Authenticate accuracy of transcription of analytical data (i.e., instrument to the Laboratory Information Management System, or laboratory notebook to reporting form).
- Standards: Determine that standards are traceable and meet requirements (method, procedure, or planning document).
- Communication: Confirm required communication procedures were followed by field and/or laboratory personnel.
- Audits: Review laboratory audit reports, accreditation, and certification records for the laboratory's performance on specific methods; review field forms to verify compliance with work plan and QAPP procedures.

8.2.3 Data Validation Review and Data Qualification

For Level IIA data validation, data quality will be assessed by comparing QC parameters to the appropriate criteria (i.e., limits) as specified in the planning documents (i.e., work plan, SAP, QAPP).

Analytical data may be qualified based on the data validation review. Qualifiers will be consistent with applicable EPA National Functional Guidelines and will be used to provide data users with an estimate of the level of uncertainty associated with the qualified result.

Data validation results will be evaluated with respect to assigned qualifiers to determine any data usability issues. The following qualifiers may be assigned during the data validation process:

J Indicates the analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

NJ The analyte has been "tentatively identified" or "presumptively identified" as present and the associated numerical value is the estimated concentration in the sample.

R The data are unusable. The sample results are rejected due to serious deficiencies in meeting QC criteria. The analyte may or may not be present in the sample.

U The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

UJ The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.

The objectives, evaluations, and actions employed during the data validation process will be guided by EPA National Functional Guidelines. Laboratories will be permitted to provide CLP-like forms in lieu of

original CLP forms. The data validation criteria will not strictly adhere to national functional guidelines, but will also take into consideration method criteria for preservation and holding times; laboratory-specified criteria for surrogate, laboratory control samples, laboratory duplicates, and matrix spikes; and the data validator's professional judgment.

9.0 PROJECTS USING EXISTING DATA

Because the Boeing Developmental Center RI is part of an ongoing program, secondary data may be used to evaluate performance and concentration trends. Historical data will be considered usable for the decisions being made on this project.

10.0 USE OF THIS QUALITY ASSURANCE PROJECT PLAN

This Quality Assurance Project Plan has been prepared for the exclusive use of The Boeing Company and applicable regulatory agencies for specific application to the Boeing Developmental Center in Tukwila, Washington. No other party is entitled to rely on the information, conclusions, and recommendations included in this document without the express written consent of LAI. Further, the reuse of information, conclusions, and recommendations provided herein for extensions of the project or for any other project, without review and authorization by LAI, shall be at the user's sole risk. LAI warrants that within the limitations of scope, schedule, and budget, our services have been provided in a manner consistent with that level of care and skill ordinarily exercised by members of the profession currently practicing in the same locality under similar conditions as this project. We make no other warranty, either express or implied.

11.0 REFERENCES

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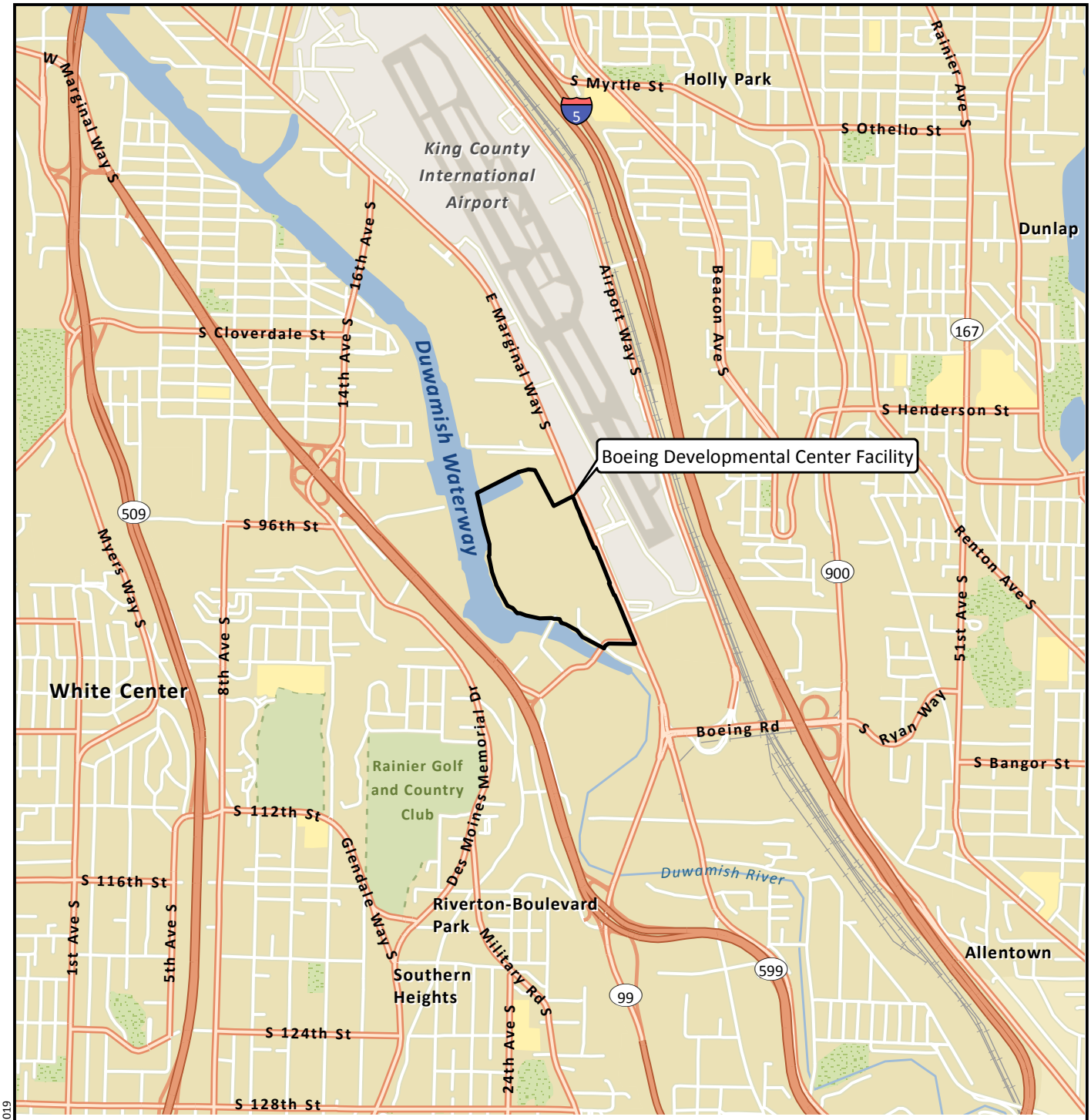


Data Source: Esri 2012

G:\Projects\025\093\118\112\F01 VicinityMap.mxd 8/2/2019

LANDAU ASSOCIATES

Boeing Developmental Center Tukwila, Washington	**Vicinity Map**	Figure **B-1**

G:\Projects\025\093\118\112\F02 FacilityMap.mxd 8/2/2019

Legend

Facility Boundary

0 300 600

Scale in Feet

Data Sources: Boeing; Esri World Imagery.

Note

1. Black and white reproduction of this color original may reduce its effectiveness and lead to incorrect interpretation.

LANDAU ASSOCIATES

Boeing Developmental Center Tukwila, Washington	**Facility Map**	Figure B-2

Table B-1
Key Personnel Project Responsibilities
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

Name	Title/Role	Organization Affiliation	Responsibilities
Lindsey Erikson	Project Manager	The Boeing Company	Manages the project for The Boeing Company.
Byung Maeng	Project Manager	Washington State Department of Ecology	Manages the project for the Washington State Department of Ecology.
Ken Reid	Consultant Project Manager	Landau Associates, Inc.	Supervises and coordinates all work for the project. These responsibilities include project planning and execution, scheduling, staffing, data evaluation, report preparation, subcontracts, and managing deliverables.
Danille Jorgensen	Quality Assurance Officer	Landau Associates, Inc.	Oversees and directs quality assurance (QA) reviews for the project, including periodic reports, analytical program requirements, and schedules before submittal to the US Environmental Protection Agency for review and comment. Responsible for inputting all field data and the maintenance of the database.
Kristi Schultz	Data Specialist	Landau Associates, Inc.	Reviews laboratory analytical data and provides data validation. Has oversight responsibility for management and integrity of the data.
Chris Kimmel	Site Health & Safety Manager	Landau Associates, Inc.	Responsible for review and implementation of the Health and Safety Plan (HASP).
Kelly Bottem	Laboratory Project Manager	Analytical Resources, Inc.	Manages laboratory analysis and reporting.

Table B-2
Data Quality Objectives
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

DQI	QC Sample or Activity Used to Assess MQO	MQO	Frequency	Sampling or Analytical DQI
Soil Samples Analyzed for Gasoline-Range Petroleum Hydrocarbons by Method NWTPH-Gx				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <35%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank, Trip Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S
Soil Samples Analyzed for Diesel- and Motor Oil-Range Petroleum Hydrocarbons by Method NWTPH-Dx				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <35%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S
Soil Samples Analyzed for Total Metals by SW-846 6010C				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Accuracy	LCS	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/Laboratory Duplicate	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <35%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S

Table B-2
Data Quality Objectives
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

DQI	QC Sample or Activity Used to Assess MQO	MQO	Frequency	Sampling or Analytical DQI
Soil Samples Analyzed for Volatile Organic Compounds by SW-846 8260D				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Bias/Contamination	Method Blank, Trip Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S
Soil Samples Analyzed for Polychlorinated Biphenyls by SW-846 8082A				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <35%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S
Water Samples Analyzed for Gasoline-Range Petroleum Hydrocarbons by Method NWTPH-Gx				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <20%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank, Trip Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S

Table B-2
Data Quality Objectives
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

DQI	QC Sample or Activity Used to Assess MQO	MQO	Frequency	Sampling or Analytical DQI
Water Samples Analyzed for Diesel- and Motor Oil-Range Petroleum Hydrocarbons by Method NWTPH-Dx				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <20%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S
Water Samples Analyzed for Total or Dissolved Metals by EPA Methods SW-846 6010C/7471A				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Accuracy	LCS	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/Laboratory Duplicate	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <20%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S
Water Samples Analyzed for Volatile Organic Compounds by SW-846 8260D				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Bias/Contamination	Method Blank, Trip Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S

Table B-2
Data Quality Objectives
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

DQI	QC Sample or Activity Used to Assess MQO	MQO	Frequency	Sampling or Analytical DQI
Water Samples Analyzed for Polycyclic Aromatic Hydrocarbons by SW-846 8270E-SIM				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <20%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S
Water Samples Analyzed for Polychlorinated Biphenyls by SW-846 8082A				
Representativeness	Cooler Temperature	<6°C	All project samples	S
Bias	Surrogates	Recoveries within laboratory-specified control limits	All project and QA samples	A
Accuracy	LCS/LCSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Precision	LCS/LCSD and MS/MSD	RPDs within laboratory-specified control limits	1 per 20 samples or one per analytical batch	A
Method performance for matrix, bias	MS/MSD	Recoveries within laboratory-specified control limits	1 per 20 samples or one per analytical batch	S&A
Precision	Field Duplicates	RPD <20%	1 per 20 samples or one per analytical group	S&A
Bias/Contamination	Method Blank	Target analytes not detected at concentrations >1/2 the PQL	1 method blank per 20 samples, 1 every 12 hours, or 1 per analytical batch	S&A
Analytical Completeness	Number of usable (not rejected) results out of total number of results	90%	NA	S&A
Field Completeness	Number of samples collected out of planned samples	95%	NA	S

Abbreviations/Acronyms:

% = percent
°C = degrees Celsius
A = analytical
DQI = data quality indicator
LCS = laboratory control spike
LCSD = laboratory control spike duplicate
MQO = measurement quality objective
MS = matrix spike
MSD = matrix spike duplicate
NA = not applicable
PQL = practical quantitation limit
QA = quality assurance
QC = quality control
RPD = relative percent difference
S = sampling
SIM = Selected Ion Monitoring

Table B-3
Soil and Groundwater Targeted Practical Quantitation Limits
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

		Soil (a)					Groundwater				
Analyte	CAS No.	2002 Preliminary Screening Level	Lower Duwamish Waterway Preliminary Cleanup Level (PCUL) (b)	Laboratory PQLs (c)	Proposed Screening Level (d)	Units	2013 Proposed Cleanup Level	Duwamish Waterway Preliminary Cleanup Level (PCUL) (e)	Laboratory PQLs (b)	Proposed Screening Level (d)	Units
Total Petroleum Hydrocarbons		NWTPH-Gx					NWTPH-Gx				
Gasoline Range	86290-81-5	100 (f)	30	5.0	30	mg/kg	800	--	100	800	µg/L
		NWTPH-Dx					NWTPH-Dx				
Diesel Range	N/A	2,000 (f)	260	5.00	260	mg/kg	--	--	100	500 (g)	µg/L
Motor Oil Range	N/A	--	2,000	10.0	2,000	mg/kg	--	--	200	500 (g)	µg/L
Total Metals		Method 6010C/6020A					Method 6020A/7470A				
Arsenic	7440-38-2	7	7.0	5.00	7.0	mg/kg	8.0	8.0	0.2	8.0	µg/L
Barium	7440-39-3	--	--	--	--	--	--	200	0.5	200	µg/L
Cadmium	7440-43-9	--	--	--	--	--	--	1.2	0.1	1.2	µg/L
Chromium, Total	7440-47-3	--	--	--	--	--	--	--	0.5	--	µg/L
Copper	7440-50-8	36	36	0.5	36	mg/kg	8.0	3.1	0.5	3.1	µg/L
Lead	7439-92-1	--	--	--	--	--	--	8.1	0.1	8.1	µg/L
Mercury	7439-97-6	--	--	--	--	--	--	0.025	0.1	0.1	µg/L
Zinc	7440-66-6	100	86	4.0	86	mg/kg	--	81	4.0	81	µg/L
Dissolved Metals							Method 6020A/7470A				
Arsenic	7440-38-2	--	--	--	--	--	8.0	8.0	0.2	8.0	µg/L
Barium	7440-39-3	--	--	--	--	--	--	200	0.5	200	µg/L
Cadmium	7440-43-9	--	--	--	--	--	--	1.2	0.1	1.2	µg/L
Chromium, Total	7440-47-3	--	--	--	--	--	--	--	0.5	--	µg/L
Copper	7440-50-8	--	--	--	--	--	8.0	3.1	0.5	3.1	µg/L
Lead	7439-92-1	--	--	--	--	--	--	8.1	0.1	8.1	µg/L
Mercury	7439-97-6	--	--	--	--	--	--	0.025	0.1	0.1	µg/L
Zinc	7440-66-6	--	--	--	--	--	--	81	4.0	81	µg/L
Volatile Organic Compounds		Method EPA 8260C/D					Method EPA 8260C/D				
1,1,1,2-Tetrachloroethane	630-20-6	--	38,000	1.00	38,000	µg/kg	--	7.4	0.200	7.4	µg/L
1,1,1-Trichloroethane	71-55-6	3,300,000	370,000	1.00	370,000	µg/kg	--	5,500	0.200	5,500	µg/L
1,1,2,2-Tetrachloroethane	79-34-5	--	1.7	1.00	1.7	µg/kg	--	0.3	0.200	0.3	µg/L
1,1,2-Trichloroethane	79-00-5	230	5.0	1.00	5.0	µg/kg	--	0.9	0.200	0.9	µg/L
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	--	2,400,000,000	2.00	2,400,000,000	µg/kg	--	180	0.200	180	µg/L
1,1-Dichloroethane	75-34-3	350,000,000	180,000	1.00	180,000	µg/kg	--	11	0.200	11	µg/L
1,1-Dichloroethene	75-35-4	20	25,000	1.00	20	µg/kg	2,300	130	0.200	130	µg/L
1,2,3-Trichlorobenzene	87-61-6	--	20,000	5.00	20,000	µg/kg	--	--	0.500	--	µg/L
1,2,3-Trichloropropane	96-18-4	--	33	2.00	33	µg/kg	--	--	0.500	--	µg/L
1,2,4-Trichlorobenzene	120-82-1	--	1.4	5.00	5.00	µg/kg	--	0.037	0.500	0.500	µg/L
1,2,4-Trimethylbenzene	95-63-6	--	800,000	1.00	800,000	µg/kg	--	240	0.200	240	µg/L
1,2-Dibromo-3-chloropropane	96-12-8	--	1,250	5.00	1,250	µg/kg	--	--	0.500	--	µg/L
1,2-Dichlorobenzene	95-50-1	--	36	1.00	36	µg/kg	--	4.6	0.200	4.6	µg/L
1,2-Dichloroethane	107-06-2	480	350	1.00	350	µg/kg	--	4.2	0.200	4.2	µg/L
1,2-Dichloropropane	78-87-5	--	16	1.00	16	µg/kg	--	3.1	0.200	3.1	µg/L
1,3,5-Trimethylbenzene	108-67-8	--	800,000	1.00	800,000	µg/kg	--	--	0.200	--	µg/L
1,3-Dichlorobenzene	541-73-1	--	--	1.00	--	µg/kg	--	2.0	0.200	2.0	µg/L
1,3-Dichloropropane	142-28-9	--	--	1.00	--	µg/kg	--	--	0.200	--	µg/L
1,4-Dichlorobenzene	106-46-7	--	110	1.00	110	µg/kg	--	4.9	0.200	4.9	µg/L
2-Butanone	78-93-3	2,100,000,000	48,000,000	5.00	48,000,000	µg/kg	--	1,700,000	5.00	1,700,000	µg/L
2-Chlorotoluene	95-49-8	--	1,600,000	1.00	1,600,000	µg/kg	--	--	0.200	--	µg/L

Table B-3
Soil and Groundwater Targeted Practical Quantitation Limits
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

		Soil (a)					Groundwater				
Analyte	CAS No.	2002 Preliminary Screening Level	Lower Duwamish Waterway Preliminary Cleanup Level (PCUL) (b)	Laboratory PQLs (c)	Proposed Screening Level (d)	Units	2013 Proposed Cleanup Level	Duwamish Waterway Preliminary Cleanup Level (PCUL) (e)	Laboratory PQLs (b)	Proposed Screening Level (d)	Units
2-Hexanone	591-78-6	--	400,000	5.00	400,000	µg/kg	--	--	5.00	--	µg/L
4-Chlorotoluene	106-43-4	--	--	1.00	--	µg/kg	--	--	0.200	--	µg/L
4-Isopropyltoluene	99-87-6	--	--	1.00	--	µg/kg	--	--	0.200	--	µg/L
4-Methyl-2-Pentanone (MIBK)	108-10-1	--	6,400,000	5.00	6,400,000	µg/kg	--	470,000	5.00	470,000	µg/L
Acetone	67-64-1	350,000,000	72,000,000	5.00	72,000,000	µg/kg	110,000	--	5.00	110,000	µg/L
Benzene	71-43-2	220,000	8.8	1.00	8.8	µg/kg	2.0	1.6	0.200	1.6	µg/L
Bromobenzene	108-86-1	--	640,000	1.00	640,000	µg/kg	--	--	0.200	--	µg/L
Bromochloromethane	74-97-5	--	--	1.00	--	µg/kg	--	--	0.200	--	µg/L
Bromodichloromethane	75-27-4	--	15	1.00	15	µg/kg	--	1.8	0.200	1.8	µg/L
Bromoethane	74-96-4	--	--	2.00	--	µg/kg	--	--	0.200	--	µg/L
Bromoform	75-25-2	--	78	1.00	78	µg/kg	--	12	0.200	12	µg/L
Bromomethane	74-83-9	--	1,200	1.00	1,200	µg/kg	--	13	1.00	13	µg/L
Carbon Disulfide	75-15-0	350,000,000	8,000,000	1.00	8,000,000	µg/kg	3,900	400	0.200	400	µg/L
Carbon Tetrachloride	56-23-5	--	2.9	1.00	2.9	µg/kg	--	0.35	0.200	0.35	µg/L
Chlorobenzene	108-90-7	--	1,700	1.00	1,700	µg/kg	--	200	0.200	200	µg/L
Chloroethane	75-00-3	--	--	1.00	--	µg/kg	--	19,000	0.200	19,000	µg/L
Chloroform	67-66-3	2,500	806	1.00	806	µg/kg	9.4	1.2	0.200	1.2	µg/L
Chloromethane	74-87-3	--	--	1.00	--	µg/kg	--	150	0.500	150	µg/L
cis-1,2-Dichloroethene	156-59-2	350,000,000	160,000	1.00	160,000	µg/kg	130	--	0.200	130	µg/L
cis-1,3-Dichloropropene	10061-01-5	--	11	1.00	11	µg/kg	--	2.0	0.200	2.0	µg/L
Dibromochloromethane	124-48-1	--	12	1.00	12	µg/kg	--	2.2	0.200	2.2	µg/L
Dibromomethane	74-95-3	--	800,000	1.00	800,000	µg/kg	--	--	0.200	--	µg/L
Ethylbenzene	100-41-4	250,000	260	1.00	260	µg/kg	1.7	31	0.200	1.7	µg/L
Ethylene Dibromide (1,2-Dibromoethane)	106-93-4	--	500	1.00	500	µg/kg	--	0.27	0.200	0.27	µg/L
Hexachlorobutadiene	87-68-3	--	11	5.00	11	µg/kg	--	0.01	0.500	0.500	µg/L
Iodomethane	74-88-4	--	--	1.00	--	µg/kg	--	--	1.00	--	µg/L
Isopropylbenzene	98-82-8	--	8,000,000	1.00	8,000,000	µg/kg	270	--	0.200	270	µg/L
m,p-Xylene	179601-23-1	7,000,000,000	16,000,000	2.00	16,000,000	µg/kg	1,500 (h)	--	0.400	1,500 (h)	µg/L
Methylene Chloride	75-09-2	7,000	430	2.00	430	µg/kg	--	100	1.00	100	µg/L
Naphthalene	91-20-3	140,000	40	5.00	40	µg/kg	26	1.4	0.500	1.4	µg/L
n-Butylbenzene	104-51-8	--	4,000,000	1.00	4,000,000	µg/kg	--	--	0.200	--	µg/L
n-Propylbenzene	103-65-1	--	8,000,000	1.00	8,000,000	µg/kg	--	--	0.200	--	µg/L
o-Xylene	95-47-6	7,000,000,000	16,000,000	1.00	16,000,000	µg/kg	1,500 (h)	430	0.200	430	µg/L
sec-Butylbenzene	135-98-8	--	8,000,000	1.00	8,000,000	µg/kg	--	--	0.200	--	µg/L
Styrene	100-42-5	4,400,000	300,000	1.00	300,000	µg/kg	--	8,200	0.200	8,200	µg/L
tert-Butylbenzene	98-06-6	--	8,000,000	1.00	8,000,000	µg/kg	--	--	0.200	--	µg/L
Tetrachloroethene	127-18-4	100	30	1.00	30	µg/kg	5.3	2.9	0.200	2.9	µg/L
Toluene	108-88-3	1,450,000	920	1.00	920	µg/kg	1,300	130	0.200	130	µg/L
Total Xylenes	1330-20-7	--	16,000,000	2.00	16,000,000	µg/kg	1,500	330	0.600	330	µg/L
trans-1,2-Dichloroethene	156-60-5	180,000	5,200	1.00	5,200	µg/kg	940	1,000	0.200	940	µg/L
trans-1,3-Dichloropropene	10061-02-6	--	10	1.00	10	µg/kg	--	2.0	0.200	2.0	µg/L
trans-1,4-Dichloro 2-Butene	110-57-6	--	--	5.00	--	µg/kg	--	--	1.00	--	µg/L
Trichloroethene	79-01-6	540	4.4	1.00	4.4	µg/kg	1.4	0.7	0.200	0.7	µg/L
Trichlorofluoromethane	75-69-4	--	24,000,000	1.00	24,000,000	µg/kg	--	120	0.200	120	µg/L
Vinyl Acetate	108-05-4	--	80,000,000	5.00	80,000,000	µg/kg	--	7,800	0.200	7,800	µg/L
Vinyl Chloride	75-01-4	3,300	1.0	1.00	1.0	µg/kg	2.4	0.18	0.200	0.18	µg/L
PAHs							EPA Method 8270D/E SIM				
1-Methylnaphthalene	90-12-0	--	--	--	--	--	--	--	0.0100	--	µg/L

Table B-3
Soil and Groundwater Targeted Practical Quantitation Limits
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

		Soil (a)					Groundwater				
Analyte	CAS No.	2002 Preliminary Screening Level	Lower Duwamish Waterway Preliminary Cleanup Level (PCUL) (b)	Laboratory PQLs (c)	Proposed Screening Level (d)	Units	2013 Proposed Cleanup Level	Duwamish Waterway Preliminary Cleanup Level (PCUL) (e)	Laboratory PQLs (b)	Proposed Screening Level (d)	Units
2-Methylnaphthalene	91-57-6	--	--	--	--	--	--	--	0.0100	--	µg/L
Acenaphthene	83-32-9	--	--	--	--	--	--	5.3	0.0100	5.3	µg/L
Acenaphthylene	208-96-8	--	--	--	--	--	--	--	0.0100	--	µg/L
Anthracene	120-12-7	--	--	--	--	--	--	2.1	0.0100	2.1	µg/L
Benzo(a)anthracene	56-55-3	--	--	--	--	--	--	0.00016	0.0100	0.0100	µg/L
Benzo(a)pyrene	50-32-8	--	--	--	--	--	--	0.000016	0.0100	0.0100	µg/L
Benzo(g,h,i)perylene	191-24-2	--	--	--	--	--	--	--	0.0100	--	µg/L
Benzofluoranthenes, Total	N/A	--	--	--	--	--	--	--	0.0100	--	µg/L
Chrysene	218-01-9	--	--	--	--	--	--	0.016	0.0100	0.016	µg/L
Dibenz(a,h)anthracene	53-70-3	--	--	--	--	--	--	0.000016	0.0100	0.0100	µg/L
Dibenzofuran	132-64-9	--	--	--	--	--	--	--	0.0100	--	µg/L
Fluoranthene	206-44-0	--	--	--	--	--	--	1.8	0.0100	1.8	µg/L
Fluorene	86-73-7	--	--	--	--	--	--	3.7	0.0100	3.7	µg/L
Indeno(1,2,3-cd)pyrene	193-39-5	--	--	--	--	--	--	0.00016	0.0100	0.0100	µg/L
Naphthalene	91-20-3	--	--	--	--	--	--	1.4	0.0100	1.4	µg/L
Phenanthrene	85-01-8	--	--	--	--	--	--	--	0.0100	--	µg/L
Pyrene	129-00-0	--	--	--	--	--	--	2.0	0.0100	2.0	µg/L
cPAH TEQ (i)	N/A	--	--	--	--	--	--	0.000016	--	0.0100	µg/L
PCBs		EPA Method 8082A					EPA Method 8082A				
Aroclor 1016	12674-11-2	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Aroclor 1242	53469-21-9	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Aroclor 1248	12672-29-6	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Aroclor 1254	11097-69-1	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Aroclor 1260	11096-82-5	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Aroclor 1221	11104-28-2	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Aroclor 1232	11141-16-5	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Aroclor 1268	11100-14-4	--	--	4.00	--	µg/kg	--	--	0.0100	--	µg/L
Total PCBs	--	330	0.000027	--	0.000027	µg/kg	--	0.000007	--	0.0100	µg/L

Abbreviations and Acronyms:

-- = not applicable
µg/kg = micrograms per kilogram
µg/L = micrograms per liter
CAS = Chemical Abstracts Services
EPA = US Environmental Protection Agency
MDL = method detection limit
mg/kg =milligrams per kilogram
mg/L = milligrams per liter
N/A = not available
PAH = polycyclic aromatic hydrocarbon
PCB = polychlorinated biphenyls
PQL = practical quantitation limit
SIM = selected ion monitoring
SL = screening level

Notes:

(a) Soil results and associated laboratory practical quantitation limits will be reported on a dry weight basis.

(b) Lower Duwamish Waterway preliminary cleanup levels for nonpotable vadose zone (April 2019).

(c) Laboratory practical quantitation limits are defined as the lowest concentrations that can be accurately detected by the analytical method.

(d) The proposed screening level is selected as the lower of the Lower Duwamish Waterway PCUL or proposed 2013 proposed cleanup levels. In those instances when the laboratory PQL is greater than either of these two values, the proposed screening level is raised to the laboratory PQL.

(e) Lower Duwamish Waterway preliminary cleanup levels for nonpotable groundwater (April 2019).

(f) Model Toxics Control Act Method A industrial value.

(g) Model Toxics Control Act Method A cleanup level.

(h) 2013 proposed cleanup level for total xylenes.

(i) If one or more of the cPAHs has never been detected in any sample at the site, then a value of zero will be assigned to a non-detected concentration of that cPAH for these calculations. If a cPAH is not detected in a sample but has been detected at the site a value of one-half the reporting limit will be assigned to that cPAH for the purpose of the TEQ calculation.

Table B-4
Sample Containers, Preservatives, and Holding Times
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

Matrix	Method	Container	Preservative	Holding Time (a)	Laboratory Performing Analyses
Soil	Gasoline-range Petroleum Hydrocarbons by NWTPH-Gx	2 x 40-mL glass	Methanol	14	ARI
Groundwater	Gasoline-range Petroleum Hydrocarbons by NWTPH-Gx	40-mL glass	<6°C; Add HCl to pH<2	14	ARI
Soil	Diesel- and Oil-range Petroleum Hydrocarbons by NWTPH-Dx	8 oz wide-mouth glass	<6°C	14 days/40 days	ARI
Groundwater	Diesel- and Oil-range Petroleum Hydrocarbons by NWTPH-Dx	2 x 500-mL amber glass	<6°C	7 days/40 days	ARI
Soil	Total Metals by SW-846 6010C	4 oz wide-mouth glass	<6°C	180	ARI
Groundwater	Total/Dissolved Metals by SW-846 6010C	500 mL high density polyethylene	<6°C; Total metals or field filtered, HNO_3 to pH <2	180	ARI
Groundwater	Total/Dissolved Mercury by SW-846 7471B	500 mL high density polyethylene	<6°C; Total metals or field filtered, 5 mL 1:1 HNO_3	28	ARI
Soil	VOCs by SW-846 8260D	40-mL amber glass	<6°C; $NaHSO_4$ (2 vials), Methanol (2 vials)	14 days	ARI
Groundwater	VOCs by SW-846 8260D	40-mL glass, no headspace	<6°C; HCl to pH<2 (b)	14 days (7 days unpreserved or pH >2)	ARI
Groundwater	PAHs by SW-846 8270E-SIM	2 x 500-mL amber glass	<6°C	7 days/40 days	ARI
Soil	PCBs by SW-846 8082A	8 oz wide-mouth glass	<6°C	365 days/40 days	ARI
Groundwater	PCBs by SW-846 8082A	2 x 500-mL amber glass	<6°C	365 days/40 days	ARI

Acronyms/Abbreviations:

°C = degrees Celsius
ARI = Analytical Resources, Inc.
HCl = Hydrochloric acid
HNO_3 = nitric acid
mL = milliliter
$NaHSO_4$ = sodium hydrogen sulfate
oz = ounces
PAH = polycyclic aromatic hydrocarbon
PCB = polychlorinated biphenyl
SIM = selected ion monitoring
VOC = volatile organic compound

Notes:

(a) Time from sample collection to extraction/time from sample extraction to analysis.
(b) Analysis of acid-reactive volatiles (if applicable) must be completed from unpreserved samples per the analytical method.

Table B-5
Data Validation Elements
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

QC Element	Evaluation Criteria	Qualification	Comments
Case Narrative	A case narrative shall be included with all laboratory packages.	Depending on issues presented in case narrative, additional qualification to the data may be warranted.	
Chain of Custody	A COC shall be included with all laboratory packages.	If discrepancies are noted on the COC, then the laboratory report may be revised to correct any issues.	
Preservation	Preservation conditions as noted in laboratory report are compared to method-specified requirements.	Depending on the preservation issue, data may be qualified as estimated (J/UJ) or rejected.	
Headspace	VOA vials should be free of headspace and air bubbles.	If sample was analyzed from a vial that contained headspace or bubbles, data will be qualified as estimated (J/UJ).	Applicable only to VOAs.
Sample Filtration	Samples that are field filtered shall be identified as such on the COC. Filtered metals will be reported as dissolved fraction.	If discrepancies are identified or problems with filtration are noted, then a revised lab report may be issued.	Applicable only to dissolved metals.
Holding Times	Holding times are compared to method-specified hold times.	If hold times are exceeded, then all results for the method are qualified as estimated (J/UJ). If hold times are grossly exceeded, then detected results are qualified as estimated (J) and no detected results are rejected (R).	
Method Blanks	Detections of target analytes should be < PQL for the analyte or < level of acceptable blank contamination specified in the QAPP	If sample result is less than the blank concentration and between MDL and PQL, raise result to PQL and flag "U." If sample result is less than the blank concentration and greater than the PQL, flag "U." Apply method blank results to all samples in the same analytical batch.	

Table B-5
Data Validation Elements
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

QC Element	Evaluation Criteria	Qualification	Comments
Field/Equipment Blanks	Detections of target analytes should be < PQL for the analyte or < level of acceptable blank contamination specified in the QAPP	If sample result is less than the blank concentration and between MDL and PQL, raise result to PQL and flag "U." If sample result is less than the blank concentration and greater than the PQL, flag "U." Apply field blank results to samples with same collection date; apply equipment blank results to samples associated with equipment.	
Trip Blanks	Detections of target analytes should be < PQL for the analyte or < level of acceptable blank contamination specified in the QAPP	If sample result is less than the blank concentration and between MDL and PQL, raise result to PQL and flag "U." If sample result is less than the blank concentration and greater than the PQL, flag "U." Apply trip blank results to samples shipped in the same cooler.	
LCS	Recoveries are compared to laboratory-specified QC limits.	If % is <10%, qualify detected results as estimated (J) and reject nondetected results. If %R is < laboratory-specified QC limits, qualify results as estimated (J/UJ). If %R is > laboratory-specified QC limits, qualify detected results as estimated (J).	
Surrogates	Recoveries are compared to laboratory-specified QC limits.	If % is <10%, qualify detected results as estimated (J) and reject nondetected results. If %R is < laboratory-specified QC limits, qualify results as estimated (J/UJ). If %R is > laboratory-specified QC limits, qualify detected results as estimated (J).	Not applicable for inorganics

Table B-5
Data Validation Elements
Quality Assurance Project Plan
Boeing Developmental Center
Tukwila, Washington

QC Element	Evaluation Criteria	Qualification	Comments
MS	Recoveries are compared to laboratory-specified QC limits.	If % is <10%, qualify detected results as estimated (J) and reject nondetected results. If %R is < laboratory-specified QC limits, qualify results as estimated (J/UJ). If %R is > laboratory-specified QC limits, qualify detected results as estimated (J).	
Laboratory Duplicate or MSD or LCSD	RPDs are compared to laboratory-specified QC limits.	If RPDs exceed laboratory-specified QC limits, then results for the sample that was analyzed in duplicate will be qualified as estimated (J/UJ).	
Dilutions	Results shall be reported within the calibration range of the instrument.	Results reported by the laboratory that are outside the calibration range of the instrument (E-qualified) will be marked as not reportable during data validation. The detected result that is within the calibration range is the reportable result. Nondetected results will be reported from the lowest dilution run.	
Field duplicates	RPDs should be <20% for aqueous samples and <35% for soil samples. For detected results <5 times their PQLs, results should be within +- the PQL.	RPD >20% waters (>35% soils), flag detected results "J." Differences in concentrations > the PQL, flag detected results "J."	

Abbreviations and Acronyms:

% = percent
COC = chain of custody
LCS = laboratory control sample
LCSD = laboratory control sample duplicate
MDL = maximum detection limit
MS = matrix spike
MSD = matrix spike duplicate
PQL = practical quantitation limit
QAPP = Quality Assurance Project Plan
QC = quality control
RPD = relative percent difference
VOA = volatile organic analysis

Notes:

J = The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
U = The analyte was analyzed for but was not detected above the level of the reported sample quantitation limit.
UJ = The analyte was analyzed for but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.

ATTACHMENT B-1

Laboratory Standard Operating Procedures

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Gasoline Range Organics
using
Purge and Trap GC/MS

EPA Method 8260D

SOP 431S
Version 003

Revision Date: 6/27/19
Effective Date: 6/27/19

Prepared by:

Jianqing Zhou / Lani Hertzog / Van Spohn

Approvals:

Brian N. Bebee, Laboratory Section Manager

Bob Congleton, Quality Assurance Manager

Annual Review

SOP Number: 431S

Title: Gasoline Range Organics using Purge and Trap GC/MS

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This document describes the procedures for performing Volatile Gasoline Range Organics used by Analytical Resources Inc. (ARI). The procedures are based on EPA Method 8260D and EPA Method 8000C Revision 3, March 2003 referenced in Section 19.1. Some text is directly from those documents. Additional guidance is taken from EPA Method 8015C Revision 3, February 2007. BETX Volatile Organics and Volatile Gasoline Additives may also be analyzed with this procedure in conjunction with SOP#700S-Volatile Organic Analysis.

1.2. This method is applicable to most environmental sample matrices, including aqueous (ground water, surface water, waste water, TCLP extracts), solid (soil, sediment, sludge), and waste (waste solvent, oily waste, mousse, tar, polymeric emulsion, filter cake, spent carbon, etc.) samples.

1.3. ARI uses several sample preparation techniques to achieve project and/or client specific detection limits. Routine techniques are summarized in Table 01. Other preparation techniques may be employed to meet client requests.

Table 01
Typical GRO Analyzes performed by ARI

Sample Matrix	Sample size	Extraction Technique	Estimated MRL
Water (GRO)	10 mL	Direct Purge & Trap	.25µg/L
Water (BETX)	10 mL	Direct Purge & Trap	0.5µg/L
Solid (GRO)	5 g	Methanol Extraction	500µg/kg
Solid (BETX)	5 g	Methanol Extraction	25µg/kg

1.4. QLS standards are prepared and analyzed with sample batches and are used to statistically determine detection (LOD) and method reporting limits (MRL). QLS spikes are prepared and analyzed quarterly or more frequently, as necessary to establish DL, LOD and MRL.

1.5. This document describes a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2. Summary of the Procedure

2.1. This method requires separate preparation and analysis procedures. Sample preparation is outlined in Section 11.7.4 and 11.7.5. Analysis of prepared sample is accomplished using a Purge & Trap GC-MS instrument described in Section 11.8 through 11.13. The GC-MS system data acquisition, data reduction process and analyte calculations described in this document are performed with Agilent Chemstation Environmental quantitation Software. The formulae are provided for reference and may be used to manually verify calculated results.

2.2. There are two basic sample preparations.

2.2.1. Direct purge and trap where the sample is analyzed with no initial extraction or preparation.

2.2.2. Methanol is used to extract volatile organic compounds which is diluted into organic free water and analyzed.

2.3. Following sample preparation, volatile organic compounds are automatically purged from the sample and injected into the gas chromatograph using a purge-and-trap equipped GC-MS system.

2.3.1. Compounds purged from the sample using Helium are trapped in a tube containing suitable sorbent materials.

2.3.2. The sorbent tube is heated and back flushed with helium to desorb trapped sample components directly onto the GC-MS system following a split to optimize GC performance.

2.4. A narrow bore capillary GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS).

2.5. Quantification of Gas Range Organics is performed by summing up the total RIC response between time ranges determined by hydrocarbon retention time markers. Internal and Surrogate standards eluting within the GRO range are subtracted from the summed response

2.6. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant GC retention times and mass spectra.

2.7. Identified target analytes (BETX and Gasoline Additives) are quantified by comparing the detector responses of each analytes' characteristic mass ion and internal standard characteristic mass ion to the responses of these ions in a calibration curve prepared using analytes at known concentration.

2.8. Detection limits for all analytes quantitated using this SOP are set using the low point of the initial calibration curve and validated by QLS studies.

2.8.1. QLS studies are performed regularly for each analyte by each preparatory and analytical method.

2.8.2. DL, LOD and MRL values may be found for each analyte in ARI's Element LIMS.

3. Definitions

3.1. GRO Retention Time (RT) Marker Standard (C6 thru C15 n-Hydrocarbons) purchased form Absolute Standards, Inc.

3.2. CALGAS: perfluoro-tri-n-butylamine (FC-43), CAS 311-89-7.

3.3. Initial Calibration Verification (ICV): a process used to verify that the current instrument calibration is acceptable.

3.4. Second Source Calibration Verification Standard (SCVS): A standard prepared at the mid-point concentration of the initial calibration and prepared from the same source as the initial calibration.

3.5. Detection Limit (DL) – The lowest result that can reliably be distinguished in a matrix from a blank.

3.6. EICP- Extracted Ion Current Profile- A plot of the abundance of a specific ion as a function of time

3.7. Holding Blank: A blank water sample stored along with client samples. A holding blank is analyzed periodically to determine if there is cross contamination of samples introduced during storage in the laboratory. See Section 16 for contamination of holding blanks.

3.8. Initial Calibration (ICAL): a minimum of 6 points, with 7 points typical.

3.9. Secondary Calibration Verification (SCV): a process used to verify that the current instrument calibration is acceptable.

3.10. Secondary Calibration Verification Standard (SCVS): A mid-point concentration standard from a source different than that used for the initial calibration used to demonstrate the validity of the initial calibration. The SCVS is equivalent to the Second Source Standard. The second source standard must be purchased from a different manufacturer than the calibration standard whenever possible.

3.11. Internal Standard (IS): internal standards are compounds added to each standard, sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of an internal standard.

3.12. Blank Spike (BS): OFW spiked with verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system.

3.13. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, an BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS. ARI fortifies the BS/BSD with all target analytes.

3.14. LIMS (Laboratory Information Management System): Software used to compile and report final chromatographic data.

3.15. Limit of Detection (LOD) – The lowest result that can be reported while meeting method precision and accuracy requirements.

3.16. Method Reporting Limit (MRL) – The lowest result that may be reported unqualified based on the lowest curve point.

3.17. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte(s) to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method. ARI fortifies Matrix Spike samples with all target analytes.

3.18. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision.

3.19. Method Blank (MB): A sample of OFW, free of any analytes of interest that is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures.

3.20. Organic Free Water (OFW): ASTM Type 1 water produced by ARI's centralized water purification system and run through a bed of activated charcoal in the VOA laboratory.

3.21. QLS: Quantitation Limit Standard - A matrix spike prepared at reporting limit, used to determine LOD and MRL.

3.22. RIC- Reconstructed Ion Current- A plot of the total instrument response versus time

3.23. RRT-Relative Retention Time- the elution time of an analyte relative to the elution time of its associated internal standard

3.24. Scan Descriptor: Defines a specific mass range for analytes of interest.

3.25. Second Source Standard: A standard from a different manufacturer or lot number other than the standard used to calibrate an instrument. The SSS is used to prepare the Initial Calibration Verification Standard.

3.26. Solvent Blank – A clean sample (OFW and/or MeOH) analyzed using the same conditions as a regular sample. A solvent blank detects system contamination and assures the purity of the solvent. Used as a MB for MeOH extracted samples.

3.27. Surrogate – A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

3.28. Chemstation™ - A chromatography software package. ARI uses Environmental Chemstation ™ software to identify and quantify Gasoline Range Organics.

3.29. Target™ - A chromatography software package. ARI uses Target™ software to identify and quantify BETX and Gasoline Additives.

4. Interferences

4.1. See SOP 700S Section 4.

5. Safety

5.1. See SOP 700S Section 5.

6. Equipment, Maintenance and Supplies

6.1. See SOP 700S Section 6.

7. Reagents and Standards

7.1. See SOP 700S Section 7.

7.2. Retention time standard: Solution contains normal alkanes n-C_4 through n-C_{12}, 2-Methylpentane, naphthalene and 1,2,4-trimethylbenzene. The BETX standard includes toluene which is always run in conjunction with retention time standards.

8. Sample Collection, Preservation, Shipment, Storage and Disposal

8.1. See SOP 700S Section 8.

9. Quality Control

9.1. Quality Control procedures and requirements are summarized in Appendix 20.1.

9.1.1. Acceptance criteria for ARI's routine analyses listed in the column title "ARI Acceptance Criteria".

9.1.2. When DoD-QSM acceptance criteria differ, they are provided in the "DoD-QSM Acceptance" column

9.2. Some clients and/or projects may have different quality control procedures or criteria. Always read and understand any "special Instructions" supplied by an ARI Project Manager.

9.3. Instrument control:

9.3.1. QLS studies are performed regularly for each analyte by each preparatory and analytical method.

9.3.2. DL, LOD and MRL values may be found for each analyte in the ARI LQAP.

9.3.3. The GC-MS must be tuned to the specifications in Appendix 20-4 before samples are analyzed. It is required that a 5-50ng total BFB standard be analyzed prior to calibration, but not on a daily basis. An ICV, BS, BSD and a method blank be analyzed with acceptable QC before analyzing samples.

9.3.4. Internal standard (IS) area criteria in the samples must be evaluated for retention time shift and EICP areas.

9.3.4.1. If the EICP area for any IS changes by -50% to +100% from the area of the IS in the mid-point of the initial calibration, the samples must be reanalyzed.

9.3.4.2. Retention time shift of internal standards must be ± 0.06 RRT units from the CCV internal standard RT.

9.4. Method performance:

9.4.1. Samples are analyzed in 12 hour run sequences known as QC periods. Each 12 hr QC period begins when an ICVsample analysis starts and ends following the analysis of the last sample injected within 12 hours of the initial sample injection.

9.4.2. One method blank will be performed each 12-hour shift.

9.4.2.1. A method blank is run to demonstrate system cleanliness (no analytes should be detected > 1/2 MRL). Blanks may contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e., targets are not present in the samples or sample concentrations/responses are greater than 10x the blank. Surrogates are to be within the established control limits.

9.4.2.2. Corrective action must be taken when MB contamination is greater than the report MRL and the samples contain detections of the analyte that are above the reporting limit and less than 10x the concentration found in the blank. Re-analysis is not necessary if the analyte concentration falls well below the action or regulatory limit or if the analyte is deemed not important for the project. See section 16.6.

9.4.2.3. Prepare a water method blank by adding 45 mL organic-free water to a pre-cleaned auto-sampler vial.

9.4.2.4. Prepare a medium soil method blank by adding 900 µL purge and trap grade MeOH to a 45 mL VOA vial containing OFW.

9.4.3. A Blank Spike (BS) Sample must be analyzed before analyzing samples. At a minimum one (BS) must be run in each 12 hr. QC period. It is recommended an (BS) duplicate be analyzed also. The control limits for all compounds is ± 20% or ARI's published historical control limits. The maximum allowed relative percent difference (RPD) for an BS and BSD) is 30%.

9.4.3.1. Compounds that do not meet these limits must be documented on an Analyst Notes Form (Form 8042F) and included in the data package for review

9.4.3.2. Prepare a medium soil BS by adding 900 µL purge and trap grade MeOH to a 45 mL VOA vial containing OFW, then spike the sample with VSS

9.4.3.3. Prepare a soil BS by adding the VSS to 5mL of organic-free water to a final concentration equivalent to that of the CVS.

9.4.4. One set of matrix spikes is analyzed for each 20 samples/matrix/instrument (when requested and adequate sample is available) at a known concentration level within the range curved, typically at 20ng/mL for 5mL waters and 40mg/kg for soils.

9.4.4.1. The MS/MSD samples are run, and the relative percent difference must be calculated between the two control samples. The RPD for each analyte for MS/MSD should be less than 30% and note any deviation >30% in the analyst notes.

9.4.4.2. ARI will not perform MS/MSD analysis on any of the field QC samples delivered as part of a client's QA/QC program (water rinsate samples, field/trip blanks etc.)

9.4.4.3. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.4.5. QC limits are provided to bench chemists, managers, and QA review personnel as tools for assessing data quality in real-time at the point of data generation.

9.5. A holding blank will be kept in volatile Refrigerator 21 and will be analyzed every week. Holding blank data is documented in Element.

9.6. Surrogates are added to each sample, blank, and standard, and are used to evaluate the purge and trapping efficiency by measuring recovery. Surrogates are brominated, fluorinated or isotope labeled compounds not expected to be detected in samples.

9.7. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for matrix spike and matrix spike duplicates are statistically generated on an annual basis.

9.7.1. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation.

9.7.2. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. Current control limits may be found in ARI's Element LIMS.

9.7.3. All analysts using this SOP must use it in conjunction with Control Limit documentation in order to assess data quality and any possible need for corrective actions.

10. Calibration and Standardization

10.1. Summary of VOA calibration procedure:

Step	BTEX Analysis Section	Gas Analysis Section	Procedure
1	10.2	10.2	Prepare Calibration Samples
2	10.3	10.3	Verify Instrument Tune
3	10.4	10.11	Analyze BTEX Calibration samples
4	10.5		Target/Chemstation Calculates RRF & %RSD
5	10.6		Validate analyte response
6	10.7		Analyze Instrument Blank
7	10.710.8		Analyze SCV
8	10.810.9		Evaluate IS Response
9	10.910.10	10.14	Verify Retention Times
10	10.1010.11	10.10	Update Analytical Method

10.2. Prepare Calibration samples:

10.2.1. Using a new unopened vial of Gas or BETX calibration solutions prepare a set of five or more calibration samples containing all target analytes. This is accomplished by spiking

separate volumes of VOA free water with increasing volumes of the VOA spike working standard as listed in Table 03. Calibration samples are prepared in 45 mL VOA vials. The volume of the calibration samples must be equal to the volume that will be analyzed to account for purge efficiencies that vary with sample volume. The concentration of analytes in the lowest level sample must less than or equal to the method reporting limit. The concentrations in the calibration standards define the working range of the method. A set of at least 5 calibration standards containing the method analytes is required. One calibration standard should contain each analyte at the concentration of the reporting limit for that compound. The other calibration standards should contain analytes at concentrations that define the range of the method. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. ARI typically calibrates with between five and eight calibration levels covering the dynamic range of the instrument and meeting the required reporting limit of the project. The Gasoline and BETX are calibrated separately and quantified using Chemstation and Target Chromatography software respectively.

10.2.2. Gasoline and BETX calibrations are typically performed at the following concentrations.

Table 03 – Typical Calibration Solution Concentrations

Standard	Gas Range (mg/L)	BETX (µg/L)
1	0.10	0.2
2	0.25	0.5
3	0.50	1.0
4	1.0	2
5	2.5	10
6	5.0	20
7		40
8		80

10.2.3. Initial calibration standards, initial calibration verification standards and surrogates for the soil side of the Autosampler are made in a minimum amount of water. The standards are then transferred to 45 mL vials, each containing a magnetic stir bar. Internal standards (IS) and Surrogate standards (SS) are added by the Autosampler.

10.2.4. Initial calibration standards, initial calibration verification standards and surrogates for the water side of the Autosampler are made at volumes for use in 45 mL vials containing magnetic stir bars. The appropriate sample volume of the standard is transferred via the Autosampler to a sparger vessel and purged. The IS/SS solution is added by the Autosampler standard syringe.

10.2.5. Surrogates are not curved; they are spiked at the same level for all calibration points.

10.3. Verify that the instrument is properly tuned following the procedure in Appendix 20.3

10.4. (BETX) Analyze BETX calibration Samples:

10.4.1. Analyze each calibration sample using the exact conditions and procedure to be used for subsequent sample analyzes.

10.4.2. Print the initcal.rp Report" using Target™ software and evaluate each target analyte.

10.4.2.1. Verify that the automated routine has properly identified and quantified all peaks.

10.4.2.1.1. Perform any required manual integration as necessary.

10.4.2.2. Verify that the internal standard (IS) is in control.

10.5. Target™ will tabulate relative response factors (RRF), Average RRF, relative standard deviation (RSD) and % RSD using Equations 01 through 04 for each compound relative to its internal standard.

Equation 01:
$RRF = (A_X C_{IS}) / (A_{IS} C_X)$
A_X = Area of the characteristic ion for the compound being measured
A_{IS} = Area of the characteristic ion for the associated Internal Standard
C_{IS} = Concentration of the associated internal standard
C_X = Concentration of the compound being measured

Equation 02:
$Average\ RRF = \Sigma\ RRF_i / n$
where:
RRF_i = the peak response factor for each quantitation peak in the calibration standard
n = the total number of standards (usually 7)

Equation 03:	
$RSD = SD / (Ave\ RRF) =$	$\frac{\sum (RRF_i - Ave\ RRF)^2) / (n-1))^{1/2}}{Ave\ RRF}$
where:	
SD = Standard deviation of the response	

Equation 04:
%RSD = RSD * 100

10.6. Evaluate Analyte Response.

10.6.1. When the %RSD for a given target is ≤ 20%, the detector response is considered linear and the average RRF may be used to quantify that compound.

10.6.2. When %RSD is >20% for any compound, the analyst may use an alternative method to evaluate the acceptability of the calibration.

10.6.3. The curve must meet minimum RRF requirements noted in Appendix 20.2.

10.6.4. If more than 10% of the compounds included in the initial calibration exceed 20% RSD and do not meet the minimum coefficient of determination of 0.99, for alternate curve fits, the chromatographic system is considered to imprecise for analysis to begin.

10.6.5. For linear and non-linear calibration curves based on a least squares regression (LSR) model the coefficient of determination (COD) r^2 must be > 0.99.

10.6.6. Special care should be taken to monitor the RRF in the lowest calibration standard to ensure adequate sensitivity at the reporting limit. Following examination of the ICal and any corrective action, all compounds not meeting the calibration acceptance criteria must be documented on an Analysts Notes Form (8042F)

10.7. An instrument blank must be analyzed immediately following the highest point of the calibration. This blank can be used to estimate the extent of decontamination needed to eliminate carryover after analyzing a sample at similar concentration.

10.8. A secondary calibration verification (SCV) is performed by analyzing a midpoint calibration standard prepared using the SCVS. ARI will spike the full list of compounds at a mid-calibration range concentration. Calibration verification is acceptable when the recovered analytes are within ± 30% (20% for DoD analyses) of the expected concentration. Specific clients or projects may allow or require different calibration acceptance limits. When any analytes are not in the acceptable range corrective action and documentation on an Analyst Notes Form (Form 8042F) is required.

10.9. The internal standard responses and retention times in the continuing calibration standard must be evaluated during or immediately after data acquisition.

10.9.1. If the EICP area for any of the internal standards changes from -50% to +100% from the last mid-point concentration of the initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. Areas are documented in the daily run log.

10.10. If the retention time for any internal standard changes by more than 10 seconds from the last daily calibration, the chromatographic system must be inspected for malfunctions and corrections must be made, as required.

10.11. Update the analytical method file with updated RT and RRF data.

10.12. (GAS) Analyze Gas Range Organics standards using Target data analysis software.

10.13. The RSD of the gasoline curve should be ≤ 20%. Gasoline is typically very linear, and for this reason, the RSD should not exceed 20%. Other methods of evaluating linearity, as described in ARI's SOP 400S, "Gas Chromatography (GC) Analysis Procedure Method 8000", alternate curves types will not be used for Gas and GRO quantitations; however, alternate analytes (i.e. light fuels Stoddard/Mineral Spirits, JP4, Aviation Fuel, etc.) may be quantitated using other fit techniques if needed.

10.14. Surrogates are calculated from the BETX calibration and method using the Average response Factor determined from the surrogates in the BETX standard mix.

10.15. Area Summation

10.15.1. In order to determine accurate calibration factors, the total area of each standard must be correctly calculated. The total area for northwest gasoline is defined as the area sum of all the peaks detected within the range between Toluene and Naphthalene. Additional gasoline ranges (Oregon, Alaska, and California ranges are used if requested).

10.15.2. The daily retention time standard is used to determine actual retention times. The analyst should set the gas range start time 0.05 minutes before starting marker compound, and the range stop time 0.05 minutes after the ending marker compound. That way, both peaks will always be included in the gas range total.

10.15.3. Suggested Integration Parameters:

Table 8

Parameter	Setting
Initial Threshold	8.00
Initial Peak Width	0.005
Initial Area Reject	0
Shoulder Detection	OFF

10.15.4. Each peak will be integrated to baseline. Manual baselines may be required for some standards and samples in order to achieve proper integration.

10.15.5. It is frequently necessary for the analyst to adjust the integration parameters and /or perform manual integration in order to correctly integrate the GC signal. This includes, but is not limited to, splitting shoulders off of peaks, and adding or subtracting “set baseline now” events.

10.15.6. The analyst is responsible for insuring that all peaks are integrated properly. The peak should be integrated from the point where it rises up from the baseline to where it returns to the baseline. The integration should not extend to include baseline noise, nor should it “climb” up the side of the peak.

10.15.7. At no time should the integration extend above the baseline.

10.15.8. There should be no gaps in the integration. All area should be integrated.

10.15.9. Baseline rise should not be included in the area of the chromatogram. The analyst is responsible for distinguishing baseline rise from any chromatographic effects caused by the sample. If there is any doubt, overlay the chromatogram of the blank with that of the standard or sample.

10.15.10. Please refer to Manual Integration SOP 1021S for assistance with manual integrations.

10.15.11. The analyst must initial and date all raw instrument data.

10.16. The analyst notes from the Initial Calibration must be included with every job analyzed using the corresponding initial calibration.

11. Procedure

11.1. Procedure Summary

Table 04 – Procedure Summary		
Step	**Process**	**See Section**
1	Project Evaluation	11.2
2	Set or Verify Instrument Operating Parameters	11.3
3	Verify Spiking Solution in the autosampler	11.4
4	Prepare Samples for Analysis	11.5
5	Set up Analytical Run	11.6
6	Initiate sample analysis	11.7
7	Verify Instrument Tune and Calibration	11.8
8	Evaluate Mass Spectra	11.9
9	Evaluate QC Analyses	11.10
10	Export Data to Element	11.11

11.2. Project Evaluation

11.2.1. Holding times: Review project documentation to determine when sample holding time will expire. If there is any chance the sample will not be analyzed with the required holding time, notify your laboratory supervisor and/or the appropriate project manager.

11.2.2. Special requirements: Non-routine analytical requirement may be required for a specific project or sample. Review all project documentation and make sure you understand any special requirement before proceeding with analysis.

11.2.3. Historic Data may be available for a continuing project or sampling site. Use this data to pre-determine any special sample handling necessary.

11.3. Set up the GC/MS/Autosampler system as outlined in Tables 06, 07 and 08:

11.3.1. This should be done prior to the preparation of the sample to avoid loss of volatiles from prepared standards and samples.

Table 06 – Typical Instrument Operating Parameters	
Mass Spectrometer	
Mass scan range	35 – 300 amu

Scan time	1 sec/scan or less
Electron volts	70 volts (nominal)
Gas Chromatogram	
Initial Temperature	43 – 46 °C
Temperature Program	46-240°C at 12°C/min
Final temperature:	240°C, hold 4 min
Source temperature:	According to manufacturer's specs, 150-250°C
Transfer nozzle/line:	180-250°C
Carrier Gas:	Helium at 25-50 mL/min
Purge & Trap	
Purge	8-11 minutes
He flow rate	25 – 50 mL/min
Sample Heater	40 °C
Desorb preheat	250°C
Desorb	1-6 minutes at 250°C
Bake	4-10 minutes at 260°C
Valve temperature	50-110°C
Mount temperature	30-110°C
Line	50-200°C

11.4. Table 07 – Typical Autosampler Set-up - Manual Mode

Parameter	Autosampler Options	Recommended Set-up	
		Water	Soil
Flush Volume	5, 10, 15, 20 mL	10	5
Select matrix	Water or Soil	Water	Soil
Standard	Yes or No	Yes	Yes
Sample Volume	5, 10, 15, 20 mL	5 or 10	--
Dilution	0 – 95 %	0	--
Flushes	0 - 10	3	--
Stir Time	0 – 15 min	1	--
Settle Time	0 – 15 min	0	--
Stir Speed	L, M, H	M	--
Desorb Time	0 – 10 min	1	--
Flow Rate	0 – 150 mL/min	40	
Line Heat	25 – 125 °C	--	80
Pre-heat	0 – 10 min	0	0
Water Volume	0 – 10 mL	--	7
Pre-purge	0 – 10 min	0	0

Purge time	0 – 20 min	10	10
Flushes	0 - 10	--	1
Soil Stir	Yes or No	--	Yes
Desorb time	0 – 10 min	--	2
Water Trap Volume	Yes or No	--	0

11.5. Table 08 – Typical Autosampler Set-up - Auto Mode

Parameter	Options	Recommended Set-up	
		Water	Soil
Start delay	0 – 99.5 hours	0	0
Cycle time	0 – 199 min	0	24
Auxiliary output	Yes or No	No	No
Last water or soil	Vial number	1 – 30	1 - 30
Blank Last	Yes or No	No	No
Flush Volume	5, 10, 15, 20 mL	5 or 10	5
Select Matrix		Water	Soil
Standard	Yes or No	Yes	Yes
Sample Volume	5, 10, 15, 20 mL	5 or 10	--
Dilution	0 – 95 %	0	--
Flushes	0 - 10	2	--
Stir Time	0 – 15 min	1	--
Settle Time	0 – 15 min	0	--
Stir Speed	L, M, H	M	--
Desorb Time	0 – 10 min	1	--
Flow Rate	0 – 150 mL/min	40	40
Line Heat	25 – 125 °C	--	80
Pre-heat	0 – 10 min	--	0
Water Volume	0 – 10 mL	--	7
Pre-purge	0 – 10 min	0	0
Purge time	0 – 20 min	10	10
Flushes	0 - 10	--	1
Soil Stir	Yes or No	--	Yes
Desorb time	0 – 10 min	--	2
Water Trap Volume	Yes or No	--	No

11.6. Verify Spiking Solutions

11.6.1. Verify the IS / SS standard volume in the Autosampler reservoir. Add standard as necessary.

11.7. Prepare Samples for Analysis: Samples must be properly prepared for analysis using the processes outlined in Table 09.

Table 09 – Sample Preparation Procedures

Sample Matrix	Method	Technique	Details in Section:
All	Sample Screening	Sample Dilution	11.5.2
Water	5030B	Direct P&T	11.5.4
Soil	5035	Direct P & T	11.5.5
Solid	5035	Methanol Extraction	11.5.5
Soil		From Total Solids Jar	11.5.3.2
Waste	3585	Waste Dilution	11.5.5.4

11.7.1. **Prepare the Instrument:** The Purge and Trap GC-MS instrument must be readied before samples are prepared for analyses to allow minimum time lapse between preparation and analysis.

11.7.2. **Sample screening:**

11.7.2.1. Any sample with characteristics (color, odor, client information etc.) indicating it may contain high levels should be screened prior to analysis. Screening may also help prevent un-necessary contamination of the purge-and-trap system. Samples are screened by analyzing them at dilution.

11.7.2.1.1. Aqueous samples: dilute the samples with an appropriate volume of OFW and analyze as a normal sample.

11.7.2.1.2. Extract solid samples with methanol and dilute a small aliquot of the methanol into 45mL OFW for analysis.

11.7.2.1.3. A portable PID may be used to assess the sample.

11.7.3. All client samples, QA samples and standards must be spiked with surrogate (SS) and internal standards (IS) prior to analysis. The SS and IS are normally added to the sample by the auto-sampler. When samples are analyzed manually, the analyst must spike each sample individually.

11.7.4. **Aqueous Sample Preparation:**

11.7.4.1. Screen aqueous samples when historic data or their appearance indicated that they may contain high concentrations (> 2mg/L) of volatile compounds. When the screening indicates a high concentration of volatiles dilute the sample with OFW.

11.7.4.2. Aqueous samples are normally received by ARI in 45 mL VOA vials. The VOA vials are placed directly on the auto-sampler for analysis. The auto-sampler will spike surrogate and internal standard into the sample prior to the purge process.

11.7.4.3. Manual Sample Preparation: Remove the plunger from a 5mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and

carefully pour the sample into the syringe barrel to just short of overflowing. Replace syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 or 10 mL. Transfer remaining sample to a 45mL VOA vial with a Teflon™ sealed cap or fill a second syringe at this time to maintain sample integrity.

11.7.4.4. For matrix spike, matrix spike duplicate, and BS analyses, add the appropriate amount of spiking solution to the 45mL vial containing the sample to be purged to a known concentration level within the range curved.

11.7.4.5. Appropriate concentration range for analysis.

11.7.4.5.1. Use screening data, historic project information, sample appearance or other ancillary information to determine appropriate purge or dilution volumes prior to analysis.

11.7.4.5.2. The amount a sample may be diluted is determined by the purge volume and final concentration of target analytes.

11.7.4.5.3. Prepare dilutions in a 45 mL vial taking care to maintain sample integrity by keeping atmospheric exposure of the sample to a minimum

11.7.4.5.4. Add a stir bar to the 45 mL vial or leave a small pea bubble in the vial to facilitate mixing while shaking the sample.

11.7.4.5.5. Dilutions in excess of 5000X may be prepared using an intermediate Methanol (or OFW) dilution taken directly from the sample vial.

11.7.4.5.6. Always perform a final review of multiple analyses from the same sample and note any major deviations in analyte concentrations on the analyst notes Form 8042F.

11.7.4.6. Compositing samples prior to GC/MS analysis

11.7.4.6.1. The samples must be cooled at >0 to 6°C during this step to minimize volatilization losses. Combine an equal amount of each sample to be composited in a volumetric flask. Invert and shake 3 times and transfer to a sample vial or a 5mL gas tight syringe.

11.7.4.6.2. Samples composited in this fashion will be qualified in the analyst notes.

11.7.5. **Solid Samples (Soil & Sediment) Preparation:**

11.7.5.1. Screen solid samples when historic data or their appearance indicated that they may contain high concentrations (> 2mg/L) of volatile compounds. When the screening data indicates a high concentration of volatiles, use less methanol extract in the analysis.

11.7.5.2. Solids samples are normally reported on a dry weight basis. Always perform a dry weight determination (Appendix 20.8) unless the project plan requires data reported on an “as received” basis.

11.7.5.3. Methanol Extraction for medium level soil or waste samples. This method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol.

11.7.5.3.1. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Using a top loading balance weigh 5g (wet weight) of sample into a tarred 20 mL vial. Record the actual weight to 0.1g. Determine the percent dry weight of the sample as described in Appendix 20.4. Measure 5mL of Methanol into the vial. Stir the sample Methanol mixture for 2 to 3 minutes using a vortex mixer.

11.7.5.3.2. Pipet a portion of the extract to a clean amber Teflon sealed vial for storage (limiting headspace). The remainder may be disposed. Store the extracts at >0 to 6°C in Refrigerator 25, prior to analysis.

11.7.5.3.3. After determining the required dilution, add the appropriate amount of extract to the Autosampler vial (100µL to 10µL / 5mL). To a 45 mL vial filled with OFW, add 900 µL of the sample extract for a total volume of 45 mL. Cap the vial and place it on the autosampler for analysis.

11.7.5.3.4. If a dilution is required, add less sample extract to the 45 mL vial of OFW.

11.7.5.3.5. For a matrix spike, prepare the sample as normal and then add an appropriate amount of the BS spike solution to the vial. Matrix spikes are typically spiked at the BS level. Purge and start analysis of the sample.

11.8. Set Up Analytical Run

11.8.1. Samples are analyzed in 12 hour run sequences known as QC periods. Each 12 hr QC period begins when an RT/ICV sample analysis starts and ends following the analysis of the last sample injected within 12 hours of the ICV sample injection.

11.8.2. Setup an analytical run by placing 45 mL sample vials containing either standards or client samples in the autosampler tray in the order listed in Table 09.

Table 09 – Example Analytical Run Sequence

Sample Sequence	Sample Type
1*	RT standard
2*	Initial Calibration Standard (ICV)
3	Blank Spike (BS)
4	Blank Spike Duplicate (BSD)
5	Method Blank
6 through 50	Prepared Client Samples
* These may be combined	

11.8.3. The autosamplers may run in manual or automatic mode.

11.8.4. Enter the sample identifications into the Chemstation software

11.9. Initiate Sample Analysis

11.9.1. Proceed with the analysis. Analyze all blanks on the same instrument as that used for the samples. The standards and blanks should also contain 900µL of the purge-and-trap grade MeOH to simulate the sample conditions when analyzing extracted solid samples.

11.9.2. The instrument system will transfer sample to the purge and trap sampling device and perform the GC-MS analysis automatically.

11.9.3. The analyst is responsible for assuring that the automated peak identifications and integrations are acceptable.

11.10. Verify Instrument Tune and Calibration

11.10.1. The 12 hr QC period starts with the ICV injection time and ends with the injection time of the last run inside the 12 hours. BFB and retention time (RT) standards may be combined as long as both criteria can be met.

11.10.2. Review chromatographic data to assure all peaks are identified and integrated correctly following the procedures in SOP 1021S.

11.10.3. Verify that the response of all internal standards is -50% to +100% of the compound's response in the most recent initial calibration mid-point standard.

11.10.4. The GC/MS system must be hardware tuned to meet the ion abundance criteria in Appendix 20.4 for analysis of ≤ 50 ng BFB. Analysis must not begin until all criteria have been met. Compliance with the criteria must be demonstrated prior to every calibration.

11.10.4.1. Evaluate the BFB in the following manner.

11.10.4.1.1. Acquire and average the entire peak (all scans) or three scans (the peak apex scan and the scans immediately preceding and following the apex).

11.10.4.1.2. Subtract background, this is required and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not subtract part of the BFB peak.

11.10.5. Daily GC/MS calibration and initial calibration verification

11.10.5.1. An initial calibration verification standard at mid-concentration containing each compound of interest, including all required surrogates, must be performed once every 12 hours prior to sample analysis. Compare the response factor data of the standard each 12 hour shift that samples are to be analyzed against the average response factor from the initial calibration for a specific instrument.

11.10.5.2. Determine the percent drift (%D) for all analytes in the daily continuing calibration.

11.10.5.3. The calibration for all compounds with a %D ≤ 20 is acceptable.

11.10.5.3.1. Method 8260 allows up to 20% of the target analytes to be greater than 20%. If more than 20% of the analytes have %D > 20% corrective action is required prior to analysis.

11.10.5.3.2. Non-detects for compounds with >20%D may be reported when it can be demonstrated that there is adequate sensitivity to detect the compound if it were present. Such compounds must be documented on an Analysts Notes Form (Form 8042F). Any reported values must be Q-flagged.

11.11. Evaluate Mass Spectra

11.11.1. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum. If not, the compound may be flagged with “M” if the analyst feels the identification is real (this favors false positives).

11.11.2. The relative intensities of the major ions should generally agree with the reference spectra.

11.11.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.11.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

11.11.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.11.6. An analyte is identified by comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the initial calibration. These standard reference spectra may be obtained through analysis of the calibration standards. The characteristic ions are defined as the three ions of greatest intensity, or any ions over 30% intensity relative to the base ion, if less than three such ions occur in the reference spectrum. Two criteria must be satisfied to verify identification: (1) elution of sample component at or near the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component mass spectrum and the standard component mass spectrum.

11.11.7. The intensities of the characteristic ions must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where 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 will be accepted as meeting this criterion.

11.11.8. The sample component RRT must compare within ±0.06 units of the RRT of the standard component. For reference, the standard must be run within the same 12-hour QC period as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted, ion-current profiles for ions unique to the component of interest.

11.11.9. All ions present in the standard mass spectra at a relative intensity greater than 10% (the most abundant ion in the spectrum is equal to 100% intensity) should be present in the sample spectrum.

11.11.10. The relative intensities of ions specified in Appendix 20.3 must agree within plus or minus 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample abundance must be between 20% and 80%.). If not, the compound may be flagged with an "m" if the analyst determines that the identification is valid (favors false positive).

11.11.11. Structural isomers that produce very similar mass spectra should be 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 and reported as the sum of both compounds.

11.11.12. 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 co-elute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

11.11.13. Secondary ion quantitation is allowed only if there are sample matrix interferences with the primary ion.

11.11.14. All dilution efforts should try to keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. To determine the dilution factor, compare a minor ion in the saturated analyte against the daily standard.

11.12. Evaluate the QA samples as outlined in Section 12

11.12.1. Daily GC/MS initial calibration verification, BS criteria, and the MB must demonstrate the system is free of interferences, before analyzing samples.

11.12.2. If the analysis shows the sample to have a concentration of analytes that exceed their highest standard, the sample must be rerun at a dilution. Analyst considerations for chromatographic “system overload” are analytes that are above the linear range, saturation of the mass spectrometer, chromatography overload, or analyte/interference carryover. Professional judgment must be used by the analyst as to the modification of the analytical sequence. If system contamination is present, an OFW blank must be analyzed. If the blank analysis is not free of analytes/interferences, the system should undergo maintenance, such as baking the trap or purging with methanol to decontaminate the system. If a blank is not run, as with auto-samplers, the following sample must be checked for carryover and rerun if it contains the same compounds which showed saturation. This must continue until no analyte is detected > ½ the MRL.

11.13. Export data to Element

12. Data Analysis and Calculations

12.1. Quantitative BETX analysis:

12.1.1. It is the operator’s responsibility to verify all compound identifications performed by the GC-MS data system. Use retention time, spectral data, data system calculated fit, and the operator’s expertise to determine whether analytes found by the system are real.

12.1.2. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

12.1.3. If secondary ion quantitation is necessary due to interference, then a short quantitation report list is generated. This quantitation contains the integrated areas of the affected compounds, based on the secondary ion(s) for that compound, and of the relevant internal standards. Identical reports must be generated for the sample with interference and for the relevant initial calibration verification. The report for the initial calibration verification is used to generate a relative response factor for the affected compound based on its secondary ion. This relative response factor is then used in the calculations for that compound in the affected sample. The short quantitation report may be hand calculated by the analyst as long as it is signed and dated by the analyst.

12.1.4. The concentration of each identified analyte in the sample is calculated as follows:

12.1.4.1. Aqueous samples

Concentration (µg/L) =	$\frac{(Ax)(Is)}{(Ais)(RF)(VO)}$
where:	

Ax = Area of characteristic ion for compound being measured.
Is = Amount of internal standard injected (ng)
Ais = Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured.
VO =Volume of water purged (mL), taking into consideration any dilutions made.

12.1.5. Sediment /Soil, Sludge, and Waste:

12.1.5.1. High-concentration:

Concentration (µg/Kg) =	$\frac{(Ax)(Is)(Vt)}{(Ais)(RF)(Vi)(Ws)}$
where:	
Ax = Area of characteristic ion for compound being measured.	
Is = Amount of internal standard injected (ng)	
Vt = Volume of total extract (L) (use 5,000µL or a factor of this when dilutions are made).	
Ais = Area of characteristic ion for the internal standard.	
RF = Response factor for compound being measured.	
Vi = Volume of extract added (L) for purging	
Ws = Weight of sample extracted or purged (g). The wet weight or dry weight may be used depending upon the scientific applications of the data.	

12.1.6. Low-concentration

Concentration (µg/Kg) =	$\frac{(Ax)(Is)}{(Ais)(RF)(Ws)}$
where:	
Ax = Area of characteristic ion for compound being measured.	
Is = Amount of internal standard injected (ng)	
Ais = Area of characteristic ion for the internal standard.	
RF = Response factor for compound being measured.	
Ws = Weight of sample extracted or purged (g). The wet weight or dry weight may be used depending upon the scientific applications of the data.	

12.1.7. Sediment/soil samples are generally reported on a dry weight basis (sludge and wastes are also reported on a dry weight basis). In either instance, the percent dry weight of the sample should be reported along with the data.

12.2. Quantitative Gas Range Analysis

12.2.1. After the calibration curve has been analyzed, the Response Factor (RF) for each hydrocarbon range must be determined using the following formula:

RF = A / C
where:

A = Total peak area for the hydrocarbon range
C = Concentration of the hydrocarbon analyte

12.2.2. After calculating the RF for each hydrocarbon range for each calibration standard, the average RF is calculated by summating the RF for each calibration standard and dividing by the number of calibration standards. The formula is:

Average RF = Σ RF_i / n
where:
RF_i = the response factor for each hydrocarbon range in the calibration standard
N = the total number of standards (usually 6)

12.2.3. Relative Standard Deviation- The relative standard deviation of the response factors for each hydrocarbon range is determined by dividing the standard deviation of the RFs by the peak's average RF. The formula is:

$$\text{RSD} = \text{SD} / (\text{Ave RF}) = \frac{((\Sigma (RF_i - \text{Ave RF})^2) / (n-1))^{1/2}}{\text{Ave RF}}$$

12.2.4. Percent Difference- the percent difference calculations for CVSs involve dividing the difference between the CVS RF and the average RF by the average RF and converting this number to percent. The equation is:

%D = 100(Conc – Concmp) / Concmp
where:
Concc = the quantitated concentration in the CVS
Concmp = the concentration of the midpoint in the ICal (250)

12.2.5. TPH Identification- A sample is tentatively determined to contain a specific TPH analyte when the GC-FID response within a defined retention time (RT) window match the GC-FID response of a standard in the same RT window.

12.2.6. The Retention Time (RT) windows are defaulted to 0.05 minutes.

12.2.7. When samples appear to contain weathered or treated TPH, or mixtures of various TPH distillates, use of standards may not be straightforward (or technically appropriate). In such cases, the analyst must decide which TPH pattern most closely represent the range of TPH present and will quantify total TPH by quantifying the most appropriate GC-MS response range based on the analyst's knowledge and experience. Weathered patterns and complex mixtures should be noted on the Analyst Notes form.

12.2.8. All TPH surrogate peaks should show consistent RT relative to the initial calibration. Large chromatographic interferences may cause inconsistent shifting by moving some of the peaks more than others. The chromatogram of samples should be examined to ensure that false negatives aren't created by this manner of chromatographic overload.

12.3. Gas Range Organics Sample Quantitation

12.3.1. Water

Concentration (µg/L) = $\frac{(Ax)(FEV)(DF)}{(RF)(Vo)(Vi)}$
where:
A_X = Total area of the quantitation range for the analyte being measured
FEV = Final effective extract volume (mL)
RF = response factor for compound being measured
Vo = Volume of water extracted (ml)
Vi = Volume of extract injected (µL)
DF = Sample Dilution Factor (1 for undiluted samples)

12.3.2. Soil calculations involve correcting the results for both the percent moisture of the sample. Because water and methanol are miscible, the results must be corrected for the additional dilution that occurs from the water present in the sample.

12.3.2.1. The total liquid content must be calculated first.

Total liquid (TL), ml=(MeOH Amt) + ((100-%TS)) *AmtExt)
Where:
MeOH Amt is the amount of methanol added to the sample in ml
%TS is the percent total solids of the sample, or 1-% moisture
AmtExt is the amount of sample extracted in grams

12.4. The dry weight equivalent of the sample must be calculated next. This is the amount, in grams, of the sample that is actually purged.

DwtEquiv, g = {(%TS/100)*(AmtExt/TL)}*(dilExt)*(mlExt/mlV)*PV
Where:
dilExt is the factor by which the extract may have been diluted prior to injection into the autosampler vial.
ml Ext is the amount of extract injected into the autosampler vial
ml V is the volume of the autosampler vial.
PV is the purge volume in milliliters.
%TS, AmtExt and TL are defined in Section 12.1.2.1

12.5. Using the above values, the gasoline range organics (GRO) concentration of the sample may be calculated.

GRO (mg/kg) = (Range Area/RF)*(PV/DwtEquiv)
Where:
Range Area: subtracting the area of any surrogate eluting in that range.
RF is the response factor from the curve.
PV and DwtEquiv are as defined above.

12.6. Analysis records

12.6.1. Each analytical run will be recorded in the instrument run log in Element, including the vial ID and pH of each sample for aqueous samples. This log book serves as a routine maintenance log and the chain-of-custody for analyzed samples. Any change of operator must be included in the notations.

12.6.2. Soil extractions and 5035 analyses are noted on the Volatile Organics Extraction Bench Sheet 8043F, which is included with the analysis data.

12.6.3. Total solids are recorded on the Total Solids bench Sheet 5050F and included with the analysis data.

13. Method Performance

13.1. See SOP 700S Section 13

14. Pollution Prevention

14.1. See SOP 700S Section 14

15. Data Assessment and Acceptance Criteria

15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 of this document.

15.2. Method Blanks- The method blank must contain less than 1/2 the reporting limit of the targeted analytes or corrective action is required.

15.3. Internal Standards- All samples' internal standard EICP areas following the continuing calibration standard must meet the technical acceptance criteria listed in Section 9.

15.4. Surrogate Recoveries

15.4.1. All method blanks, blank spike samples, matrix spikes, matrix spike duplicates, duplicates or other samples must have acceptable surrogate recoveries. Surrogate recoveries are considered unacceptable when:

15.4.1.1. Any surrogate has a recovery that is outside ARI or project specific control limits.

15.4.2. These requirements do not apply to subsequent analysis of samples where a prior analysis of the sample shows unacceptable surrogate recovery. This may demonstrate a matrix effect.

15.4.3. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet surrogate acceptance criteria, even when we meet in house limits.

15.4.4. Surrogate recovery acceptance windows are ideally determined statistically from method and matrix specific laboratory data updated on a periodic basis. Certain methods or clients may specify project specific surrogate recovery acceptance windows.

15.4.5. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.

15.5. Blank Spikes (BS)

15.5.1. The BS recovery values should fall within the specified recovery acceptance limits. If a BSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.

15.5.2. BS recovery acceptance windows are ideally determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Project or method specific limits may supersede laboratory acceptance criteria.

15.5.3. Evaluate BS/BSD RPD and note any deviation >30% in the analyst notes.

15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.6.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified recovery acceptance limits. If an MSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.

15.6.2. MS/MSD recovery and RPD acceptance is advisory and data should not necessarily be rejected based upon MS/MSD recovery. MS/MSD recovery should be compared to BS/BSD recovery to determine if recovery trends are present. Certain projects or clients may require project specific MS/MSD recovery and RPD acceptance windows.

15.6.3. Evaluate MS/MSD RPD and note any deviation >30% in the analyst notes.

15.7. Holding Times

15.7.1. Samples must be run within holding times (seven days for unpreserved water samples and fourteen days for solid samples, Methanol extracts and preserved water samples).

15.7.2. In the event that re-analysis due to an out of control event requires that samples be re-analyzed after their holding time has elapsed the analyst should analyze and report both data sets, whenever practical, distinguishing between the initial analysis and re-analysis on all deliverables. This will document that the samples were originally analyzed within holding times and may allow for comparisons that will determine whether any of the more volatile analytes were lost in the interval between analyses.

16. Corrective Actions for Out of Control Events

16.1. Corrective actions may include any, but are not limited to, the following:

16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the analyst notes.

16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.3. Re-preparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.4. Re-analysis – if available another vial or aliquot of the sample is run on the gas chromatograph.

16.1.5. Re-extraction – a portion of the remaining sample is extracted.

16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in ELEMENT.

16.1.7. Re-calibration – a new initial calibration is evaluated and the associated samples reanalyzed.

16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.

16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.

16.2. When an Initial Calibration for an analyte exceeds 20% RSD or .990 R^2 (BETX only)

16.2.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.2.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single

standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

16.2.1.2. If the analyte is outside 20% and is a poor performer then proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.3. When a Continuing Calibration Verification (CCV) fails.

16.3.1. Perform the appropriate corrective action(s) from Section 16.1 and re-calibrate the instrument.

16.3.2. DoD-QSM requires that %D for all analytes in the ICV or CCV be ≤ 20% (50% for end of batch CCV). For DoD analyses, if no samples have been analyzed and less than 1 hour elapsed since the failed CCV, two additional consecutive ICVs or CCVs may be analyzed. This is not required; the analyst may default to Section 16.3.1

16.3.2.1. When both of these CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.3.2.2. If either of the two CCVs fail or their analysis cannot be started within one-hour, associated samples may not be reported and the instrument must be re-calibrated.

16.4. Internal Standards

16.4.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.1.1. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.

16.4.1.2. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.

16.4.1.3. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.4.1.4. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".

16.5. Surrogates

16.5.1. Examine the bench sheet to verify spiking levels are correct.

16.5.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.5.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.6. Method Blanks- Corrective action for a method blank which fails acceptance criteria may involve re-preparation of a secondary method blank and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.7. Blank Spike Samples

16.7.1. Examine the bench sheet to verify spiking levels are correct.

16.7.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8. Matrix Spike/Matrix Spike Duplicates

16.8.1. Examine the bench sheet to verify spiking levels are correct.

16.8.2. Recoveries are advisory and should not necessarily result in reextraction.

16.8.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.9. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve, a dilution must be performed such that the analyte’s quantitated value is within the curve range.

16.9.1. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

16.9.2. When peaks from an analyte saturate the detector:

16.9.2.1. The analyst must flag all affected analytes with an S flag.

16.9.2.2. The analyst should evaluate samples following a saturation or over range hit to determine if carry over has occurred.

16.10. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when initial calibration verification responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.

16.10.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst must have the PM approve and document all such decisions. It is preferable that the Client

be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)

16.10.2. All QC limit issues (including initial calibration verification limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

16.11. Mass Spectrometer Tuning

16.11.1. When the MS does not produce an acceptable mass spectrum when injected with 5 to 50 µg/mL of BFB, re-inject the BFB. If the spectrum again fails to meet the criteria found in Appendix 20.4, the MS must be re-tuned.

16.11.2. If the re-tuned mass spectrum still fails to meet the criteria found in Appendix 20.4, the GC-MS may require maintenance. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.12. Holding blanks should meet the same criteria as the method blanks detailed below.

16.12.1. Corrective action must be taken when holding blank contamination is greater than ½ the reporting limits for any analyte.

16.12.2. Holding blanks requiring corrective action must also be submitted to the QA department for further review.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Section 16.2 for guidance on dealing with out-of-control initial calibrations.

17.2. See Section 16.3 for guidance on dealing with out-of-control initial calibration verifications.

17.3. See Section 16.4 for guidance on dealing with internal standard out-of-control events.

17.4. See Section 16.5 for guidance on dealing with surrogate out-of-control events.

17.5. See Section 16.6 for guidance on dealing with method blank related out-of-control events.

17.6. See Section 16.7 for guidance on dealing with BS/BSD related out-of-control events.

17.7. See Section 16.8 for guidance on dealing with MS/MSD related out-of-control events.

17.8. See Section 16.9 for guidance on dealing with over range samples.

17.9. See Section 16.10 for guidance on dealing with project managers.

17.10. See Section 16.11 for guidance on dealing with out-of-control tuning events.

17.11. See Section 16.12 for guidance on holding blanks.

18. Waste Management

18.1. See SOP 700S Section 18

19. Method References

19.1. "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Method 8260D Revision 4, February 2017.

19.2. USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration Revision OLM03.1, August 1994.

19.3. “Determinative Chromatographic Separations”: Method 8000C, Test Methods for Evaluating Solid Waste (SW-846), Revision 3, March 2003.

19.4. Department of Defense (DoD) Quality Systems Manual – Version 4.2 October 2010

19.5. “Sample Preparation for Volatile Organic Compounds” EPA Method 5000, Revision 0, December 1996

19.6. “Nonhalogenated Organics by Gas Chromatography: Method 8015C Revision 3, February 2007.

20. Appendices

20.1. Appendix 20.1: Quality Control Requirements

20.2. Appendix 20.2: 8260D GAS/BETX target analyte list

20.3. Appendix 20.3: BFB ion abundance criteria

20.4. Appendix 20.4: Chromatograms of Typical VOA standard

20.5. Appendix 20.5: Example page from GC/MS VOA organics logbook

20.6. Appendix 20.6: Sample Screening

20.7. Appendix 20.7: Dry weight determination

20.8. Appendix 20.8 Chromatogram of typical Gas standard

Appendix 20.1 - Method 8260D Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	DoD Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method (see ARI SOP 1017S)	QC acceptance criteria published by DoD, if available; otherwise method specified criteria.	Same	1) Recalculate results 2) Locate and correct the source of the problem and repeat the test for all parameters of interest.	Not applicable (NA)	This is a demonstration of ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., BS or PT sample) as described in ARI SOP 1017S. An analyst must completed a successful demonstration of capability before analyzing client samples
Method detection limit (MDL) study	At initial set-up and subsequently once per 12-month period.	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.		Run MDL verification check at higher level and set MDL higher or reconduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Tuning	Prior to calibration	Refer to method for specific ion criteria. Option A or B see appendix 20.4	Method specific tuning criteria from 8260D option B must be used.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units of the daily CCal	DoD requires re-analysis of the ICal	Correct problem, then rerun CCal**.**	Flagging criteria are not appropriate.	
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	Option 1: RSD for each analyte ≤ 20% Option 2: linear least squares regression $r^2 > 0.99$ Option 3: non-linear regression - coefficient of determination (COD) $r^2 \geq 0.99$ (Max 10% of target analytes may fail) (6 points shall be used forsecond order)	Same	Correct problem then repeat initial calibration.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification (SCV)	Once after each initial calibration	Value of second source for all analytes within ± 30% of expected value (initial source)	Value of second source for all analytes within ± 20% of expected value (initial source)	Correct problem, verify second source standard. Rerun verification. If that fails, correct problem and repeat ICal	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Retention time established for all analytes and surrogates	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	Same	NA	NA	

Appendix 20.1 - Method 8260D Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	DoD Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration verification (ICV)	Daily, before sample analysis, and every 12 hours of analysis time	%Difference/Drift for all target analyes: ≤ 20%D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration.) Up to 20% of analytes may exceed ≤ 20%D	Method specific minimum RF factors are applied	Correct problem, then rerun ICV. If that fails, repeat initial calibration.	DoD: Apply Q-flag if no sample material remains and analyte exceeds criteria. ARI: Apply Q-flag to any analytes that exceed ≤ 20%D	.
Internal standards verification	In all field samples and standards	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL EICP area within - 50% to + 100% of ICAL midpoint standard	Same	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for failed standards.	Sample results are not acceptable without a valid IS verification.
Method blank	One per preparatory batch	No analytes detected > ½ MRL. For common laboratory contaminants, no analytes detected ≥ 5 X the MRL.	No analytes detected > ½ MRL. For common laboratory contaminants, no analytes detected > the MRL.	Correct problem, if required, reprep then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch	
Blank Spike (BS) containing all reported analytes & surrogates	One BS per preparatory batch	QC acceptance criteria specified published in ARI's LQAP.	Same unless QC acceptance criteria specified by DoD.	Correct problem, then reprep and reanalyze the BS and all samples in the associated batch, if sufficient sample material is available	If corrective action fails apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch	
Matrix spike (MS)	One MS/MSD per preparatory batch per matrix when sufficient sample is available	For matrix evaluation, use QC acceptance criteria specified by for BS.	Same unless QC acceptance criteria specified by DoD.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply *-flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are out of control, evaluated data to determine the source of difference and to determine if there is a matrix effect or analytical error.
Surrogate spike	All field and QC samples	QC acceptance criteria specified by DoD, if available; otherwise method-specified criteria or laboratory's own in-house criteria	Same	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	For the specific analyte(s) in all field samples collected from the same site matrix as the parent, apply *-flag if acceptance criteria are not met. For QC samples, apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Alternative surrogates are recommended when there is obvious chromatographic interference.

Appendix 20.1 - Method 8260D Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	DoD Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Results report-ed between LOD & MRL	NA	NA	NA	NA	Apply J-flag to all results between LOD and MRL.	

Appendix 20.2
ARI's Routine Method 8260C Target Analytes
Internal Standards, Quantitation Ions, and Calibration Criteria

BETX Internal Standard Associated Analyte[1]	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
Pentafluorobenzene (IS)[1]	363-72-4	168	99	--	--	--
D4-1,2-Dichloroethane(surrogate)	NA	65	130	--	20	20
Benzene	71-43-2	78	52, 77	0.5	20	20
Chlorobenzene-d5 (IS)	108-90-7	117	82	--	--	--
Ethylbenzene	100-41-4	91	106	0.1	20	20
m-Xylene	108-38-3,	106	91	0.1	20	20
p-Xylene	106-42-3	106	91	0.1	20	20
o-Xylene	95-47-6	106	91	0.3	20	20
4-Bromofluorobenzene(surrogate)	400-00-4	95	174	--	20	20
1,4-Difluorobenzene (IS)		114	88	--	--	--
Toluene-d8(surrogate)	108-88-3	98	100	--	20	20
Toluene	108-88-3	92	91	0.4	20	20
1,4-Dichlorobenzene-d4 (IS)	106-46-7	150	152	--	--	--
d4-1,2-Dichlorobenzene(surrogate)	95-50-1	150	152	--	20	20
Gasoline Range RT Marker Stds						
n-Butane(C4)	106-97-8	RIC	NA	NA	NA	NA
n-Pentane(C5)	109-66-0	RIC	NA	NA	NA	NA
n-Hexane(C6)	110-54-3	RIC	NA	NA	NA	NA
n-Heptane(C7)	142-82-5	RIC	NA	NA	NA	NA
n-Octane(C8)	111-65-9	RIC	NA	NA	NA	NA
n-Nonane(C9)	111-84-2	RIC	NA	NA	NA	NA
n-Decane(C10)	124-18-5	RIC	NA	NA	NA	NA
n-Undecane(C11)	1120-21-4	RIC	NA	NA	NA	NA
n-Dodecane(C12)	112-40-3	RIC	NA	NA	NA	NA
2-Methylpentane	107-83-5	RIC	NA	NA	NA	NA
1,2,4-Trimethylbenzene	95-63-6	RIC	NA	NA	NA	NA
Naphthalene	91-20-3	RIC	NA	NA	NA	NA

1 – Compound designations: IS = Internal Standard, SS = Surrogate Standard

Appendix: 20.3
BFB ION ABUNDANCE CRITERIA[1]

Option A: CLP OLM04.2 criteria‡

BFB MASS INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
50	8 to 40% of mass 95
75	30 to 66% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	50-120% of mass 95
175	4 to 9% of mass 174
176	greater than 93% but less than 101% of mass 174
177	5 to 9% of mass 176

Option B: 8260D SUGGESTED ION ABUNDANCE CRITERIA[1]

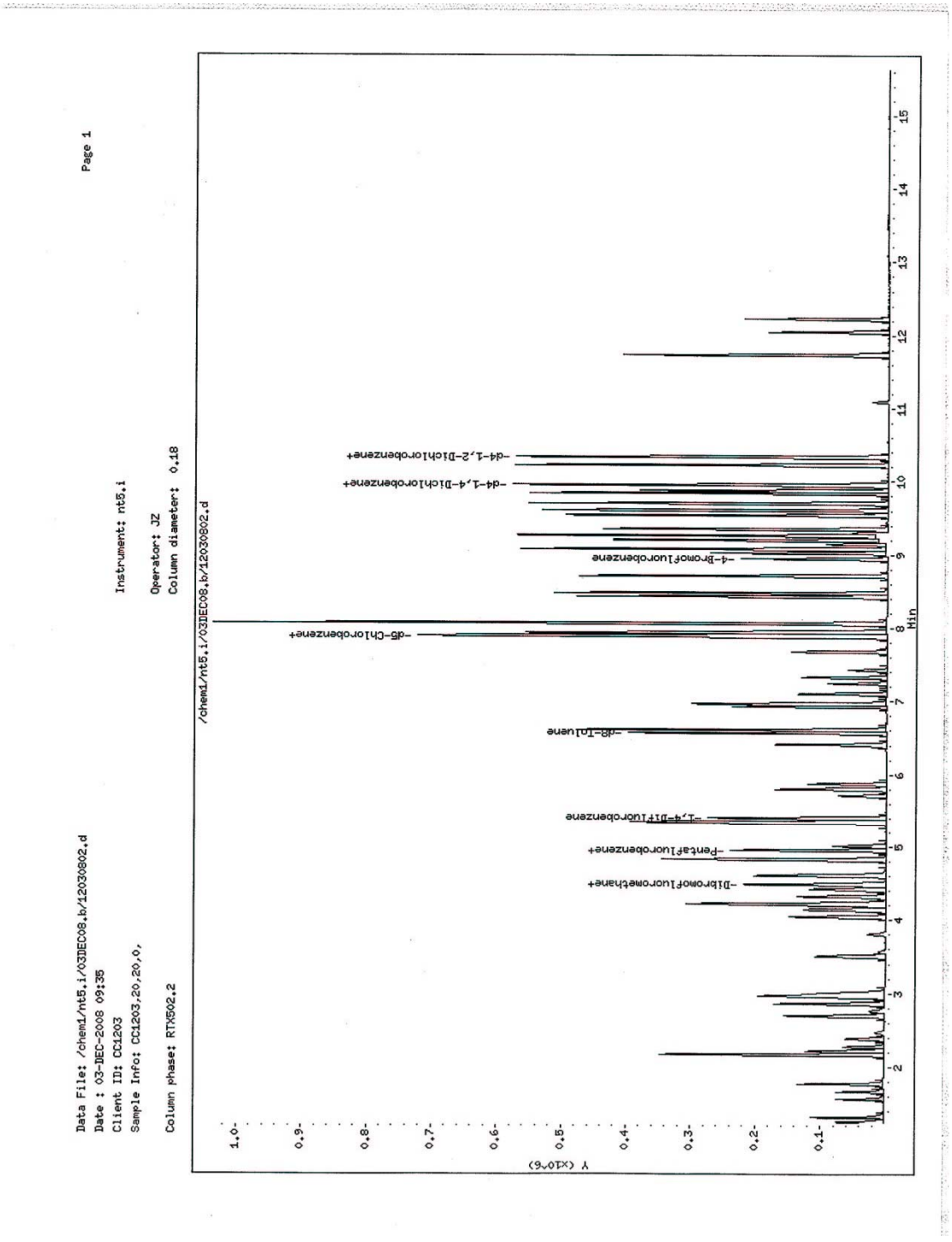
BFB MASS INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)[2]
95	50-200% of mass 174
96	5.0 to 9.0% of mass 95[3] (5-15% when using H_2 carrier)
173	less than 2.0% of mass 174
174	50.0-200% of mass 95
175	5.0 to 9.0% of mass 174
176	95.0% -105% of mass 174
177	5.0 to 10% of mass 176

[1] Method 8260C allows the use of alternate abundance criteria, including CLP. Option B is the default option. Either set of criteria may be used without affecting data quality.
[2] Raw data is rounded to three significant figures and one or less decimal point before comparison to the abundance criteria.
[3] All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundances of m/z 174 may be up to 120% that of m/z 95.

20.9.

Appendix 20.4
Chromatogram of Calibration Standard



Appendix 20.5
GC/MS Volatile Organics Logbook

Analytical Resources Inc.: Organics Instrument Log
NT-3 Serial No.: 10582321978

Date:_____ Analysis: _____ Analyst: _____
GC Program: _____ Column No: _____ Column Type:_____
Instrument Tune (.U or .CT.):_____ EM Voltage: _____
Calibration File:_____ Curve Date: _____

IS/SS	Ical/Ccal	LCS/ICV

Maintenance / Comments

Maintenance Verification (Identify ICal or CCal that demonstrates the instrument is in control):

Every line must contain information or be lined out. Make all entries legible. Start a new page for each QC period.

Form 8038F NT-3 12/12/2008 Revision 001
Organic Instrument Log **Page 02499** 1/16/06

Appendix 20.6
Sample Screening

1.1. Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system.

Aqueous Samples

Place an appropriate volume of aqueous sample in a 45 mL vial and fill the vial with organic free water (OFW). Analyze the sample as a normal sample and determine the appropriate dilution for final analysis.

Solid Samples (Soil & Sediment)

For screening soils, oils, and solid materials, place 1g of sample into a scintillation vial with 5mL VOA grade Methanol and vortex until well mixed. Dilute 100 µL of the methanol solution into 45 mL OFW. Analyze the sample as a normal sample and determine the appropriate dilution for final analysis.

Waste Samples

Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with organic-free reagent water.

Initial and serial dilutions can be made in a 100mL volumetric flask with organic-free reagent water.

Alternatively, prepare dilutions directly in a 5mL syringe filled with organic-free reagent water by adding at least 180µL, but not more than 900µL, of liquid sample.

OVM may be used to determine approximate dilution levels.

Appendix 20.7
Dry Weight Determination

1.2. Determine the percent dry weight of the soil/sediment sample. Other wastes should be reported on a wet-weight basis.

Weigh 5-10g of the sample into a tared weighing dish.

Place the weighted sample in a 104 ± 2°C oven overnight (12 hour minimum).

Remove the sample from the oven and allow it to equilibrate to ambient temperature.

Calculate the sample per cent dry weight:

$$\% \text{ dry weight} = \frac{\text{sample weight dry (g)}}{\text{sample weight wet (g)}} \times 100$$

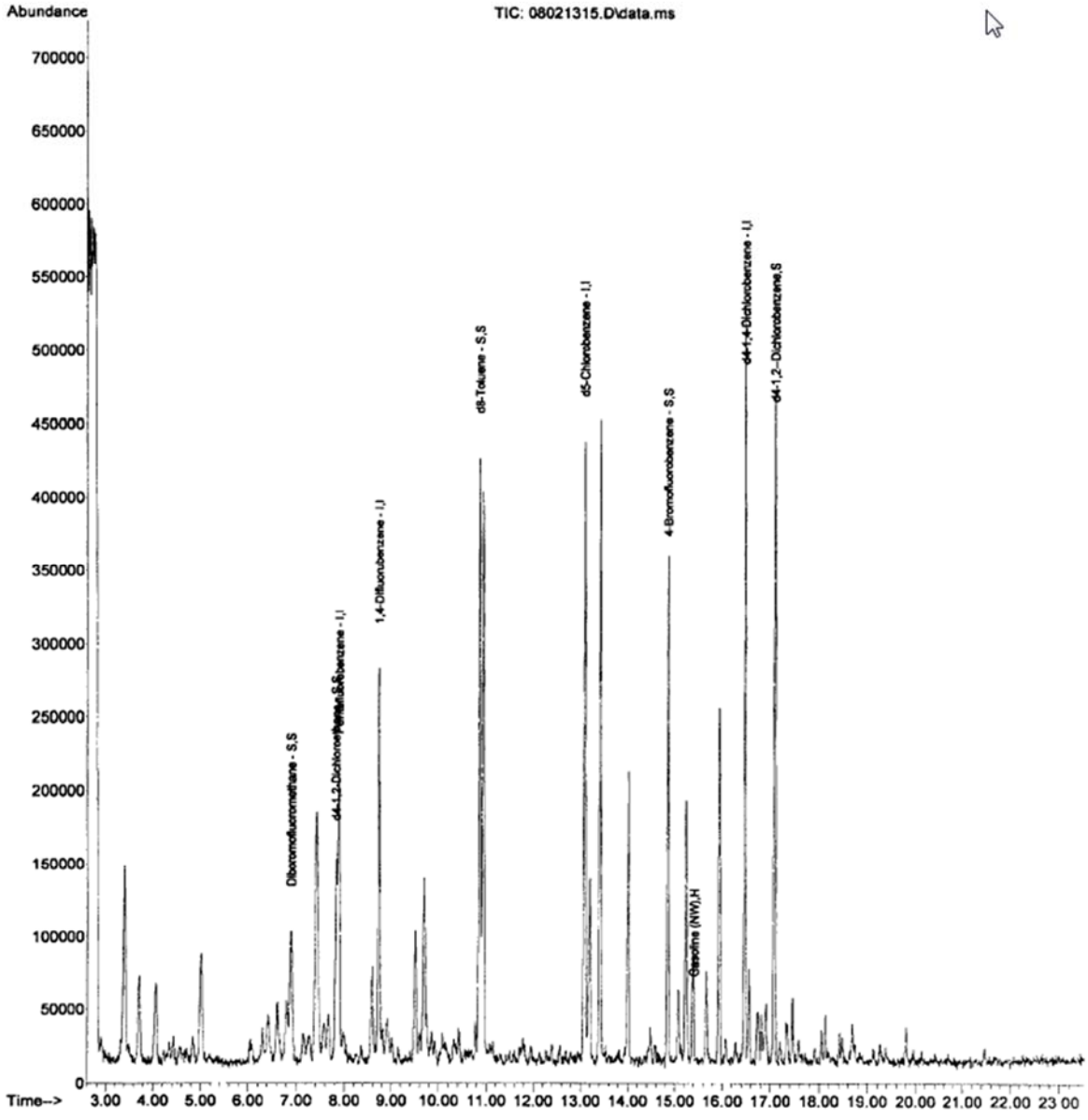
Appendix 20.8

EXAMPLE CHROMATOGRAM OF GAS CALIBRATION

Quantitation Report (QT Reviewed)

Data Path : C:\msdchem\1\DATA\080213\
Data File : 08021315.D
Acq On : 2 Aug 2013 9:33 pm
Operator : JZ
Sample : GASIC050802,
Misc : 13-
ALS Vial : 4 Sample Multiplier: 1

Quant Time: Aug 03 10:06:19 2013
Quant Method : C:\msdchem\1\METHODS\NW080213.M
Quant Title : TPHG QUANTITATION
QLast Update : Sat Aug 03 10:01:41 2013
Response via : Initial Calibration



RTCHECKJ.M Thu Aug 15 13:52:33 2013 Page: 2

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Diesel Range Organic Compounds (DRO)
Residual Range Organic Compounds (RRO)
Methods NWTPH-Dx, AK102 and AK103 and 8015C

SOP 407S
Revision 014.3

Revision Date: 12/2/16
Effective Date: 12/2/16

Prepared by:

Josh Rains, Max Litwin & Van Spohn

Approvals:

Brian N. Bebee, Laboratory Section Manager

David R. Mitchell, Quality Assurance Manager

Annual Review

SOP Number: 407S

Title: Diesel Range Petroleum DRO) Hydrocarbons Residual Range Organic (RRO) Compounds Methods NWTPH-Dx, AK102 and AK103

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This procedure measures the concentration of diesel range organics (DRO) and residual range organic (RRO) (motor oil) in aqueous and solid samples. The procedure includes options that meet the requirements of analytical methods listed in Table 1 and referenced in Section 19.

Table 1 – Analytical Methods

Parameter	Method	Hydrocarbon Range		Reporting Limit (PPM)	
		Beginning	End	Water mg/L	Soil mg/kg
LOW DRO	NWTPH-D	Dodecane (nC_{12})	Tetracosane (nC_{24})	0.1	5
DRO	NWTPH-D	Dodecane (nC_{12})	Tetracosane (nC_{24})	1.0	50
DRO	AK-102	Decane (nC_{10}) peak start	Pentacosane (nC_{25}) peak start	0.1	5
LOW RRO	NWTPH-Dx	Tetracosane (nC_{24})	Octatriacontane (nC_{38})	0.2	10
RRO	NWTPH-Dx	Tetracosane (nC_{24})	Octatriacontane (nC_{38})	2.0	100
RRO	AK-103	Pentacosane (nC_{25}) peak start	Hexatriacontane (nC_{36}) peak end	0.2	10
JP-4	NWTPH-D	Toluene	Tetradecane (nC_{14})	0.1	10
DRO	8015C	Decane (nC_{10})	Octacosane (nC_{28})	0.1	5
BunkerC	NWTPH-Dx	Decane (nC_{10})	Octatriacontane (nC_{38})	0.50	25
Jet-A	NWTPH-Dx	Decane (nC_{10})	Octadecane (nC_{18})	0.1	5
Kerosene	NWTPH-Dx	Toluene	Octadecane (nC18)	0.1	5
Creosote	NWTPH-Dx	Octane (nC_8)	Docosane (nC_{22})	0.1	5
Mineral Spirits (Stoddard)	NWTPH-Dx	Octane (nC_8)	Dodecane (nC_{12})	0.1	5
Mineral Oil	NWTPH-Dx	Tetracosane (nC_{24})	Octatriacontane (nC_{38})	0.2	10

1.2. This method is designed to detect the presence of diesel fuel and or motor oil in environmental samples. Other organic distillates (JP-8, hydraulic fluid, Bunker C, Creosote, Stoddard/mineral spirits, Diesel#1, Transformer oil, Mineral oil, synthetic oils, Jet A, JP4, Lube Oil, Crude, Kerosene, etc.) are also detectable under the conditions of this method. When review of the chromatogram indicates the presence of such compounds or unknown individual organic compounds, the analyst

will inform ARI's Project manager and record the observance on the reviewer checklist. These products are identified using pattern recognition techniques.

1.3. This SOP uses GC-FID to identify and quantify petroleum hydrocarbons. The method reporting limits (MRL) for this procedure are listed in Table 1

1.4. Data is generally reported on a "dry weight" basis and moisture content must be determined for all solid samples.

1.5. This procedure describes the analysis of sample extracts prepared in ARI's Organic Extractions Laboratory. This method must be used by or under the supervision of analysts experienced in the use of gas chromatography to identify and quantify organic compounds using GC-FID. The analysts must be skilled in the interpretation of gas chromatograms as quantitative tools.

2. Summary of the Procedure

2.1. This method describes gas chromatographic conditions used to detect, identify and quantify semi-volatile, solvent extractable petroleum fractions as defined in Table 1. Quantitation is performed by comparing the total FID response between method specific markers to the same response produced by a known quantity of a commercial petroleum distillate. Preparation of the commercial standard is method specific as described in Section 7. Environmental samples are extracted in ARI's Organic Extractions Laboratory and delivered to the GC laboratory for analysis.

2.2. Surrogate standards are added to a measured volume or weight of sample which is extracted using an appropriate organic solvent and extraction technique. The resulting extract is concentrated to a specified final volume. Project or Protocol required Quality Assurance Samples are prepared and analyzed using identical techniques.

2.3. A variety of cleanup steps may be applied to the extracts, depending on the nature of any co-extracted matrix interferences and the requested target analytes. All cleanup techniques must be applied to all sample extracts including QC samples (BLK, BS, MS, MRL, etc.).

2.4. Acid/Silica Gel cleanups are often used for NW Diesel.

2.5. Following any cleanup, the extract is concentrated to a designated final effective volume and delivered to ARI's Gas Chromatography Laboratory for identification and quantification of Total Petroleum Hydrocarbons.

2.6. The extract is injected onto a GC using an auto-sampler and splitless injection technique.

2.7. Analytes are detected and quantified using FID detectors.

2.8. Identified Target analytes are quantified using range quantitation as described in Section 12.

3. Definitions

3.1. Initial Calibration Verification (ICV): a process used to verify that the current instrument calibration is acceptable. Performed at the beginning of an analytical sequence.

3.2. Continuing Calibration Verification (CCV): a process used to verify that the current instrument calibration is acceptable. Performed on an ongoing basis after every 10 field samples.

3.3. Continuing Calibration Verification Standard (CCVS): A standard prepared at the mid-point concentration of the initial calibration, and prepared from the same source as the initial calibration used to perform the ICV/CCV.

3.4. DRO – Diesel Range Organic compounds.

3.5. Method Detection Limit (MDL) – The lowest result that can reliably be distinguished in a matrix from a blank.

3.6. FID (Flame Ionization Detector) – detectors sensitive to organic molecules.

3.7. Second Source Calibration Verification Standard (SCV): A mid-point concentration standard from a source different than that used for the initial calibration used to demonstrate the validity of the initial calibration. The second source standard must be purchased from a different manufacturer than the calibration standard whenever possible.

3.8. Instrument Blank (IB): A QC sample made by adding surrogates to clean solvent used to measure instrument background.

3.9. Blank Spike (BS) – A sample matrix, free from the analytes of interest, spiked with verified amounts of analyzes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system.

3.10. Blank Spike Duplicate (BSD) – A sample matrix, free from the analytes of interest, spiked with verified amounts of analyzes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system.

3.11. Matrix Spike (MS): - A sample prepared by adding a known mass of target analyte to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on a method's recovery efficiency.

3.12. Element: Computer hardware and software system used to compile and report final analytical data.

3.13. Limit of Detection (LOD) – The lowest result that can be reported while meeting method precision and accuracy requirements.

3.14. Method Reporting Limit (MRL) – The lowest result that may be reported unqualified based on the lowest curve point.

3.15. Matrix Spike Duplicate (MSD): - A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.16. Method Blank (BLK) – A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

3.17. DI Water - Deionized reagent water, all references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.

3.18. RRO – Residual Range Organic compounds.

3.19. Surrogate – A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

3.20. MRL Check (MRL) - A laboratory control spike prepared at reporting limit or MRL, used to calculate the detection limit.

3.21. Target Software - Software used to integrate and reduce raw chromatographic data.

4. Interferences - Sources of interference in this method can be grouped into three broad categories:

4.1. Contaminated solvents, reagents and/or sample processing hardware.

4.1.1. Interferences by phthalate esters introduced during sample preparation can pose a major problem. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

4.1.1.1. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and by checking all solvents and reagents for phthalate contamination.

4.1.1.2. Method interferences may be reduced by washing all glassware with hot, soapy water and then rinsing them with warm tap water, acetone, and methylene chloride.

4.1.1.3. Glassware should be baked at 400°C for a minimum of 4 hours after washing to further reduce interference problems.

4.1.1.4. High purity reagents must be used to minimize interference problems.

4.2. Contaminated GC carrier gas, parts, column surfaces and/or detector surfaces

4.2.1. Chromatographic interference

4.2.1.1. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination (if needed).

4.3. Matrix Interferences

4.3.1.1. Bio-organics may be eliminated by Silica Gel and Acid cleanup. (EPA Method 3630 and WADOE Method).

4.3.1.2. Interferences co-extracted from the samples will vary considerably from sample to sample. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

5. Safety

5.1. The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.

5.2. Always wear appropriate PPE (personal protective equipment) when working with environmental samples and/ or organic solvents. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, etc. are provided for your protection

5.3. Safety Data Sheets (SDS) that outline hazards, exposure treatments and regulatory guidelines are available for all chemicals used in this procedure and should be consulted as the need may arise. The SDS file is located in the central project management area. SDS are also available online at www.SDShazcon.com, and online via the vendor's website.

5.4. Sample extracts may contain hazardous waste; treat them as potential health hazards.

5.5. All handling of standards and samples should be done in a fume hood.

6. Equipment and Supplies

6.1. Gas chromatograph

6.1.1. Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including:

6.1.2. Autosampler – capable of holding 1 to 100 extracts, and programmable to inject sample extracts.

6.1.3. Analytical fused-silica capillary columns - Columns used may vary depending on currently available technology (other columns may be used so long as they generate equivalent data):

6.1.3.1. Column: RTX-1, 20 m, 0.25 mm ID, 0.1 µm film (or equivalent).

6.1.3.1.1. Alternate ZB – 1, 20m, 0.25mm ID, 0.25 µm film

6.1.3.2. FID detector

6.1.4. Data system – Chemstation must be interfaced to the GC. The system must allow the recording of instrument response as a function of time.

6.1.4.1. The data must be securely stored for at least seven years from date of acquisition.

6.2. Syringes - 10 µL, 25 µL, 50 µL, 100 µL, 500 µL, 1000 µL

6.3. Balance - Analytical, 0.0001 g

6.4. Autosampler vials- 2 ml clear glass vials with PTFE lined crimp caps.

7. Reagents and Standards

7.1. All concentrated stock standards and neat compounds must be equilibrated to room temperature before they are measured or weighted. When measuring the volume of standard solutions use a syringe with capacity of about 2 times the volume being measured. When measuring less than ½ the syringe volume, choose a smaller syringe, if possible.

7.2. Surrogate Standards

7.2.1. 10mg/mL o-terphenyl Stock Solution: Accurately weighing about 0.5g of the neat surrogate compound, ortho-terphenyl, into a 50mL volumetric flask and fill it to volume with methylene chloride. The neat must be at least 97% pure or corrected for purity.

7.2.2. 10mg/mL n-triacontane Stock Solution: Accurately weighing about 0.5g of the neat surrogate compound, n-triacontane, into a 50mL volumetric flask and fill it to volume with methylene chloride. The neat must be at least 97% pure or corrected for purity. Caution: n-triacontane is difficult to dissolve in methylene chloride. The surrogate solution should be prepared at room temperature and addition of *iso*-Octane, gentle heating and/or sonication of the solution may be required to completely dissolve the n-triacontane.

7.2.3. Surrogate Spike Solution: Add 0.1125g of o-terphenyl and 0.1125g of n-triacontane to a 100mL volumetric flask and dilute to volume with methylene chloride. The Surrogate Spike Solution will contain o-terphenyl and n-triacontane at 1125µg/mL

7.3. Calibration Standard

7.3.1. Prepare a Diesel Calibration Solution containing commercial Diesel #2 at 2500µg/mL and o-Terphenyl at 450µg/mL using methylene chloride. Also used for AK102.

7.3.2. Prepare a Motor Oil Range Calibration Solution containing commercial SAE 30 weight motor oil at 5000µg/mL and n-triacontane at 450µg/mL using methylene chloride. Verify you are using SAE 30 weight and not SAE 10-30 weight.

7.3.3. For AK103 Prepare a Motor Oil Range Calibration solution containing commercial SAE 30 and 40 weight motor oil (1:1) at 5000µg/mL and n-triacontane at 450µg/mL using methylene chloride.

7.4. Initial Calibration Verification Standards

7.4.1. A secondary source standard prepared in the same manner as the Calibration Standard. The second source standard must be purchased from a different manufacturer than the calibration standard whenever possible.

7.5. Continuing Calibration Verification Standards

7.5.1. Prepare by diluting a diesel or motor oil calibration solution 1:5.

7.6. Diesel Spike Solution

7.6.1. Prepare a diesel spike solution of containing Diesel # 2 at 15,000µg/ml in Acetone.

7.6.2. AK102/103 spike solution contains Diesel#2, SAE 30 and 40 weight motor oil at a total concentration of 7500ug/ml in Acetone.

7.7. Retention Time Standard (RT)

7.7.1. A retention time standard contains the even carbon number alkanes from n-C_8 to n-C_{40}, plus Toluene, n-C_{25} at varying concentrations, and 112.5µg/mL of each surrogate (o -terphenyl & n-triacontane) in methylene chloride.

7.8. Instrument Blank

7.8.1. An instrument blank contains o-terphenyl and n-triacontane at 112.5µg/mL each in methylene chloride.

8. Sample Collection, Preservation, Shipment, Storage, Holding time and Disposal.

8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 °C.

8.2. Samples must be stored at ARI, at >0 to 6 °C until final disposal.

8.3. Samples must be extracted within holding times determined from the day of sampling. The standard holding time for water samples is seven days. The standard holding time for solid samples is 14 days.

8.4. Solid and sediment samples may be stored at -10°C to -20°C to extend the holding time to one year.

8.5. Extracts are delivered to Refrigerator 15 in the instrument laboratory by extractions technicians.

8.5.1. Analysts in the instrument lab will assume custody of the sample extracts, reassign the location in Element to refrigerator 17 and begin the analysis.

8.5.2. Extracts must be stored at >0 to 6 °C and protected from light.

8.5.3. Extracts must be analyzed within 40 days of extraction initiation.

8.5.4. Extracts must be stored in the location assigned in Element.

8.5.5. Extracts may be disposed 40 days after the analysis has been completed.

8.5.6. Extracts will be disposed in the large blue barrel in the satellite accumulation area designated for extract vials. Disposed extracts are now marked in Element as disposed.

9. Quality Control

9.1. Surrogates

9.1.1. Surrogates are compounds chemically similar to the targeted analytes, but not expected to be found in environmental samples used to evaluate extraction efficiency by measuring recovery. Surrogates are added to every sample analyzed.

9.2. Method Blanks

9.2.1. A method blank is a volume of a clean reference matrix (DI for water samples, or purified solid matrix for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

9.2.2. Method blank extraction and analysis are performed as follows:

9.2.2.1. Whenever samples from different jobs are extracted by the same procedure up to 20 samples may be batched together with the same method blank.

9.2.2.2. Every 20 field samples, excluding matrix spike/matrix spike duplicates, that are of a similar matrix (water, soil/sediment) or similar concentration (soil/sediment only) would constitute a separate analytical batch.

9.2.2.3. Method blanks must be analyzed on each GC system used to analyze associated samples if mandated by project-specific requirements. Otherwise a single analysis of the method blank is sufficient. If instrument caused contamination is suspected, the method blank should be reanalyzed to determine if this is so.

9.2.2.4. Each method blank must contain all surrogates used for sample extracts.

9.3. Blank Spikes

9.3.1. To evaluate the accuracy of the analytical method independent of matrix-related effects, a matrix-specific blank spike (BS) must be included in each preparation batch.

9.3.2. A BS is a volume of clean reference matrix (DI for water samples, or sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The BS must contain all surrogates required by the method. Typically, the BS (and BSD when applicable) is spiked with Diesel for NWTPH-Dx and Diesel + Motor Oil for AK102 / AK103.

9.3.3. In instances where insufficient sample volumes exist to perform an MS/MSD analysis, an BS/BSD may be used to assess the precision of the analytical method. The BS Duplicate is prepared and analyzed identically to the BS.

9.3.4. BS samples should be prepared at the same frequency as method blanks (every 20 field samples of the same matrix prepared at the same time by the same method.)

9.3.5. BS (and BSD) samples must contain all surrogates used for sample extracts.

9.3.6. The RPDs between the BS and BSD must be measured and reported.

9.3.7. Evaluate the BS/BSD RPD and note any deviation >30% in the reviewer checklist.

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

9.4.1. To evaluate the effects of the sample matrix on the methods used for TPH analyses a sample per batch is prepared in triplicate (one un-spiked sample, and the spiked MS/MSD set.)

9.4.2. A matrix spike and matrix spike duplicate must be extracted and analyzed for every 20 field samples of a similar matrix or whenever samples are extracted by the same procedure at the same time.

9.4.3. As part of a client's QA/QC program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to the laboratory for analysis. The laboratory will not perform MS/MSD analysis on any of the field QC samples.

9.4.4. If a client designates a sample to be used as an MS/MSD, then that sample must be used.

9.4.5. If there is insufficient sample remaining in any of the samples to perform an MS/MSD, the laboratory shall immediately contact the client to inform them of the situation. The client will either approve that no MS/MSD is required, require that a reduced sample aliquot be used for the MS/MSD analysis or request that a BS/BSD (See Section 9.3.3) analysis be performed. The laboratory shall document the decision in the case narrative.

9.4.6. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.4.7. The RPDs between the MS and MSD must be measured and reported.

9.4.8. Evaluate the MS/MSD RPD and note any deviation >30% in the reviewer checklist.

9.5. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for matrix spike and matrix spike duplicates are statistically generated on a periodic basis.

9.5.1. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation.

9.5.2. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. Current control limits may be found on the ARI Intranet.

9.5.3. All analysts using this SOP must use it in conjunction with Control Limit documentation in order to assess data quality and any possible need for corrective actions.

9.6. Initial Demonstration of Proficiency- Each analyst must demonstrate initial proficiency with each sample preparation and determinative method combination performed, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat these procedures whenever new staff is trained or significant changes in instrumentation are made. Review EPA Methods 8000C and 3500 for information on how to accomplish this demonstration.

10. Calibration and Standardization

10.1. The GC-FID instrument is calibrated in the diesel range using 6 standards and in the residual range using 5 or 6 standards. A minimum of 5 points is required for all DRO and RRO calibration curves. The curves must have a %RSD of less than 20%. The AK102/103 curves must have a %RSD of less than 20%. The average calibration factor is used to quantify detected analytes.

10.1.1. Calibration range will be 50 - 2500 µg/mL for diesel range. Using the diesel range stock prepared above, individually prepare the calibration standards at concentrations of 50, 100, 250, 500, 1000 and 2500 µg/mL in methylene chloride. The calibration range for motor oil range will be 100 – 5000 µg/mL. Individually prepare the residual range stock to concentrations of 100, 250, 500, 1000, 2500 and 5000 µg/mL.

10.1.2. The lowest concentration calibration standard analyzed during the initial calibration establishes the reporting limit, adjusted for the final volume of the extract and amount of sample extracted, for that compound.

10.2. Specific hydrocarbon ranges requested by the client may be calibrated using either a single or a multi-point calibration. ARI maintains a library of chromatograms to aid in identification of various hydrocarbon distillates.

10.3. The reviewer checklist from the Initial Calibration must be included with every job run under the corresponding initial calibration.

10.4. Sequences are always started with an alkane (retention time) standard containing the even carbon number alkanes from n-C_8 to n-C_{40}, plus Toluene, n-C_{25}, and the surrogates o -terphenyl and n-triacontane, then an instrument blank. Curves are then run for any analyte requiring a new calibration, and calibration verification standards are run to validate the appropriate curves from a previous run(s).

10.4.1. The alkane standard analyzed at the beginning of each sequence is used to determine actual retention times for the various alkane ranges, and the retention time are updated in the method every 24 hours.

10.4.2. A new macro version is generated and saved every time the macro is updated with both calibration factors and calibration dates. The analyst must be extremely careful when entering values in the macro, and must double check each modified macro for accuracy and completeness prior to using it.

10.4.3. Once the macro is updated, it will calculate and report both total area and concentration for each defined range. Surrogate areas are automatically subtracted from the diesel and motor oil range total. The surrogate area values being subtracted are reported in the macro so it can be easily verified.

10.4.4. The analyst enters each range concentration into ELEMENT. ELEMENT then incorporates the sample amount, final extract volume, and dilution factor to calculate the final concentration of the sample.

10.5. Initial and Continuing Calibration Standards (ICV/CCV) must be run at the start and end of a run sequence and after every 10 field sample injections within the sequence. Calibration factors for each CCV must be within 15% D (25% D for AK102/103) of the average calibration factor of the working curves. If a CCV fails to meet the 15% D (25% D for AK102/103) limit and corrective action does not resolve the problem, a new curve must be generated for that analyte.

10.6. A sequence may continue as long as the CCV is within 15%D (25% D for AK102/103) of the average calibration factor from the curve and no more than 24 hours have elapsed since analysis of the last Retention Time Standard (Section 9). When evaluating the CCV for a specific project only the relevant ranges must meet QC limits for the run to continue and the data to be valid. For example, if motor oil range CCV failed, it would not affect the data for a project requesting diesel range only.

10.7. Each day continuing calibration standards must be evaluated to determine if the calibration is still valid. The analyst should evaluate peaks and responses and examine the standard chromatogram for evidence of leaks or other problems with the instrument.

10.8. The GC lab accepts custody of sample extracts when they are signed into the GC sample log book designated for the fuels refrigerator and the extract custody is then the responsibility of the GC laboratory. Extracts are subsequently signed out of Refrigerator 15 by an analyst who assumes custody of the extracts until they are signed back into the refrigerator or into archive.

10.9. See Corrective Action Section 9.0 for any deviations from this procedure.

Table 2: Method ICal Acceptance Criteria

Analytical Method	Ical RSD	ICV %D	CCV
NWTPH-D	≤ 20%	≤ 15%	≤ 15%

AK-102	≤ 20%	≤ 25%	≤ 25%
8015C	≤ 20%	≤ 15%	≤ 15%

10.10. Suggested Integration Parameters:

Table 4: Typical Integration Parameters

Parameter	Setting
Initial Start Threshold	1.00
Initial End Threshold	1.00
Initial Area Threshold	25000.00
Initial P-P Resolution	1.00
Initial Bunch Factor	5
Initial Negative Peaks	OFF
Initial Tension	10

10.11. Each peak will be integrated to baseline, by the Falcon Integration Parameters. Manual baselines may be required for some standards and samples to achieve proper integration. See SOP 1021 for guidance on manual integration.

10.12. Calibration Verification

10.12.1. Calibration verification standards (ICV/CCV) are standards run at the beginning and end of each sequence, after every 10 field samples or fewer.

10.12.2. The percent drift (%D) of the CCV must be within 15% of the true value for Method NWTPH-D and 8015C, and within ±25% for Method AK-102 & AK103. See ARI SOP 400S, "Gas Chromatography (GC) Analysis Procedure Method 8000C," for %D calculation.

10.12.3. If the response for a CCV goes high, that is, the calculated concentration is > 115% (125% for AK-102 or AK-103) of the expected value, but the analyte was undetected in the samples affected by the CCV, the samples do not need to be re-analyzed. The fact that the CCV is high indicates that if the analyte is present, it would have been detected. This is not the case for a CCV that fails <85%.

10.12.4. If a CCV fails to meet criteria a second CCV may be run, if the second CCV passes and the bracket reported then both CCVs need to be noted in the Reviewer checklist.

10.12.5. If an analyte is present in the sample above the linear range of the curve, the sample must be run at a dilution with the analyte within the calibration range, with acceptable CCVs and ideally near the CCV concentration.

11. Procedure

11.1. Sample Screening: It is highly recommended that all samples suspected of containing high concentrations of fuels, be screened prior to analysis, as they may contain high enough concentrations of petroleum products to overload the column and/or the detectors.

11.2. Gas Chromatograph Analysis:

11.2.1. Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods.

11.2.2. Set the GC operating conditions so that Toluene is distinguished from the solvent peak, target compounds do not co-elute and there is minimal column bleed. Suggested GC operating conditions are listed in Table 4 (samples must be run using the same instrument conditions as the initial calibration).

Table 4: Typical GC Operating Conditions	
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	35 - 165°C at 35C°/min
	165 -250°C at 30C°/min
	250 -350°C at 20C°/min
Final temperature:	330°C, hold for 2 minutes
Injector temperature:	300°C
Detector temperatures:	350°C
Detector make-up gas flows	40 mL/min
Column flow	2.5 mL/min
Injector:	Grob-type, splitless injection
Injector Pulse	15 psi at 0.45 minutes
Split flow	Not Applicable
Sample volume:	1 µL
Carrier gas:	Hydrogen

11.2.3. If a new analysis sequence is being started, verify the calibration curve by analysis of the ICV.

11.2.4. Calculate the percent difference between the ICV/CCV response factor and the average calibration factor from the curve (as in section 6.8). Percent difference should be < 15% for NWTPH-D and 8015C and < 25% for AK-102 & AK103.

11.2.4.1. Rinses before CCVs are not allowed unless rinses are placed before all injections in the analytical sequence.

11.2.5. An instrument blank must be run in every sequence to determine the area generated from normal baseline noise under the conditions prevailing within the 24-hour period. This laboratory QC sample is integrated over the DRO and/or RRO area in the same manner as samples. The concentration of target analytes must be less than the ½ MRL. If not, instrument maintenance must be performed to remove contamination from the chromatographic system.

11.2.6. A Retention Time (RT) standard must be run every 24-hour period at the start of each analytical sequence.

11.2.6.1. Retention time ranges are defined by adding or subtracting 0.05 minutes from the apex of the peak for the designated hydrocarbon marker.

11.2.6.2. The Target method used to identify the range markers is then updated with the revised RT window data.

11.2.6.3. Deviation from the 24-hour period must be noted in the Reviewer checklist.

11.2.7. Sample extracts are introduced into the instrument in the same manner as the calibration standards.

11.2.8. Each method blank and blank spike should be run as closely as possible to the sample batch to which they are associated. That way, the results for these blanks will more accurately reflect the condition of the samples at the time of analysis.

11.2.9. Whenever a sample with a high concentration of target analytes is analyzed, the potential for carryover exists. If possible, the analyst should analyze a blank following the analysis of "dirty" samples.

11.2.10. If no blank was analyzed, the following samples should be examined for evidence of carryover. If carryover appears to be a problem, the samples should be re-analyzed.

11.2.11. When the sample cannot be re-extracted due to insufficient volume, notify the Project Manager. Report the sample as analyzed and explain why it was not re-extracted on the Reviewer checklist form.

11.2.12. When sample concentrations exceed the limits of the initial calibration, dilute the extract and re-analyze. Samples must be diluted so that all target analyte peaks are on scale.

11.2.13. Matrix spikes and matrix spike duplicates do not require dilution.

11.2.14. A CCV must be analyzed after every 10 field samples. A CCV must, also, be analyzed at the end of each sequence.

11.2.15. All samples should be bracketed by CCVs that meet the criteria in Section 10.6.

11.2.16. When a CCV fails, all affected samples (those samples run after the last passing CCV) must be re-analyzed.

11.2.17. A sequence may continue as long as the CCVs meet the criteria in Section 10.6.

12. Data Analysis and Calculations

12.1. After the calibration curve has been analyzed, the Response Factor (RF) for each hydrocarbon range must be determined using the following formula:

$RF = A / C$
where:
A = Total peak area for the hydrocarbon range
C = Concentration of the hydrocarbon analyte

12.2. After calculating the RF for each hydrocarbon range for each calibration standard, the average RF is calculated by summating the RF for each calibration standard and dividing by the number of calibration standards. The formula is:

$\text{Average RF} = \Sigma RF_i / n$
where:
RF_i = the response factor for each hydrocarbon range in the calibration standard
N = the total number of standards (usually 6)

12.3. Relative Standard Deviation- The relative standard deviation of the response factors for each hydrocarbon range is determined by dividing the standard deviation of the RFs by the peak's average RF. The formula is:

$$RSD = SD / (Ave\ RF) = \frac{((\Sigma (RF_i - Ave\ RF)^2) / (n-1))^{1/2}}{Ave\ RF}$$

12.4. Percent Difference- the percent difference calculations for CCVs involve dividing the difference between the CCV RF and the average RF by the average RF and converting this number to percent. The equation is:

$\%D = 100(Conc - Concmp) / Concmp$
where:
Concc = the quantitated concentration in the CCV

Concmp = the concentration of the midpoint in the ICal (250)

12.5. TPH Identification- A sample is tentatively determined to contain a specific TPH analyte when the GC-FID response within a defined retention time (RT) window match the GC-FID response of a standard in the same RT window.

12.5.1. The Retention Time (RT) windows are defaulted to 0.05 minutes as discussed in Section 11.2.6.

12.5.2. When samples appear to contain weathered or treated TPH, or mixtures of various TPH distillates, use of standards may not be straightforward (or technically appropriate). In such cases, the analyst must decide which TPH pattern most closely represent the range of TPH present and will quantify total TPH by quantifying the most appropriate GC-FID response range based on the analyst's knowledge and experience. Weathered patterns and complex mixtures should be noted on the Reviewer checklist form.

12.5.3. All TPH surrogate peaks should show consistent RT relative to the initial calibration. Large chromatographic interferences may cause inconsistent shifting by moving some of the peaks more than others. The chromatogram of samples should be examined to ensure that false negatives aren't created by this manner of chromatographic overload.

12.6. Sample Quantitation

12.6.1. Water

Concentration (µg/L) = $\frac{(Ax)(FEV)(DF)}{(RF)(Vo)(Vi)}$
where:
A_X = Total area of the quantitation range for the analyte being measured
FEV = Final effective extract volume (mL)
RF = response factor for compound being measured
Vo = Volume of water extracted (ml)
Vi = Volume of extract injected (µL)
DF = Sample Dilution Factor (1 for undiluted samples)

12.6.2. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)

Concentration (µg/kg) = $\frac{(Ax)(FEV)(DF)}{(RF)(Vi)(Ws)(DW)}$
where:
A_X = Total area of the quantitation range for the analyte being measured
FEV = Final effective extract volume (mL)

DF = Sample Dilution Factor (1 for undiluted samples)
RF = response factor for compound being measured
Vi = Volume of extract injected (µL)
Ws = Weight of sample extracted in grams
DW = % Dry weight of sample

13. Method Performance

13.1. The QA department measures method performance using a combination of continuing MRL studies, quarterly Verification standards, performance evaluation samples, standard reference materials, and the monitoring of surrogate and spike recoveries.

13.1.1. Detection limits- the LOD for all analytes quantitated using this SOP are set using the low point of the initial calibration curve and validated by MRL studies.

13.1.2. MRL studies are performed each quarter for each analyte by each preparatory and analytical method.

13.1.3. LOD and MRL values may be found for each analyte on the ARI's Web Site

13.2. Laboratory precision and bias measurements are performed by monitoring surrogate and spike recoveries in samples and quality control samples.

13.2.1. Control limits are calculated from these recoveries.

13.2.2. These control limits are disseminated to the bench chemists and ELEMENT administrator for use in monitoring method performance in real time.

13.2.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found on the ARI's Web Site.

13.3. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in Appendix 2.2 of ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC must be documented in the instrument maintenance logbook.

13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.

14. Pollution Prevention

14.1. All GC split vents will be connected to an exhaust vent.

14.2. All syringe rinses are discharged into activated charcoal. Spent charcoal is properly disposed of as "Solvent Contaminated Solids" by ARI's designated Treatment, Storage and Disposal Facility.

14.3. Disposed expired standards into the designated barrel in the hazardous waste room.

14.4. Autosampler vials containing sample extracts are placed in the satellite accumulation station in the GC store room for eventual removal by an EPA approved Treatment, Storage and Disposal Facility.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 of this document.

15.2. Requirements for Method Blanks are detailed in Section 9.

15.3. Internal Standards- All samples' internal standard peak areas must meet the technical acceptance criteria listed in Section 9 of this SOP.

15.4. Surrogate Recoveries

15.4.1. All method blanks, blank spikes, matrix spikes, matrix spike duplicates, sample duplicates, or other samples must have acceptable surrogate standard recoveries. Surrogate recoveries are acceptable when they are within ARI's statistically generated control limits or limits set by client specific limits.

15.4.2. Any surrogate recovery that is "out-of-control" required that a corrective action be initiated.

15.4.2.1. These requirements do not apply to subsequent dilutions of samples where a prior analysis of the diluted sample extract shows acceptable surrogate recovery.

15.4.2.2. When mandated by contract-specific requirements, corrective actions must be performed for unacceptable surrogate recovery even when the criteria are labeled as advisory in the reference method.

15.4.3. Surrogate acceptance criteria are matrix specific. When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.

15.5. Blank Spike Samples

15.5.1. Blank spike (BS) recovery must fall within specified recovery acceptance limits or corrective action is required.

15.5.1.1. BS recovery acceptance criteria are determined statistically from historic laboratory data. Criteria specified by client specific requirements may supersede ARI's historic values.

15.5.1.2. When mandated by a particular quality system or contract-specific requirements corrective actions is required in response to unacceptable BS criteria, even when the criteria are labeled as advisory in the reference method.

15.5.2. When an BSD is analyzed, relative percent difference (RPD) acceptance limits also apply, if specified by contract or quality system.

15.5.3. The RPD between spiked analyte concentrations in an BS and an BSD should be < 30%. If the RPD exceeds 30% this must be noted in the reviewer checklist.

15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.6.1. MS spike recoveries are advisory and should not be used to reject batch data.

15.6.2. Spike acceptance criteria are matrix specific. When analyzing for which no specific acceptance criteria are available, the closest approximation of available acceptance criteria may be used for advisory purposes only.

15.6.3. When an MSD is analyzed, relative percent difference (RPD) acceptance limits also apply, if specified by contract or quality system.

15.6.3.1. The RPD between spiked analyte concentrations in an MS / MSD should be 30%. If the RPD exceed 30% this must be noted in the reviewer checklist.

15.7. Holding Times

15.7.1. Samples should be extracted within the sample holding time (7days for waters and 14 days for soils) and extracts should be analyzed within 40 days from the initial date of extraction.

15.7.2. In the event that re-analysis due to an out of control event requires that samples be re-analyzed after their holding time has elapsed (7 days for water and 14 days for solids) the analyst should analyze and report both data sets, whenever practical, distinguishing between the initial analysis and re-analysis on all deliverables. This will document that the samples were originally run within holding times and may allow for comparisons that will determine whether data quality was affected by the samples being analyzed out of holding.

15.7.3. If any samples extracts are analyzed after the 40-day holding time has elapsed, the analyst shall document this in the analytical notes accompanying the data so that it may be included in the narrative.

16. Corrective Actions for Out of Control Events

16.1. Corrective actions may include any, but are not limited to, the following:

16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the reviewer checklist.

16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.3. Re-preparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.4. Reanalysis – the extract aliquot that was originally prepared is reinjected and run on the gas chromatograph again.

16.1.5. Re-extraction – a re-extraction request is filled out (Form 0030F). Copies of the form are provided to the extractions department, the project manager, the QA manager and the lab manager. The remaining sample is extracted.

16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in ELEMENT.

16.1.7. Recalibration – a new initial calibration is evaluated, and the associated samples reanalyzed.

16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.

16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.

16.2. When an Initial Calibration Verification (ICV) RSD for an analyte exceeds the method requirement.

16.2.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.2.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option, and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is expressly prohibited, since the analyst has generated data that demonstrate that the linear model does not apply to all the data.

16.3. When an Initial or Continuing Calibration Verification (ICV or CCV) fails:

16.3.1. Perform the appropriate corrective action(s) from Section 16.1 and re-calibrate the instrument.

16.3.2. DoD-QSM requires that %D for all analytes in the ICV or CCV be ≤ 20% (50% for end of batch CCV). For DoD analyses, if no samples have been analyzed and less than 1 hour elapsed since the failed CCV, two additional consecutive ICVs or CCVs may be analyzed. This is not required; the analyst may default to Section 16.3.1.

16.3.2.1. When both CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.3.2.2. If either of the two CCVs fail or their analysis cannot be started within one hour, associated samples may not be reported and the instrument must be re-calibrated.

16.4. Surrogates

16.4.1. Examine the bench sheet to verify spiking levels are correct.

16.4.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.5. Method Blanks- Corrective action for a method blank which fails acceptance criteria may involve re-extraction and reanalysis of all associated samples and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.6. Blank Spikes

16.6.1. Examine the bench sheet to verify spiking levels are correct.

16.6.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.7. Matrix Spike/Matrix Spike Duplicates

16.7.1. Examine the bench sheet to verify spiking levels are correct.

16.7.2. Recoveries are advisory and should not necessarily result in re-extraction.

16.7.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve, a dilution must be performed such that the analyte's quantitated value is within the curve range.

16.8.1. All dilutions should keep the response of the major constituents near the midpoint of the linear range of the curve.

16.8.2. When peaks from an analyte saturate the detector:

16.8.2.1. The analyst should analyze an Instrument Blank consisting of clean solvent until the system has been decontaminated.

16.9. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.

16.9.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)

16.9.2. All QC limit issues (including continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

16.10. If contaminants (including target and non-target compounds) continue to cause significant interference, even after all relevant cleanups have been performed; the sample should be re-extracted at a level appropriate to the amount of contamination. The re-extraction level should be based on the initial analysis. The experience and discretion of the analyst and section supervisor will be relied upon for re-extraction decisions. The PM will be notified if re-extraction at a different level is required.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Sections 16.2 and 16.3 for guidance on dealing with initial and continuing calibration out-of-control events.

17.2. See Section 16.4 for guidance on dealing with surrogate out-of-control events.

17.3. See Section 16.5 for guidance on dealing with method blank related out-of-control events.

17.4. See Section 16.6 for guidance on dealing with blank spike related out-of-control events.

17.5. See Section 16.7 for guidance on dealing with MS/MSD related out-of-control events.

17.6. See Section 16.8 for guidance on dealing with over range related out-of-control events.

18. Waste Management

18.1. All extract vials must be disposed of by placing them in the blue hazardous waste drum in the lab set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.

18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.

18.3. All spent charcoal must be disposed of by placing it in the charcoal disposal bin located in the extractions lab.

18.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

19.1. Alaska Laboratory Method for the Analysis of Diesel Range Organics (AK102), published in Appendix D of State of Alaska Department of Environmental Conservation, Contaminated Sites Program, Underground Storage Tanks Procedures Manual, April 8, 2002.

19.2. Alaska Laboratory Method for the Analysis of Residual Range Organics (AK103), published in Appendix D of State of Alaska Department of Environmental Conservation, Contaminated Sites Program, Underground Storage Tanks Procedures Manual, March 1,1999.

19.3. Washington State Department of Ecology, "Analytical Methods for Petroleum Hydrocarbons", Publication No ECY97-602, "NWTPH-Dx – Semivolatile Petroleum Products Method for Soil and Water, June, 1997

19.4. This SOP incorporates guidelines from U.S. EPA, "Test Methods for Evaluating Solid Waste" (SW-846), and Method 8000C, Revision 3, March 2003.

19.5. Department of Defense, Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/25/2010

19.6. EPA Method 8015C, "Non-Halogenated Organics by Gas Chromatography", Revision 3, February 2007

20. Appendices

20.1. TPH Quality Control Requirements

20.2. Chromatogram Library of Common Petroleum Products

Appendix 20.1: In House Quality Control Requirements

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	DoD-QSM Acceptance	Corrective Action	Flagging Criteria
Demonstration of capability (DOC). DOC requirements are outlined in ARI SOP 1017S.	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method.	ARI spike recovery QA limits	Same	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria.	Not applicable (NA)
Quantitation Limit Spike (MRL) study	At initial set-up and run continuously; and quarterly MRL verification checks shall be performed.	See 40 CFR 136B. MRL verification checks must produce a signal at least 3 times the instrument's noise level.	Same	Run MRL verification check at higher level and set LOD higher or re-conduct study.	NA
Retention time (RT) window width for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	ARI uses a default retention time window of 0.5 minutes	Same.	NA	NA
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	One of the options below: Option 1: RSD for each analyte ≤ 20% Option 2: non-linear regression: coefficient of determination (COD) r2 ≥ 0.99 (6 points required)	Same	Correct problem then repeat initial calibration.	Flagging criteria are not appropriate.
Second source initial calibration verification (SCV)	Once after each initial calibration	Value of second source for all analytes within ± 30% of expected value (initial source)	Same	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat initial calibration.	Flagging criteria are not appropriate.

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	DoD-QSM Acceptance	Corrective Action	Flagging Criteria
Retention time window position established for each analyte and surrogate	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	Same	NA	NA
Retention time Window verification for each analyte and surrogate	Each calibration verification standard	Analyte within established window	Same	Correct problem, then reanalyze all samples analyzed since the last acceptable retention time check. If they fail, redo ICAL and reset retention time window.	Flagging criteria are not appropriate for initial verification.
Calibration verification continuing [CCV]	CCV: After every 10 field samples and at the end of the analysis sequence	All analytes within ± 15% of expected value from the ICAL	Same	CCV: Correct problem then repeat CCV and reanalyze all samples since last successful calibration verification.	CCV:. Flagging criteria are not appropriate.
Method blank	One per preparatory batch	No analytes detected	Same	Correct problem, then see criteria in box D-5; if required, reprep then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch
Blank Spike (BS) containing all analytes and surrogates to be reported	One BS per preparatory batch	ARI BS control limits	Same	Correct problem, then reprep and reanalyze the BS and all samples in the associated preparatory batch, if sufficient sample material is available.	If corrective action fails and there is insufficient sample material report and discuss in the case narrative.
Matrix spike (MS)	One MS per preparatory batch per matrix.	ARI MS control limits	Same	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-qualifier if acceptance criteria are not met.

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	DoD-QSM Acceptance	Corrective Action	Flagging Criteria
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	ARI BS control limits	Same	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-qualifier if acceptance criteria are not met.
Surrogate spike	All field and QC samples	ARI control limits	Same	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	For the specific analyte(s) in all field samples collected from the same site matrix as the parent, apply J-qualifier if acceptance criteria are not met.
Confirmation of positive results (second column or second detector)	All positive results must be confirmed.		Same	NA	Apply J-qualifier if RPD > 40% Discuss in the case narrative.
Results reported between LOD and MRL	NA		NA	NA	Apply J-qualifier to all results between LOD and MRL.

20.3 Chromatogram Library of Common Petroleum Products

20.3.1 Diesel

20.3.2 Motor Oil

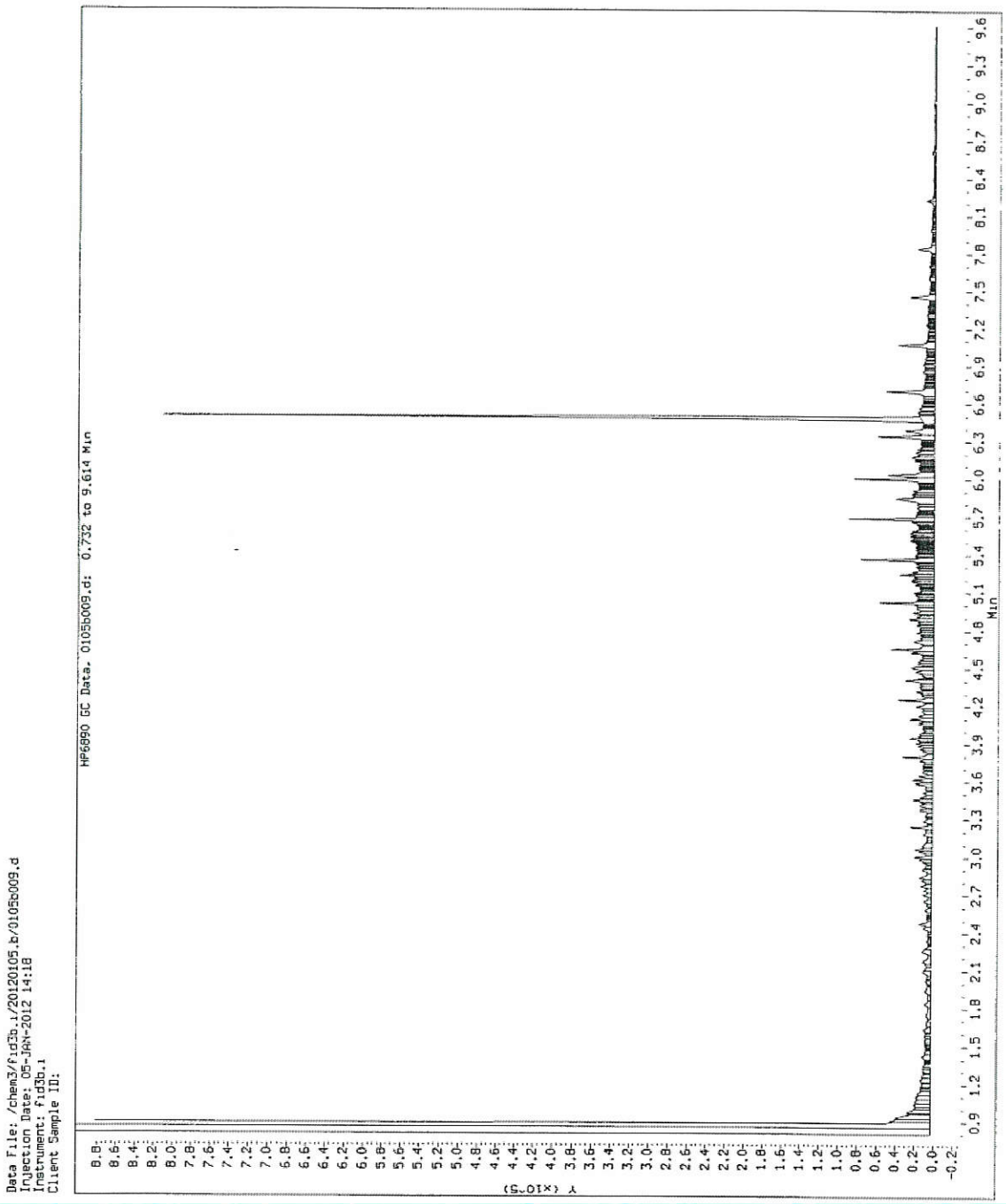
20.3.3 AK103 (30/40Wt Mix)

20.3.4 JetA

20.3.5 Gas/Diesel Mix

20.3.6 BunkerC

Diesel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Instrument: fid3b.i
Client Sample ID:
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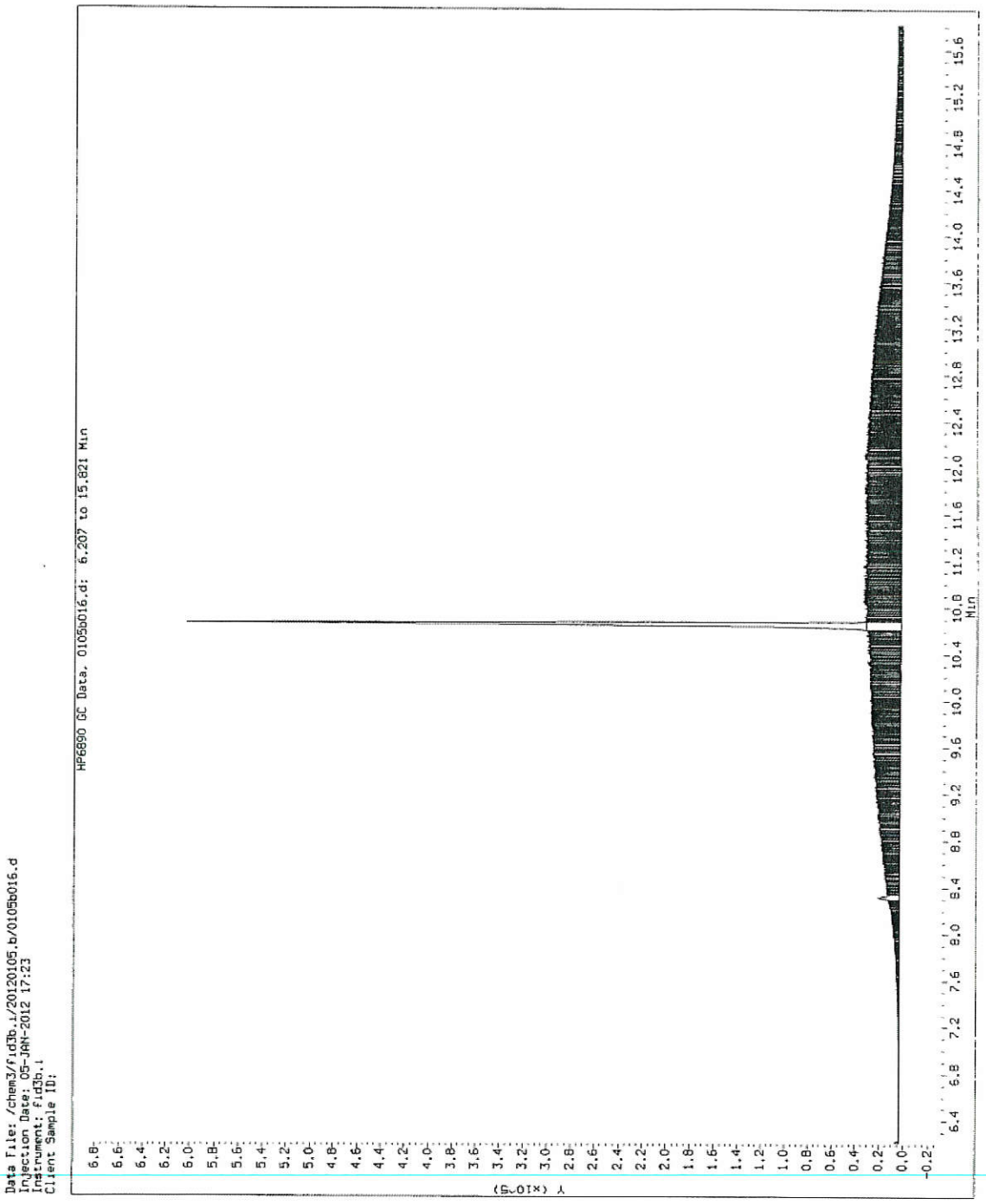
Y (X10^5)
Min

Motor Oil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Client Sample ID:
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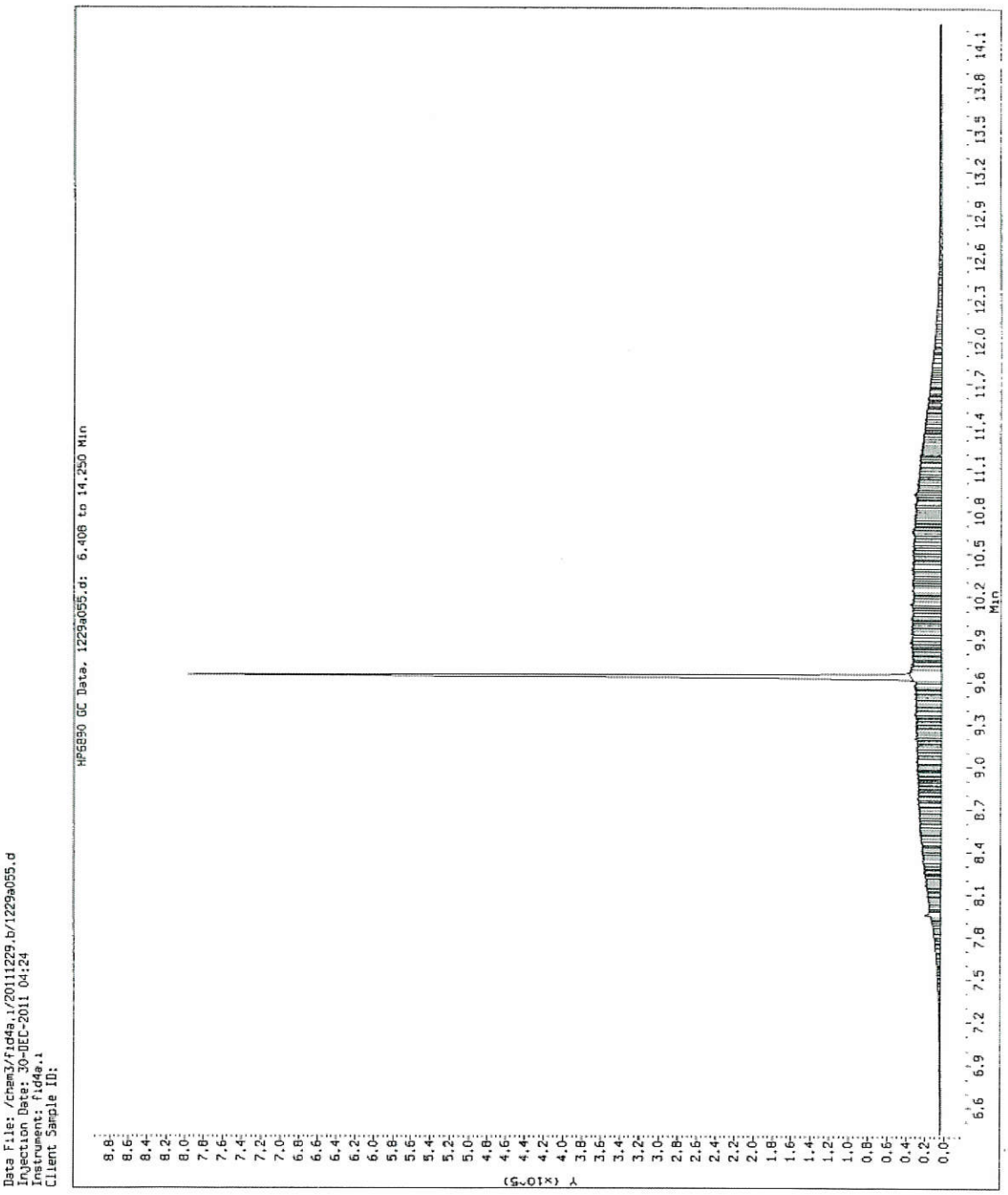
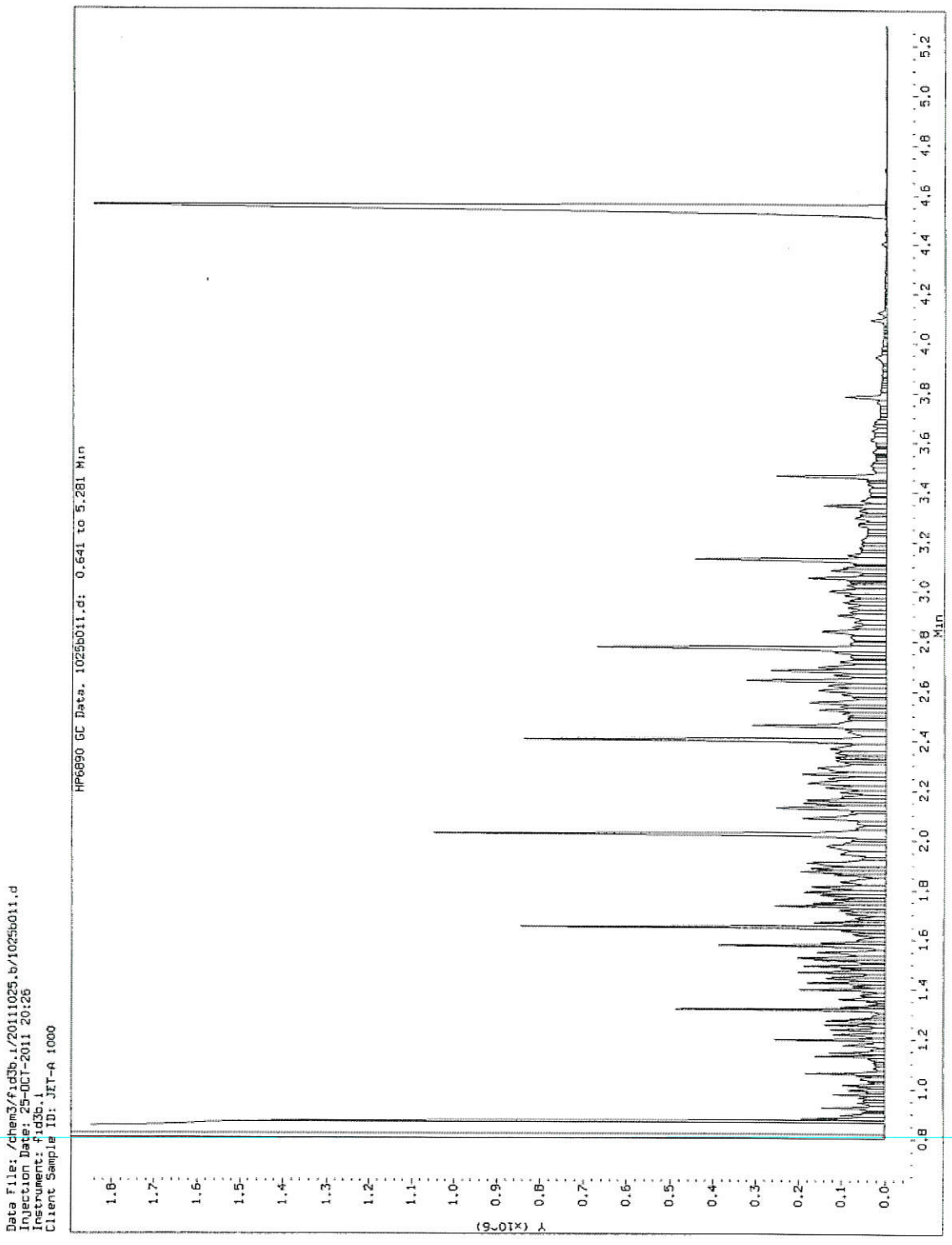
Y (x10^-5)
Min

AK103 (30/40 Wt Mix)



Jet A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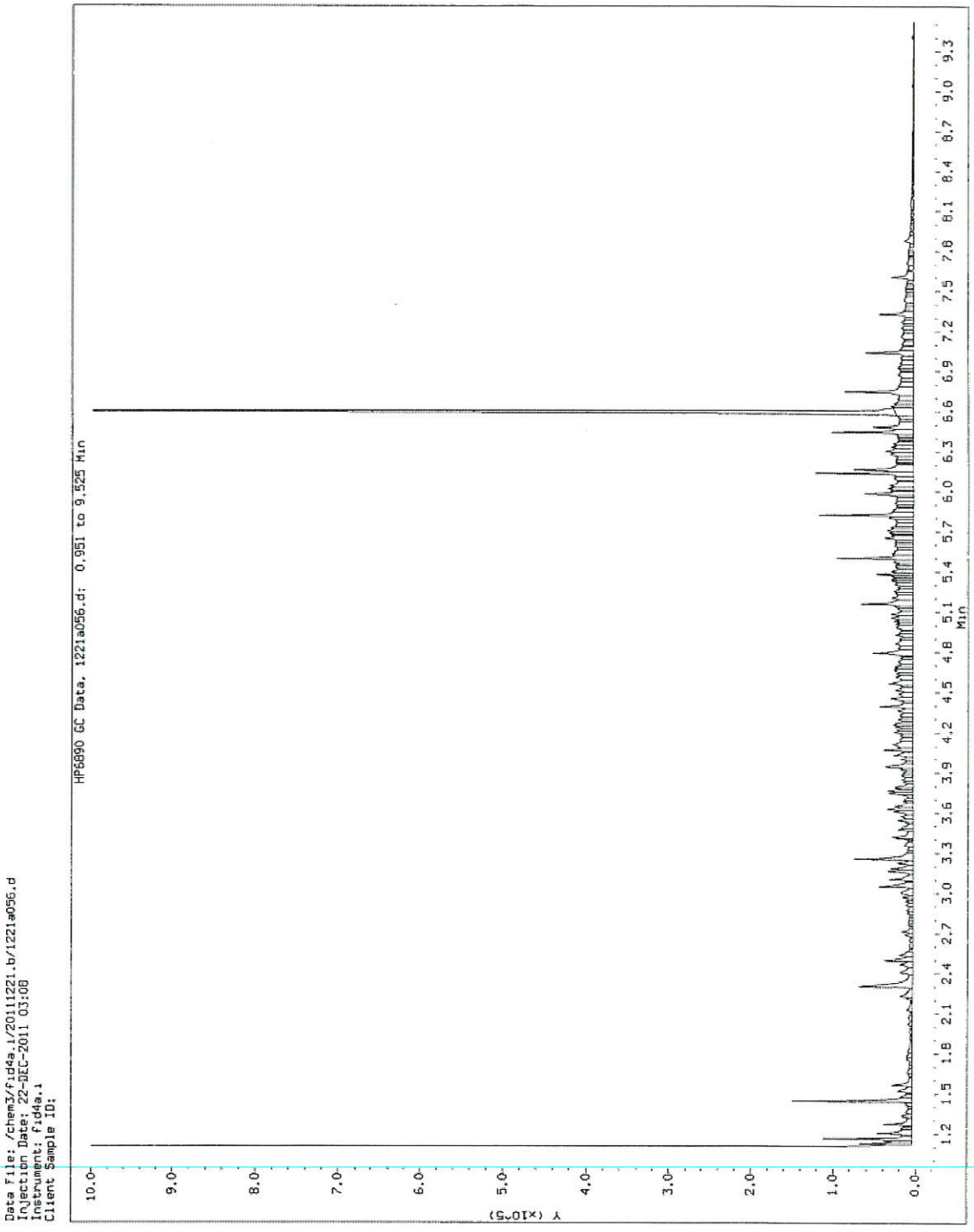
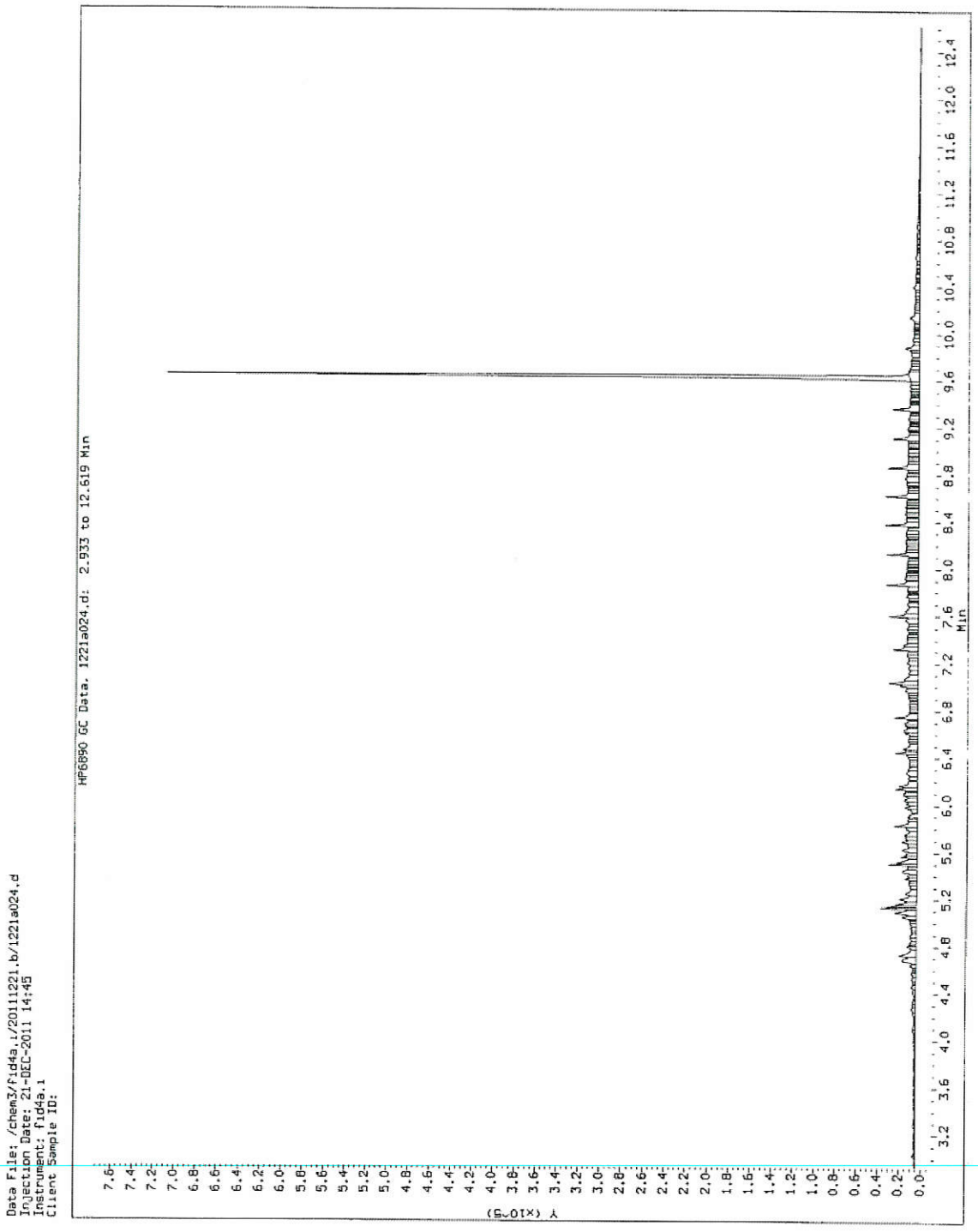
Min
y (x10^6)

Gas/Diesel Mix



Bunker C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Instrument: fid4a.i
Client Sample ID:
HP6890 GC Data. 1221a024.d: 2.933 to 12.619 Min
Min
y (x10^3)

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Volatile Organics Analysis
(Gas Chromatography/Mass Spectrometry)

SOP 700S
Version 021

Revision Date: 5/15/19
Effective Date: 5/15/19

Prepared by:

Patrick Basilio, Paul Campbell, Lani Hertzog Van Spohn

Approvals:

Brian N. Bebee, Laboratory Section Manager

David R. Mitchell, Quality Assurance

Manager

Annual Review

SOP Number: 700S

Title: Volatile Organics Analysis
(Gas Chromatography/Mass Spectrometry)

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This document describes the procedures for performing volatile organic analyses (VOA) used by Analytical Resources Inc. (ARI). The procedures are based on EPA Method 8260D and EPA Method 8000D Revision 5, March, 2018 referenced in Section 19.1 – 19.3. The procedures described also meet the requirements of EPA Method 624.1 (Reference 19.6). The modifications required when analyzing samples using EPA Method 624.1 are outlined in Appendix 20.12. The procedure will identify and quantify volatile organic compounds that have boiling points below 200˚C and that are insoluble or slightly soluble in water. Water-soluble volatile compounds may be included in this analytical technique, however, for the more soluble compounds, the quantitation limits are approximately ten times higher because of poor purging efficiency. ARI's routine target analytes for this procedure are listed in Appendix 20.3. Samples may be analyzed for additional analytes on a project specific basis.

1.2. This method is applicable to most environmental sample matrices, including aqueous (ground water, surface water, waste water, TCLP extracts), solid (soil, sediment, sludge), air samples in Tedlar bags and waste (waste solvent, oily waste, mousse, tar, polymeric emulsion, filter cake, spent carbon, etc.) samples.

1.3. ARI uses several sample preparation techniques to achieve project and/or client specific detection limits. Routine techniques are summarized in Table 01. Other preparation techniques may be employed to meet client requests.

Table 01
Typical VOA Analyzes performed by ARI

Sample Matrix	Sample size	Extraction Technique	Estimated LOQ
Water	5 mL*	Direct Purge & Trap	1 – 5 µg/L
Water	10 mL	Direct Purge & Trap	0.2 – 5 µg/L
Soil / Sediment	5 g	Direct Purge & Trap	1.0 – 5.0 µg/kg
Medium Level Solids	5 g	Methanol Extraction	50 – 250 µg/kg

*Trip blank run on soil instrument only

1.4. Batch QLS standards are prepared and analyzed with sample batches and are used to statistically determine detection (LOD) and reporting (LOQ) limits. QLS spikes are prepared and analyzed quarterly or more frequently, as necessary to establish DL, LOD and LOQ.

1.5. This document describes a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2. Summary of Procedure

2.1. This method requires separate preparation and analysis procedures. Sample preparation is outlined in Section 11.5. Analysis of prepared sample is accomplished using a Purge & Trap GC-MS instrument described in Section 11.3. Software in the GC-MS system automates the data acquisition and reduction process. Most calculations described in this document are performed automatically by the Target™ Software running on the Target Server. The formulae are provided for reference and may be used to manually verify calculated results.

2.2. There are two basic sample preparations.

2.2.1. Direct purge and trap where the sample is analyzed with no initial extraction or preparation.

2.2.2. Methanol is used to extract volatile organic compounds which is diluted into organic free water and analyzed.

2.3. Following sample preparation, volatile organic compounds are automatically purged from the sample and injected into the gas chromatograph using a purge-and-trap equipped GC-MS system.

2.3.1. Compounds purged from the sample using Helium are trapped in a tube containing suitable sorbent materials.

2.3.2. The sorbent tube is heated and back flushed with helium to desorb trapped sample components directly onto the GC-MS system following a split to optimize GC performance.

2.4. A narrow bore capillary GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS).

2.5. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant GC retention times and mass spectra.

2.6. Identified target analytes are quantified by comparing the detector responses of each analytes' characteristic mass ion and internal standard characteristic mass ion to the responses of these ions in a calibration curve prepared using analytes at known concentration.

2.7. Detection limits for all analytes quantitated using this SOP are set using the low point of the initial calibration curve and validated by QLS studies.

2.7.1. QLS studies are performed regularly for each analyte by each preparatory and analytical method.

2.7.2. DL, LOD and LOQ (RL) values may be found for each analyte in the ARI LQAP.

3. Definitions

3.1. CALGAS: perfluoro-tri-n-butylamine (FC-43), CAS 311-89-7.

3.2. Initial Calibration Verification (ICV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable at the beginning of an analytical sequence.

3.3. Continuing Calibration Verification (CCV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable during an analytical sequence.

3.4. Initial Calibration Verification Standard (ICVS): A standard prepared at the mid-point concentration of the initial calibration, and prepared from the same source as the initial calibration used to perform the ICV and CCV calibration checks

3.5. EICP- Extracted Ion Current Profile- A plot of the abundance of a specific ion as a function of time

3.6. Holding Blank: An OFW blank sample stored along with client samples. A holding blank is analyzed weekly to determine if there is cross contamination of samples introduced during storage in the laboratory. See Section 16 for contamination of holding blanks.

3.7. Initial Calibration (ICAL): a minimum of 5 points, with 7 points typical.

3.8. Second source calibration verification (SCV): A midpoint concentration standard from a source different than that used for the initial calibration used to demonstrate the validity of the initial calibration. The second source standard must be purchased from a different manufacturer than the calibration standard whenever possible.

3.9. Internal Standard (IS): internal standards are compounds added to each standard, sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of an internal standard.

3.10. Blank Spike (BS): OFW spiked with verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system.

3.11. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, an BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS. ARI fortifies the BS/BSD with all target analytes.

3.12. Element: Software used to compile and report final chromatographic data.

3.13. Method detection Limit (MDL): The lowest result that can reliably be distinguished in a matrix from a blank. MDL may also be referred to as Detection Limit (DL).

3.14. Limit of Detection (LOD) – The lowest result that can be reported while meeting method precision and accuracy requirements.

3.15. Method reporting limit (MRL): The lowest result that may be reported unqualified based on the lowest curve point. MRL may also be referred to as Limit of Quantitation (LOQ).

3.16. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte(s) to a specified amount of sample matrix for which an independent estimate of target analyte

concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method. ARI fortifies Matrix Spike samples with all target analytes.

3.17. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision.

3.18. Method Blank (MB): A sample of OFW, free of any analytes of interest that is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures.

3.19. Organic Free Water (OFW): ASTM Type 1 water produced by ARI's centralized water purification system and run through a bed of activated charcoal in the VOA laboratory.

3.20. Minimum Reporting Limit standard (MRL): A blank spike prepared at method reporting limit, used to determine MDL, LOD and MRL.

3.21. RIC- Reconstructed Ion Current- A plot of the total instrument response versus time

3.22. RRT-Relative Retention Time- the elution time of an analyte relative to the elution time of its associated internal standard

3.23. Scan Descriptor: Defines a specific mass range for analytes of interest.

3.24. Instrument Blank (IB): A clean laboratory matrix (OFW and/or MeOH) is analyzed using the same conditions as a regular sample. A solvent blank detects system contamination and assures the purity of the solvent.

3.25. Surrogate – A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

3.26. Target™ - A chromatography software package. ARI uses Target™ software to identify and quantify GC and GC-MS target analytes

3.27. Synchronous scan – Simultaneous acquisition of both SIM scan and full scan data.

4. Interferences

4.1. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary.

4.2. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. To reduce carryover, sample syringes must be rinsed with organic-free water following each use. When an unusually concentrated sample is analyzed or suspected, it should be followed by the analysis of an instrument blank.

4.3. Contamination may occur by diffusion of volatiles through the septa into the sample during shipment or storage. Analysis of a trip blank and/or a holding blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.4. All glassware associated with preparation is baked at 50 ±10 °C overnight to further reduce interferences.

4.5. Only high purity reagents and solvents are used to minimize interference.

5. Safety

5.1. The toxicity and carcinogenicity of each reagent used in this method is not precisely defined. However, all compounds and solutions should be treated as health hazards, and exposure of these chemicals to skin and clothing should be minimized to the lowest possible level by whatever means available.

5.2. Skin contact with all chemicals should be minimized by the use of nitrile gloves, safety glasses, and laboratory coats.

5.3. Standard solutions should be handled in the fume hoods to avoid chemical exposure.

5.4. All GC split vents and vacuum pump exhaust are connected to an exhaust vent.

5.5. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDS) is available to all personnel involved in the chemical analysis. ARI maintains SDS sheets for all chemicals used in the laboratory. Consult the SDS whenever you have questions concerning the handling of a potentially dangerous substance. Information also available at www.msdshazcom.com

6. Equipment, Maintenance and Supplies

6.1. Gas chromatograph/mass spectrometer system

6.1.1. Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for purge-and-trap systems and all required accessories, including syringes, analytical columns, autosampler, and gases. The capillary column should be directly coupled to the source of the mass spectrometer.

6.1.1.1. Fused-silica capillary column - 20 m x 0.18 mm ID x with a 1 µm film thickness coated with a proprietary cross bonded stationary phase (Restek RTX-VMS or RTX-502.2 or equivalent).

6.1.2. Mass spectrometer –Hewlett-Packard 5973/5975 or equivalent capable of scanning from 35 to 300 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass

spectrum for Bromofluorobenzene (BFB) which meets all of the criteria in Appendix 20.3 when 5-50 ng BFB is desorbed onto the column.

6.1.2.1. GC/MS Interface – The GC column is connected directly to the MS ion source following a 1:40 split with SilicoSteel 0.040 inch ID

6.1.3. Purge and trap system

6.1.3.1. Varian Archon, Tekmar Teledyne Atomx or equivalent auto-samplers are used for analysis.

6.1.3.1.1. When running water samples, the auto-sampler removes samples directly from standard 45mL water sampling vials and transfers them to the purge and trap sparge vessel. The autosampler adds standards (IS & SS), drains and cleans the sparge vessel, and proceeds to the next sample.

6.1.3.1.2. When running soil samples, the auto-sampler performs a heated purge and trap by lifting the soil vial into the heated soil chamber, and sparges the sample directly onto the trap of the purge and trap unit.

6.1.3.2. Trap—Supelco trap K (VOCARB), OI Analytical 4560 Trap #10 or equivalent. The Tekmar Atomx and OI Analytical Eclipse 4660 purge-and-trap system should be capable of rapidly heating the trap to 250°C during the desorb process. The trap bake-out temperature should not exceed 260°C. A sample heater should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

6.1.4. Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.

6.1.4.1. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating ion abundances in any EICP between specified time or scan-number limits.

6.1.4.2. The data system should be equipped with an EPA/NIST Mass Spectral Library.

6.1.4.3. The data must be securely stored for at least seven years from date of acquisition.

6.2. Maintenance of GC/MS system

6.2.1. Preventative Maintenance as described below will be performed on an annual basis and entered into Element under the instrument maintenance logs section.

6.2.1.1. Fore pump oil will be replaced.

6.2.1.2. Source main board and power supply is dusted off.

6.2.1.3. GC main board is dusted off.

6.2.1.4. Autosampler is lubricated and calibrated.

6.2.2. Routine maintenance events are entered into the Element data system under the instrument maintenance logs section.

6.2.2.1. Routine maintenance may include (but are not limited to) any of the following tasks:

6.2.2.1.1. Autosampler repair

6.2.2.1.2. Column repair/replacement

6.2.2.1.3. Data system repair

6.2.2.1.4. Gas Chromatograph repair

6.2.2.1.5. Purge/Trap repair

6.2.2.1.6. Transfer line repair/replace

6.2.2.1.7. Inlet repair

6.2.2.1.8. Detector (source) repair/cleaning

6.2.2.1.9. Vacuum system repair

6.2.2.1.10. Service provided from an outside vendor will also be documented in Element

6.3. Microsyringes—10, 25, 50, 100, 250, 500, and 1,000µl

6.4. Syringes—5, 10, and 25mL, gas-tight

6.5. Balances—top loading, 0.01g readability

6.6. Glass scintillation vials—20mL, with Teflon lined screw-caps.

6.7. 45 mL sample vial with Teflon septa (pre-cleaned or baked at 50 ±10 °C to dryness).

6.8. Disposable Pasteur pipettes.

6.9. Volumetric flasks, Class A - 5mL, 10mL, 25mL, 50mL, 100mL and 500mL, with ground glass stoppers

6.10. Spatula—Stainless steel

6.11. Centrifuge that can accommodate 20 and 45mL vials.

7. Reagents and Standards

7.1. Methanol, CH_3OH: – Purge and Trap quality, demonstrated to be free of analytes. Methanol will be stored separately from other solvents.

7.2. Sodium Bisulfate – used for 5035 soil preservation

7.3. Organic-free water: - All references to water in this method refer to purified water produced by ARI's Deionized (DI) Water System.

7.3.1. The laboratory DI water system is ASTM Type 1 greater than 18.2 mega ohms resistivity.

7.3.2. The Volatile laboratory water is passed through an activated carbon column. Cartridges are changed when the chloroform exceeds 0.1ppb or methylene chloride levels exceed 0.2 ppb.

7.4. Stock Standards are high concentration (1000µg/ml, 2000µg/ml, 5000µg/ml) solutions of target analytes, calibration standards, internal standards and surrogates used to prepare working standards. Procedures for handling Stock Standards are described in SOP 704S.

7.4.1. Certified standards are purchased from outside vendors. Two sources from different manufacturers are obtained when feasible or at least two different lot numbers from the same manufacturer.

7.4.2. The use of a secondary source from the same manufacturer is not recommended and all attempts in a timely manner will be made to locate a second manufacturer.

7.5. Working Standards are used directly in the analytical process to fortify samples or calibrate instruments. Working standards are diluted from stock standards or purchased directly from commercial sources. The concentration of all purchased working standards must be certified by the supplier and have a Certificate Analysis (CoA) on file at ARI as described in SOP 1013S "Chemical Receiving and Monitoring". Procedures for handling Working Standards are described in SOP 704S.

7.5.1. Surrogate standards (SS) – Recommended surrogates are d8-Toluene, 4-Bromofluorobenzene, d4-1,2-Dichlorobenzene, and d4-1,2-Dichloroethane. Other compounds may be used as surrogates depending on analytical requirements. Prepare a surrogate standard spiking solution at a concentration of 25-250µg/ml in methanol.

7.5.2. Internal standards (IS) – The recommended internal standards are chlorobenzene-d5, 1,4-difluorobenzene, 1,4-dichlorobenzene-d4 and pentafluorobenzene. Other compounds that have similar retention times may be used. Prepare an internal standard (IS) working solution so that the IS concentration in a sample will match the mid-point concentration of the instrument calibration curve. Internal standards are added to the sample by an autosampler using an injection loop. The injection loop size varies by instrument. When making the internal standard mix, adjust the concentration to the loop size for each specific instrument.

7.5.3. 4-Bromofluorobenzene (BFB) standard: Prepare a 25 µg/mL solution of BFB in Methanol.

7.5.4. VOA Spiking Standard (VSS) – Used to prepare MS, MSD, BS and BSD samples and calibration standards. Certified working standards containing all of the VOA analytes are purchased from a commercial vendor. Purchased standards are combined and/or diluted to prepare the appropriate spiking solution. The spiking solution is also used to prepare calibration standards.

7.5.4.1. The standard is prepared in methanol, with each compound present at 20µg/mL except Acrolein and the ketones which are at 100µg/.

7.5.4.2. When a targeted analyte is not available in a commercial certified working standard, the appropriate concentration should be determined, and the solution prepared in a water-soluble solvent (usually methanol or acetone) at that concentration.

7.5.5. Calibration standards - Calibration standards are prepared from the VOA Spiking Standard at the time of calibration as described in Section 10.2.

7.5.6. Second Source Calibration Verification (SCV) is a certified working standard containing the same VOA analytes as the VSS but from a different source. The VSS and SCV may be purchased from different vendors or as different lot numbers from the same vendor. This standard is used to verify the concentration of the VOA spiking solution following an initial calibration.

7.6. Preservation solutions

7.6.1. Sodium Bisulfate solution is made by adding 400g to 2L of organic free water (equivalent to 1gm/5ml) and stirring until dissolved.

8. Sample Collection, Preservation, Shipment, Storage and Disposal.

8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 ºC.

8.2. Samples must be stored at ARI, at >0 to 6 ºC until final disposal.

8.3. Water samples must be stored at >0 to 6°C and analyzed within 7 days of sampling if not preserved with 1:1 HCl. Preserved aqueous samples must be analyzed within 14 days. Soil samples are to be stored at >0 to 6°C and must be analyzed within 14 days of sampling.

8.4. Preserved soil samples (Method 5035) are preserved with either 5ml of Sodium Bisulfate solution or 5ml Methanol.

8.5. Unpreserved solid samples for Method 5035 must be analyzed or preserved within two days of sampling.

8.6. A holding blank will be kept in refrigerator 21 and to be analyzed with samples at specified intervals (Section 9.5).

8.7. VOA Chain of Custody

8.7.1. Samples for VOA analysis are delivered to Refrigerator 21 by sample receiving and the sample custody is changed in element to reflect the refrigerator and storage box where the samples were placed.

8.7.2. To locate a sample, the VOA analyst will locate the sample bin for the workorder in Element under Sample control->Workorder->Samples->containers->Home location. The home location sample bin is determined by login. The Volatile sample bins are labeled with two locations, one is the home location (R-21) and the other is the archival location (R-36) using the same bin

number. This is done to facilitate reassigning the samples to another refrigerator without physically transferring the samples to another bin.

8.7.3. The analyst will remove the samples from refrigerator 21 or refrigerator 41 for hazardous samples.

8.7.4. In Element, the analyst will add the samples to the appropriate batch with the barcode reader or manually. Samples added to the batch will now show a status of batched.

8.7.5. In Element, the analyst will change the sample location to VOA lab in Batch->Bench Sheet. The custody is updated to the analyst's name when they change the sample location. The sample location will be the VOA lab until the analysis is completed.

8.7.6. When the analysis is completed the analyst will return the samples back to the home location bin in refrigerator 21 (or 41) and update the location in Batch->Bench Sheet to the home location. The analyst may repeat step#1 if they need to query the sample home location. NOTE: Samples in refrigerator 41 are not assigned a bin and the sample location is simply R-41.

8.7.7. Sample bins are stored in R-21 until it begins to run out of space. The analyst will transfer the filled bins to R-36 and change the location in Element under sample control disposal using the edit location feature. Next the analyst will mark all samples now stored in R-36 as archived in sample control->disposal.

8.7.8. Final disposal is performed when R-36 is nearly full.

8.7.9. Prior to final disposal the analyst will query all the samples in the sample bin under sample control->disposal to identify samples that are hazardous waste. Samples that are hazardous are indicated by the red font. Hazardous samples must be placed in the appropriate blue waste drum for that profile. See the chemical hygiene manual for guidance on characterizing hazardous waste. Once the bin is empty in Element->sample control->disposal mark the contents of the bin as disposed and change the location of the samples to consumed.

8.7.1. Non-hazardous unpreserved soil and solid samples are taken directly to the dumpster and trash disposed.

8.7.2. Methanol preserved soil samples (5035) are disposed into a 55 gallon waste barrel dedicated for methanol preserved samples.

8.7.3. Methanol extracts of soil and solid samples (medium level analysis) are also to be disposed into the dedicated methanol waste barrel.

8.7.4. Unpreserved Water samples, preserved water samples, and soil samples preserved with Sodium Bisulfate are disposed into a dedicated hazardous waste drum outside the share fridge (#36).

9. Quality Control

9.1. Quality Control procedures and requirements are summarized in Appendix 20.1.

9.1.1. Acceptance criteria for ARI's routine analyses listed in the column title "ARI Acceptance Criteria".

9.1.2. For DoD-QSM acceptance criteria, see DoD QSM 5.1.

9.2. Some clients and/or projects may have different quality control procedures or criteria. Always read and understand any "special Instructions" supplied by an ARI Project Manager.

9.3. Instrument control:

9.3.1. A Method Detection Limits (MDL) study is performed for each analysis to provide recovery and precision for the method.

9.3.2. The GC-MS must be tuned to the specifications in Appendix 20-4 before initial calibration, and thus before samples are analyzed. The tune must be performed with 5-50ng total BFB standard. It is required that an ICV, BS, BSD and a method blank be analyzed with acceptable QC before analyzing samples.

9.3.3. Internal standard (IS) area criteria in the samples must be evaluated for retention time shift and EICP areas.

9.3.3.1. If the EICP area for any IS changes by -50% to +100% from the area of the IS in the midpoint of the initial calibration, the samples must be reanalyzed.

9.3.3.2. Retention time shift of internal standards must be ± 0.06 RRT units from the ICV internal standard RT.

9.4. Method performance:

9.4.1. Samples are analyzed in 12-hour run sequences known as QC periods. Each 12-hour QC period begins when an ICV sample analysis starts and ends following the analysis of the last sample injected within 12 hours of the initial sample injection. A BFB tune is required prior to initial calibration but is not a daily QC requirement.

9.4.2. One method blank will be performed each 12-hour shift after calibration standards and prior to the analysis of any samples.

9.4.2.1. A method blank is run to demonstrate system cleanliness (no analytes should be detected > ½ method reporting limits). Blanks may contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e., targets are not present in the samples or sample concentrations/responses are greater than 10x the blank. Surrogates are to be within the established control limits.

9.4.2.2. Corrective action must be taken when MB contamination is greater than ½ the method reporting limits and the samples contain detections of the analyte that are above the reporting limit and less than 10x the concentration found in the blank. Re-

analysis is not necessary if the analyte concentration falls well below the action or regulatory limit or if the analyte is deemed not important for the project. See section 16.2.

9.4.2.3. Methylene Chloride, Acetone and 2-Butanone are allowed at up to 5 times the method reporting limit. Method blanks containing any of these analytes > ½ the RL must be documented in the reviewer checklist for the analytical run and all associated hits flagged with a "B".

9.4.2.4. Prepare a water method blank by adding 45mL organic-free water to a pre-cleaned auto-sampler vial.

9.4.2.5. Prepare a soil method blank by adding 5mL organic-free water to a pre-cleaned auto-sampler vial.

9.4.3. A Blank spike must be analyzed before analyzing samples. At a minimum one (BS) must be run in each 12 hr. QC period. It is recommended an (BSD) be analyzed also. The control limits for all compounds is ± 20% or ARI's published historical control limits. The maximum allowed relative percent difference (RPD) for an BS and BSD) is 30%.

9.4.4. Since the BS analysis is prepared in an identical manner as the ICV a single analysis may be used for both the ICV and BS. Two copies of the data file must be present in both Target and Element to reflect the dual usage of a single analysis.

9.4.4.1. Compounds that do not meet these limits must be documented in the Element reviewer checklist.

9.4.4.2. Prepare a water BS by adding VOA Spiking Standard (VSS) to 45mL organic-free water, to a final concentration equivalent to that of the CVS.

9.4.4.3. Prepare a soil BS by adding the VSS to 5mL of organic-free water to a final concentration equivalent to that of the CVS.

9.4.5. One set of matrix spikes is analyzed for each 20 samples/matrix/instrument (when requested and adequate sample is available) at a known concentration level within the range curved, typically at 50ng/mL for 5mL and 10ng/mL for 10mL purges and 50ng/g for soils.

9.4.5.1. The MS/MSD samples are run and the relative percent difference must be calculated between the two control samples. The RPD for each analyte for MS/MSD should be less than 30% and note any deviation >30% in the reviewer checklist.

9.4.5.2. ARI will not perform MS/MSD analysis on any of the field QC samples delivered as part of a client's QA/QC program (water rinsate samples, field/trip blanks etc.)

9.4.5.3. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.4.6. QC limits are provided to bench chemists, managers, and QA review personnel as tools for

assessing data quality in real-time at the point of data generation.

9.5. A holding blank will be kept in volatile refrigerator 21 and will be analyzed every week. Holding blank data is documented in ELEMENT.

9.6. Surrogates are added to each sample, blank, and standard, and are used to evaluate the purge and trapping efficiency by measuring recovery. Surrogates are brominated, fluorinated or isotope labeled compounds not expected to be detected in samples.

9.7. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for matrix spike and matrix spike duplicates are statistically generated on an annual basis.

9.7.1. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation.

9.7.2. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. Current control limits may be found in the ARI LQAP.

9.7.3. All analysts using this SOP must use it in conjunction with Control Limit documentation in order to assess data quality and any possible need for corrective actions.

10. Calibration and Standardization

10.1. Summary of VOA calibration procedure:

Table 02 – Summary of GC-MS Calibration Procedure

Step	Section	Procedure	Manual/Computer
1	10.2	Prepare Calibration Samples	
2	10.3	Verify Instrument Tune	
3	10.4	Analyze Calibration samples	
4	10.5	Target Calculates RRF & %RSD	
5	10.6	Validate analyte response	
6	10.7	Analyze Instrument Blank	
6	10.8	Analyze SCV	
7	10.9	Evaluate IS Response	
8	10.10	Verify Retention Times	
9	10.11	Update Analytical Method	

10.2. Prepare Calibration samples:

10.2.1. Using a new unopened vial of VOA spiking solution (VSS) (Section 7.5.4.4), prepare a set of five or more calibration samples containing all target analytes. This is accomplished by spiking separate volumes of VOA free water with increasing volumes of the VOA spike working standard as listed in Table 03. Calibration samples are prepared in 45 mL VOA vials. The volume of the calibration samples must be equal to the volume that will be analyzed to account for purge efficiencies that vary with sample volume. The concentration of analytes in the lowest

level sample must less than or equal to the method reporting limit. The concentrations in the calibration standards define the working range of the method. A set of at least 5 calibration standards containing the method analytes is required. One calibration standard should contain each analyte at the concentration of the method reporting limit for that compound. The other calibration standards should contain analytes at concentrations that define the range of the method. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. ARI typically calibrates with between five and eight calibration levels covering the dynamic range of the instrument and meeting the required method reporting limit of the project. (note: Acrolein and the ketones are at 5X concentrations). To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water. Transfer the contents to a purging device.

10.2.2. Ketones and Acrolein are spiked at 5X the concentration levels of the other analytes due to their poor purge efficiency.

Table 03 – Typical Calibration Solution Concentrations

Standard	Direct Purge 5 mL water 5 g Soil	Direct Purge 10 mL Water
1	1	0.2
2	2	0.5
3	5	1.0
4	10	2.0
5	50	10
6	100	20
7	150	40
8	200	80

10.2.3. Initial calibration standards, continuing calibration standards and surrogates for the soil side of the autosampler are made in a minimum amount of water. The standards are then transferred to 45 mL vials, each containing a magnetic stir bar. Internal standards (IS) and Surrogate standards (SS) are added by the autosampler.

10.2.4. Initial calibration standards, continuing calibration standards and surrogates for the water side of the autosampler are made at volumes for use in 45 mL vials containing magnetic stir bars. The appropriate sample volume of the standard is transferred via the autosampler to a sparger vessel, and purged. The IS/SS solution is added by the autosampler standard syringe.

10.2.5. Surrogates are not curved, they are spiked at the same level for all calibration points.

10.3. Verify that the instrument is properly tuned following the procedure in Appendix 20.4

10.4. Analyze Calibration Samples:

10.4.1. Analyze each calibration sample using the exact conditions and procedure to be used for

subsequent sample analyzes.

10.4.2. View the "CLP Report" using Target™ software and evaluate each target analyte.

10.4.2.1. Verify that the automated routine has properly identified and quantified all peaks.

10.4.2.1.1. Perform any required manual integration as necessary.

10.4.2.2. Verify that the internal standard (IS) is in control.

10.5. Target™ will tabulate relative response factors (RRF), Average RRF, relative standard deviation (RSD) and % RSD using Equations 01 through 04 for each compound relative to its internal standard.

Equation 01:
$RRF = (A_X C_{IS}) / (A_{IS} C_X)$
A_X = Area of the characteristic ion for the compound being measured
A_{IS} = Area of the characteristic ion for the associated Internal Standard
C_{IS} = Concentration of the associated internal standard
C_X = Concentration of the compound being measured

10.6. Equation 02:
$\text{Average RRF} = \Sigma RRF_i / n$
where:
RRF_i = the peak response factor for each quantitation peak in the calibration standard
n = the total number of standards (usually 7)

Equation 03:	
RSD = SD / (Ave RRF) =	$\frac{\sum(RRF_i - \text{Ave RRF})^2) / (n-1))^{1/2}}{\text{Ave RRF}}$
where:	
SD = Standard deviation of the response	

Equation 04:
%RSD = RSD * 100

10.6. Evaluate Analyte Response.

10.6.1. When the %RSD for a given target is ≤ 20% (15% for DoD analyses), the detector response is considered linear and the average RRF may be used to quantify that compound.

10.6.2. When %RSD is >20% (15% for DoD analyses) for any compound, the analyst may use an alternative method to evaluate the acceptability of the calibration.

10.6.2.1. NOTE: Forcing the calibration model through the origin (for anlaytes that are consistently detected in the laboratory method blanks) allows for a better estimate of the background level of blank contaminants. An accurate estimate of background

contamination is necessary to set method reporting limits for method analytes when blank levels are problematic.

10.6.3. The curve must meet minimum RRF requirements noted in Appendix 20.3.

10.6.4. If more than 10% of the compounds included in the initial calibration exceed 20% (15% for DoD analyses) RSD and do not meet the minimum coefficient of determination of 0.99, for alternate curve fits, the chromatographic system is considered to imprecise for analysis to begin.

10.6.5. For linear and non-linear calibration curves based on a least squares regression (LSR) model the coefficient of determination (COD) r^2 must be > 0.99.

10.6.6. Special care should be taken to monitor the RRF in the lowest calibration standard to ensure adequate sensitivity at the method reporting limit. In addition, the lowest calibration point should be recalculated (not reanalyzed) using the final calibration curve in which this standard is used. The recalculated concentration, especially where linear regression fits are used, should be within +/- 50% of the standard's true concentration. The recalculated concentration of the standards above the low point should be within +/- 30%. If a failure occurs in the low point and it is equivalent to the RL, the analyte should be reported as estimated near that concentration or the RL should be reestablished at a higher concentration. Following examination of the ICal and any corrective action, all compounds not meeting the calibration acceptance criteria must be documented in the Reviewer Checklist in Element.

10.7. An instrument blank must be analyzed immediately following the highest point of the calibration. This blank can be used to estimate the extent of decontamination needed to eliminate carryover after analyzing a sample at similar concentration.

10.8. A secondary calibration verification (SCV) is performed by analyzing a midpoint calibration standard prepared using the SCV mix. ARI will spike the full list of compounds at a mid-calibration range concentration. Calibration verification is acceptable when the recovered analytes are within ± 30% (20% for DoD analyses) of the expected concentration. Specific clients or projects may allow or require different calibration acceptance limits. When any analytes are not in the acceptable range corrective action and documentation the reviewer checklist is required.

10.9. The internal standard responses and retention times in the initial calibration verification standard must be evaluated during or immediately after data acquisition.

10.9.1. If the EICP area for any of the internal standards changes from -50% to +100% from the last midpoint concentration of the initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. Areas are documented in the daily run log.

10.10. If the retention time for any internal standard changes by more than 30 seconds from the last daily calibration, the chromatographic system must be inspected for malfunctions and corrections must be made, as required.

10.11. Update the analytical method file with updated RT and RRF data.

10.12. The reviewer checklist from the Initial Calibration must be included with every job run under the corresponding initial calibration.

11. Procedure

11.1. Procedure Summary

Table 04 – Procedure Summary		
Step	**Process**	**See Section**
1	Project Evaluation	11.2
2	Set or Verify Instrument Operating Parameters	11.3
3	Verify Spiking Solution in the autosampler	11.4
4	Prepare Samples for Analysis	11.5
5	Set up Analytical Run	11.6
6	Initiate sample analysis	11.7
7	Verify Instrument Calibration	11.8
8	Evaluate Mass Spectra	11.9
9	Evaluate QC Analyses	11.10
10	Export Data to Element	11.11

11.2. Project Evaluation

11.2.1. Holding times: Review project documentation to determine when sample holding time will expire. If there is any chance the sample will not be analyzed with the required holding time, notify your laboratory supervisor and/or the appropriate project manager.

11.2.2. Special requirements: Non-routine analytical requirement may be required for a specific project or sample. Review all project documentation and make sure you understand any special requirement before proceeding with analysis.

11.2.3. Historic Data may be available for a continuing project or sampling site. Use this data to pre-determine any special sample handling necessary.

11.3. Set up the GC/MS/Autosampler system as outlined in Tables 06, 07 and 08:

11.3.1. This should be done prior to the preparation of the sample to avoid loss of volatiles from prepared standards and samples.

Table 06 – Typical Instrument Operating Parameters
Mass Spectrometer

Mass scan range	35 – 300 amu
Scan time	1 sec/scan or less
Electron volts	70 volts (nominal)
Gas Chromatogram	
Initial Temperature	43 – 46 °C
Temperature Program	46-240°C at 12°C/min
Final temperature:	240°C, hold 4 min
Source temperature:	According to manufacturer's specs, 150-250°C
Transfer nozzle/line:	180-250°C
Carrier Gas:	Helium at 25-50 mL/min
Purge & Trap	
Purge	8-11 minutes
He flow rate	25 – 50 mL/min
Sample Heater	40 °C
Desorb preheat	250°C
Desorb	1-6 minutes at 250°C
Bake	4-10 minutes at 260°C
Valve temperature	50-110°C
Mount temperature	30-110°C
Line	50-200°C

11.4. Table 07 – Typical Autosampler Set-up - Manual Mode

Parameter	Autosampler Options	Recommended Set-up	
		Water	Soil
Flush Volume	5, 10, 15, 20 mL	10	5
Select matrix	Water or Soil	Water	Soil
Standard	Yes or No	Yes	Yes
Sample Volume	5, 10, 15, 20 mL	5 or 10	--
Dilution	0 – 95 %	0	--
Flushes	0 - 10	1	--
Stir Time	0 – 15 min	0	--
Settle Time	0 – 15 min	0	--
Stir Speed	L, M, H	M	--
Desorb Time	0 – 10 min	1	--

Flow Rate	0 – 150 mL/min	40	
Line Heat	25 – 125 °C	--	80
Pre-heat	0 – 10 min	0	0
Water Volume	0 – 10 mL	--	7
Pre-purge	0 – 10 min	0	0
Purge time	0 – 20 min	10	10
Flushes	0 - 10	--	1
Soil Stir	Yes or No	--	Yes
Desorb time	0 – 10 min	--	2
Water Trap Volume	Yes or No	--	0

11.5. Table 08 – Typical Autosampler Set-up - Auto Mode

Parameter	Options	Recommended Set-up	
		Water	Soil
Start delay	0 – 99.5 hours	0	0
Cycle time	0 – 199 min	0	24
Auxiliary output	Yes or No	No	No
Last water or soil	Vial number	1 – 30	1 - 30
Blank Last	Yes or No	No	No
Flush Volume	5, 10, 15, 20 mL	5 or 10	5
Select Matrix		Water	Soil
Standard	Yes or No	Yes	Yes
Sample Volume	5, 10, 15, 20 mL	5 or 10	--
Dilution	0 – 95 %	0	--
Flushes	0 - 10	2	--
Stir Time	0 – 15 min	1	--
Settle Time	0 – 15 min	0	--
Stir Speed	L, M, H	M	--
Desorb Time	0 – 10 min	1	--
Flow Rate	0 – 150 mL/min	40	40
Line Heat	25 – 125 °C	--	80
Pre-heat	0 – 10 min	--	0
Water Volume	0 – 10 mL	--	7
Pre-purge	0 – 10 min	0	0
Purge time	0 – 20 min	10	10
Flushes	0 - 10	--	1
Soil Stir	Yes or No	--	Yes
Desorb time	0 – 10 min	--	2
Water Trap Volume	Yes or No	--	No

11.6. Verify Spiking Solutions

11.6.1. Verify the IS / SS standard volume in the autosampler reservoir. Add standard as necessary.

11.7. Prepare Samples for Analysis: Samples must be properly prepared for analysis using the processes outlined in Table 05.

Table 05 – Sample Preparation Procedures			
Sample Matrix	**Method**	**Technique**	**Details in Section:**
All	Sample Screening	Sample Dilution	11.7.2.1
Water	5030B	Direct P&T	11.7.4
Soil	5035	Direct P & T	11.7.5
Solid	5035	Methanol Extraction	11.7.5
Soil		From Total Solids Jar	11.7.5.3.3
Waste	3585	Waste Dilution	11.7.5.4

11.7.1. **Prepare the Instrument:** The Purge and Trap GC-MS instrument must be readied before samples are prepared for analyses to allow minimum time lapse between preparation and analysis.

11.7.2. **Sample screening:**

11.7.2.1. Any sample with characteristics (color, odor, client information etc.) indicating it may contain high levels should be screened prior to analysis. Screening may also help prevent un-necessary contamination of the purge-and-trap system. Samples are screened by analyzing them at dilution.

11.7.2.1.1. Aqueous samples: dilute the samples with an appropriate volume of OFW and analyze as a normal sample.

11.7.2.1.2. Extract solid samples with methanol and dilute a small aliquot of the methanol into 45 mL OFW for analysis.

11.7.2.1.3. A portable PID may be used to assess the sample.

11.7.3. All client samples, QA samples and standards must be spiked with surrogate (SS) and internal standards (IS) prior to analysis. The SS and IS are normally added to the sample by the auto-sampler. When samples are analyzed manually, the analyst must spike each sample individually.

11.7.4. **Aqueous Sample Preparation:**

11.7.4.1. Screen aqueous samples when historic data or their appearance indicated that they may contain high concentrations (> 2mg/L) of volatile compounds. When the screening indicates a high concentration of volatiles dilute the sample with OFW.

11.7.4.2. Aqueous samples are normally received by ARI in 45 mL VOA vials. The VOA

vials are placed directly on the auto-sampler for analysis. The auto-sampler will spike surrogate and internal standard into the sample prior to the purge process.

11.7.4.3. Manual Sample Preparation: Remove the plunger from a 10mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 or 10 mL. Transfer remaining sample to a 45mL VOA vial with a Teflon™ sealed cap or fill a second syringe at this time to maintain sample integrity. Manually spike the appropriate amount of internal standard/surrogate mix directly into the syringe prior to introducing the sample into the sparge vessel. This manual preparation is only done in special circumstances.

11.7.4.4. For matrix spike, matrix spike duplicate, and BS analyses, add the appropriate amount of spiking solution to the 45mL vial containing the sample to be purged to a known concentration level within the range curved.

11.7.4.5. Appropriate concentration range for analysis.

11.7.4.5.1. Use screening data, historic project information, sample appearance or other ancillary information to determine appropriate purge or dilution volumes prior to analysis.

11.7.4.5.2. The amount a sample may be diluted is determined by the purge volume and final concentration of target analytes.

11.7.4.5.3. Prepare dilutions in a 45 mL vial taking care to maintain sample integrity by keeping atmospheric exposure of the sample to a minimum

11.7.4.5.4. Add a stir bar to the 45 mL vial or leave a small pea bubble in the vial to facilitate mixing while shaking the sample.

11.7.4.5.5. Dilutions in excess of 5000X may be prepared using an intermediate Methanol (or OFW) dilution taken directly from the sample vial.

11.7.4.5.6. Always perform a final review of multiple analyses from the same sample and note any major deviations in analyte concentrations in the Element reviewer checklist.

11.7.4.6. Compositing samples prior to GC/MS analysis

11.7.4.6.1. The samples must be cooled at >0 to 6°C during this step to minimize volatilization losses. Combine an equal amount of each sample to be composited in a volumetric flask. Invert and shake 3 times and transfer to a sample vial or a 5mL

gas tight syringe.

11.7.4.6.2. Samples composited in this fashion will be qualified in the reviewer checklist.

11.7.5. **Solid Samples (Soil & Sediment) Preparation:**

11.7.5.1. Screen solid samples when historic data or their appearance indicated that they may contain high concentrations (> 2mg/L) of volatile compounds. When the screening data indicates a high concentration of volatiles, use less sample for a direct purge analysis or use less methanol extract in the analysis.

11.7.5.2. Solids samples are normally reported on a dry weight basis. Always perform a dry weight determination (Appendix 20.8) unless the project plan requires data reported on an “as received” basis.

11.7.5.3. Low concentration direct purge & trap

11.7.5.3.1. This is designed for samples containing individual purgeable compounds of < 1 mg/kg. The low-concentration method is based on purging a heated (40°C) sediment/soil sample mixed with OFW containing the surrogate and internal standards. Analyze all blanks and standards under the same conditions as the samples.

11.7.5.3.2. Use a 5g sample if the expected concentration is <0.2 mg/kg or a 0.5g-5g sample for expected concentrations between 0.2 and 2mg/kg.

11.7.5.3.3. The sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. If sample has free liquid, mix the unopened container 1 min using a Vortex mixer or mix the contents with a small metal spatula. When no free liquid is present remove the top layer to expose uncompromised sample. Weigh the sample into a tared purge device and record the actual weight to the nearest 0.1g. Samples collected following EPA Method 5035 will be pre-weighed.

11.7.5.3.4. Heat and purge the sample. Be sure the trap is cool (<35°C)

11.7.5.3.5. If saturated peaks occurred or would occur if a 0.5g sample were analyzed, the high concentration method (Medium Level soil method) must be followed.

11.7.5.4. Methanol Extraction for medium level soil or waste samples. This method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol.

11.7.5.4.1. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Using a top loading balance weigh 5g (wet weight) of sample into a tarred 20 mL vial. Record the actual weight to 0.1g.

Determine the percent dry weight of the sample as described in Appendix 20.4. Measure 5mL of Methanol into the vial. Stir the sample Methanol mixture for 2 to 3 minutes using a vortex mixer.

11.7.5.4.2. Pipet a portion of the extract to a clean amber Teflon sealed vial for storage (limiting headspace). The remainder may be disposed. Store the extracts at >0 to 6°C in refrigerator 25, prior to analysis.

11.7.5.4.3. After determining the required dilution, add the appropriate amount of extract to the Autosampler vial (100µL to 10µL / 5mL). If the extract amount to be added is less than 10µL, or a secondary dilution is needed, surrogates will be diluted to a level near or below the calibration range; additional surrogate must be added by the Autosampler standard syringe.

11.7.5.4.4. For a matrix spike in the medium level samples, add 25µL of matrix spike solution and an appropriate aliquot of this extract to 5mL of organic-free water for purging. Purge and start analysis of the sample.

11.8. Set Up Analytical Run

11.8.1. Samples are analyzed in 12 hour run sequences known as QC periods. Each 12-hr QC period begins when an ICV sample analysis starts and ends following the analysis of the last sample injected within 12 hours of the initial sample injection.

11.8.2. The ICV standard may be omitted if samples are analyzed within twelve hours of the ICAL, and the injection of the last ICAL standard may be used as the starting time reference for evaluation.

11.8.3. Setup an analytical run by placing 45 mL sample vials containing either standards or client samples in the autosampler tray in the order listed in Table 09.

Table 09 – Example Analytical Run Sequence

Sample Sequence	Sample Type
1*	Daily Initial Calibration Verification
2	BS
3	BSD
4	Method Blank
5 through 50	Prepared Client Samples
* These may be combined	

11.8.4. The autosamplers may run in manual or automatic mode.

11.8.5. Enter the sample identifications into the Chemstation software

11.9. Initiate Sample Analysis

11.9.1. Proceed with the analysis. Analyze all blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100µL of the purge-and-trap grade

MeOH to simulate the sample conditions when analyzing extracted solid samples.

11.9.2. The instrument system will transfer sample to the purge and trap sampling device and perform the GC-MS analysis automatically.

11.9.3. The analyst is responsible for assuring that the automated peak identifications and integrations are acceptable.

11.9.4. Verify Instrument Calibration. (Tuning is required prior to initial calibration, but not on a daily basis.)

11.9.5. MS tuning- prior to initial calibration, each GC/MS system must be hardware-tuned to meet the criteria in Appendix 20.3for a 50ng total or less injection of BFB. Analyses must not begin until all these criteria are met. Evaluate the ion abundance as following: Use the mean of the apex and the preceding and following scans (the mean of a symmetric pattern of scans about the apex). Background subtraction is required using a single scan no more than 20 scans prior to the elution of BFB. The tune must satisfy the ion abundance acceptance criteria listed in Appendix 20.3. Do not subtract part of the BFB peak.

11.9.6. It is also acceptable to evaluate the BFB ion abundance by averaging all scans from the entire peak and subtracting a single scan no more than 20 scans prior to the elution of BFB. The evaluation of BFB ion abundance from an entire peak must be documented in the reviewer checklist including the scans used for averaging and the single scan used for subtraction.

11.9.7. Evaluation of raw data to BFB abundance criteria will be performed after rounding to the number of significant figures listed in Appendix 20.3 for each mass.

11.9.8. BFB tuning is required prior to initial calibration, but not on a daily basis. The same conditions must be used for sample analysis.

11.9.9. The 12-hour QC period starts with the ICV injection time and ends with the injection time of the last run inside the 12 hours.

11.9.10. Additional analysis may be performed beyond the 12-hour period using a closing CCV that also meets all the requirements for an opening ICV.

11.9.11. All analyses performed in the twelve-hour QC period following the ICV standard must use the same instrument parameters (GC program, MS parameters, etc.)

11.9.12. Review chromatographic data to assure all peaks are identified and integrated correctly following the procedures in SOP 1021S.

11.9.13. Verify that the response of all internal standards is -50% to +100% of the compound's response in the most recent initial calibration midpoint standard.

11.9.14. Daily GC/MS initial calibration verification

11.9.14.1. An initial calibration check standard (ICV) at mid-concentration containing each compound of interest, including all required surrogates, must be performed once every

12 hours prior to sample analysis. Compare the response factor data of the standard each 12 hour shift that samples are to be analyzed against the average response factor from the initial calibration for a specific instrument.

11.9.14.2. Determine the percent drift (%D) for all analytes in the daily initial calibration verification.

11.9.14.3. The calibration for all compounds with a %D ≤ 20 is acceptable.

11.9.14.3.1. Method 8260 allows up to 20% of the target analytes to be greater than 20%. If more than 20% of the analytes have %D > 20% corrective action is required prior to analysis.

11.9.14.3.2. Compounds with >20%D may be reported when it can be demonstrated that there is adequate sensitivity to detect the compound if it were present. Such compounds must be documented in the reviewer checklist and the data Q-flagged for any reported value.

11.9.14.4. Evaluate the IS response in the ICV compared to the response in the mid-point of the initial calibration. The response must be within 50-200% relative to the response of that IS in the mid-point ICAL standard or the average of responses in the suite of ICAL standards.

11.10. Evaluate Mass Spectra

11.10.1. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum. If not, the compound may be flagged with “M” if the analyst feels the identification is real (this favors false positives).

11.10.2. The relative intensities of the major ions should generally agree with the reference spectra.

11.10.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.10.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

11.10.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.10.6. An analyte is identified by comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the initial calibration. These standard reference spectra may be obtained through analysis of the calibration standards. The characteristic ions are defined as the three

ions of greatest intensity, or any ions over 30% intensity relative to the base ion, if less than three such ions occur in the reference spectrum. Two criteria must be satisfied to verify identification: (1) elution of sample component at or near the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component mass spectrum and the standard component mass spectrum.

11.10.7. The intensities of the characteristic ions must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where 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 will be accepted as meeting this criterion.

11.10.8. The sample component RRT must compare within ±0.06 units of the RRT of the standard component. For reference, the standard must be run within the same 12 hour QC period as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted, ion-current profiles for ions unique to the component of interest.

11.10.9. All ions present in the standard mass spectra at a relative intensity greater than 10% (the most abundant ion in the spectrum is equal to 100% intensity) should be present in the sample spectrum.

11.10.10. The relative intensities of ions specified in Appendix 20.3 must agree within plus or minus 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample abundance must be between 20% and 80%.). If not, the compound may be flagged with an "m" if the analyst determines that the identification is valid (favors false positive).

11.10.11. Structural isomers that produce very similar mass spectra should be 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 and reported as the sum of both compounds.

11.10.12. 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 co-elute (i.e., only one

chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

11.10.13. Secondary ion quantitation is allowed only if there are sample matrix interferences with the primary ion.

11.10.14. All dilution efforts should try to keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. To determine the dilution factor, compare a minor ion in the saturated analyte against the daily standard.

11.11. Evaluate the QA samples as outlined in Section 12

11.11.1. Daily GC/MS calibration verification, BS criteria, and the MB must demonstrate the system is free of interferences, before analyzing samples.

11.11.2. If the analysis shows the sample to have a concentration of analytes that exceed their highest standard, the sample must be rerun at a dilution. Analyst considerations for chromatographic “system overload” are analytes that are above the linear range, saturation of the mass spectrometer, chromatography overload, or analyte/interference carryover. Professional judgment must be used by the analyst as to the modification of the analytical sequence. If system contamination is present, an OFW blank must be analyzed. If the blank analysis is not free of analytes/interferences, the system should undergo maintenance, such as baking the trap or purging with methanol to decontaminate the system. If a blank is not run, as with auto-samplers, the following sample must be checked for carryover and rerun if it contains the same compounds which showed saturation. This must continue until no analyte is detected > ½ the RL.

11.12. Export data to Element.

12. Data Analysis and Calculations

12.1. Quantitative analysis

12.1.1. It is the operator’s responsibility to verify all compound identifications performed by the GC-MS data system. Use retention time, spectral data, data system calculated fit, and the operator’s expertise to determine whether analytes found by the system are real.

12.1.2. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

12.1.3. If secondary ion quantitation is necessary due to interference, then a short quantitation report list is generated. This quantitation contains the integrated areas of the affected compounds, based on the secondary ion(s) for that compound, and of the relevant internal

standards. Identical reports must be generated for the sample with interference and for the relevant initial calibration verification. The report for the initial calibration verification is used to generate a relative response factor for the affected compound based on its secondary ion. This relative response factor is then used in the calculations for that compound in the affected sample. The short quantitation report may be hand calculated by the analyst as long as it is signed and dated by the analyst.

12.1.4. The concentration of each identified analyte in the sample is calculated as follows:

12.1.4.1. Aqueous samples

Concentration (µg/L) =	$\frac{(Ax)(Is)}{(Ais)(RF)(VO)}$
where:	
Ax = Area of characteristic ion for compound being measured.	
Is = Amount of internal standard injected (ng)	
Ais = Area of characteristic ion for the internal standard.	
RF = Response factor for compound being measured.	
VO =Volume of water purged (mL), taking into consideration any dilutions made.	

12.1.5. Sediment /Soil, Sludge, and Waste:

12.1.5.1. High-concentration:

Concentration (µg/Kg) =	$\frac{(Ax)(Is)(Vt)}{(Ais)(RF)(Vi)(Ws)}$
where:	
Ax = Area of characteristic ion for compound being measured.	
Is = Amount of internal standard injected (ng)	
Vt = Volume of total extract (L) (use 5,000µL or a factor of this when dilutions are made).	
Ais = Area of characteristic ion for the internal standard.	
RF = Response factor for compound being measured.	
Vi = Volume of extract added (L) for purging	
Ws = Weight of sample extracted or purged (g). The wet weight or dry weight may be used depending upon the scientific applications of the data.	

12.1.6. Low-concentration

Concentration (µg/Kg) =	$\frac{(Ax)(Is)}{(Ais)(RF)(Ws)}$
where:	
Ax = Area of characteristic ion for compound being measured.	
Is = Amount of internal standard injected (ng)	
Ais = Area of characteristic ion for the internal standard.	
RF = Response factor for compound being measured.	
Ws = Weight of sample extracted or purged (g). The wet weight or dry weight may be used depending upon the scientific applications of the data.	

12.1.7. Sediment/soil samples are generally reported on a dry weight basis (sludge and wastes are also reported on a dry weight basis). In either instance, the percent dry weight of the sample should be reported along with the data.

12.1.8. Background organic material in sample extracts, usually due to hydrocarbons typically manifests itself in the form of a broad peak or peaks in the chromatogram. When mandated by project-specific requirements, it is necessary to provide both a tentative identification and an approximate concentration for such peaks, utilizing the following procedures.

12.1.9. A tentative spectral identification for such a peak is established by comparison of multiple spectra from the peak with those in the NIST library. A minimum of three un-enhanced scans, one each from near the beginning, middle and end of the peak shall be used. An EICP containing the three most abundant ions common to each of the three spectra shall be plotted for the region of the chromatogram encompassing the peak.

12.2. Analysis records

12.2.1. Each analytical run will be recorded in the associated Element sequence in PDF form. PDFs of the Element sequence, target run log, target manual integrations log, and the target security log will be attached to the sequence (see appendix 20.5). The MS EM level, column ID, and tune file ID must be recorded in the sequence user fields. Sample pH and container IDs will be recorded in the batch bench sheet and a batch PDF showing the sample pH and container IDs will be attached to the batch. For soil samples, the PDF should show the %total solids rather than the pH.

12.2.2. Soil extractions and 5035 analyses are noted on the Volatile Organics Extraction Bench Sheet 8043F, which is to be scanned and attached to the Element batch.

12.2.3. When total solids are performed by the volatiles staff, they are recorded on the Total Solids bench Sheet 5050F, which is then scanned to the associated Element sequence.

13. Method Performance

13.1. The QA department measures method performance using a combination of continuing QLS studies, quarterly Verification standards, performance evaluation samples, standard reference materials, and the monitoring of surrogate and spike recoveries.

13.1.1. Detection limits- the LOD for all analytes quantitated using this SOP are set using the low point of the initial calibration curve and validated by QLS studies.

13.1.2. QLS studies are performed each quarter for each analyte by each preparatory and analytical method.

13.1.3. LOD and LOQ values may be found for each analyte on the ARI's Web Site

13.2. Laboratory precision and bias measurements are performed by monitoring surrogate

and spike recoveries in samples and quality control samples.

13.2.1. Control limits are calculated from these recoveries.

13.2.2. These control limits are disseminated to the bench chemists and Element administrator for use in monitoring method performance in real time.

13.2.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found on the ARI's Web Site.

13.3. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in Appendix 2.2 of ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC must be documented in the instrument maintenance logbook.

13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.

14. Pollution Prevention

14.1. A hazardous waste satellite accumulation station is provided for disposal of all solvent or potentially hazardous samples.

14.2. All syringe rinsing must be performed over charcoal to minimize the exposure of the environment to solvent.

14.3. All GC split vents will be connected to an exhaust vent.

14.4. All MS vacuum pumps will have a charcoal exhaust filter.

14.5. Autosampler waste is neutralized in the large neutralization tank in the warehouse.

14.6. Charcoal containers must be kept closed when not in use to prevent fugitive vapors from escaping and eliminate the possibility of spilling contents.

14.7. All spent vials are placed into the 'Autosampler Vials' Satellite Accumulation waste drum for proper disposal after analysis is finished.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 of this document.

15.2. Method Blanks- The method blank must contain less than 1/2 the method reporting limit of the targeted analytes or corrective action is required.

15.3. Internal Standards- All samples' internal standard EICP areas following the initial calibration verification standard must meet the technical acceptance criteria listed in Section 9.

15.4. Surrogate Recoveries

15.4.1. All method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates or other

samples must have acceptable surrogate recoveries. Surrogate recoveries are considered unacceptable when:

15.4.1.1. Any surrogate has a recovery that is outside ARI or project specific control limits.

15.4.2. These requirements do not apply to subsequent analysis of samples where a prior analysis of the sample shows unacceptable surrogate recovery. This may demonstrate a matrix effect.

15.4.3. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet surrogate acceptance criteria, even when we meet in house limits.

15.4.4. Surrogate recovery acceptance windows are ideally determined statistically from method and matrix specific laboratory data updated on a periodic basis. Certain methods or clients may specify project specific surrogate recovery acceptance windows.

15.4.5. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.

15.5. Blank spikes (BS)

15.5.1. The BS recovery values should fall within the specified recovery acceptance limits. If an BSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.

15.5.2. BS recovery acceptance windows are ideally determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Project or method specific limits may supersede laboratory acceptance criteria.

15.5.3. Evaluate BS/BSD RPD and note any deviation >30% in the reviewer checklist.

15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.6.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified recovery acceptance limits. If a MSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.

15.6.2. MS/MSD recovery and RPD acceptance is advisory and data should not necessarily be rejected based upon MS/MSD recovery. MS/MSD recovery should be compared to BS/BSD recovery to determine if recovery trends are present. Certain projects or clients may require project specific MS/MSD recovery and RPD acceptance windows.

15.6.3. Evaluate MS/MSD RPD and note any deviation >30% in the reviewer checklist.

15.7. Holding Times

15.7.1. Samples should be run within holding times (seven days for unpreserved water samples

and fourteen days for solid samples, Methanol extracts and preserved water samples).

15.7.2. In the event that re-analysis due to an out of control event requires that samples be re-analyzed after their holding time has elapsed the analyst should analyze and report both data sets, whenever practical, distinguishing between the initial analysis and re-analysis on all deliverables. This will document that the samples were originally analyzed within holding times and may allow for comparisons that will determine whether any of the more volatile analytes were lost in the interval between analyses.

16. Corrective Actions for Out of Control Events

16.1.1. Corrective actions may include any, but are not limited to, the following:

16.1.2. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the reviewer checklist.

16.1.3. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.4. Repreparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.5. Reanalysis – if available another vial or aliquot of the sample is run on the gas chromatograph.

16.1.6. Re-extraction – a portion of the remaining sample is extracted.

16.1.7. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in ELEMENT.

16.1.8. Recalibration – a new initial calibration is evaluated and the associated samples reanalyzed.

16.1.9. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.

16.1.10. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.

16.2. When an Initial Calibration for an analyte exceeds 20% RSD or .990 R^2

16.2.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.2.1.1. When the failure appears to be the result of an improperly prepared calibration

standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option, and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

16.2.1.2. If the analyte is outside 20% and is an active analyte then proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.3. When an Initial Calibration Verification (ICV) fails:

16.3.1. At the discretion of the analysts, a second ICV may be immediately run after the failing ICV. If the second ICV meets all ICV criteria then the sequence may begin.

16.3.2. If the second inject6ion of the ICV fails, perform the appropriate corrective action(s) from Section 16.1 and re-calibrate the instrument.

16.3.3. DoD-QSM requires that %D for all analytes in the ICV or CCV be ≤ 20% (50% for end of batch CCV). For DoD analysis, immediately analyze two additional consecutive ICVs.

16.3.3.1. When both of these ICVs meet acceptance criteria, the analytical sequence may be continued.

16.3.3.2. If either of the two CCVs fail or their analysis cannot be run, perform corrective actions and repeat the analytical sequence.

16.3.3.3. If a CCV is used both as an ICV and CCV (in the middle of an analytical sequence) then the ICV requirements must be applied.

16.3.4. When a Continuing Calibration Verification (CCV) fails:

16.3.4.1. Perform any appropriate corrective action(s) from Section 16.1 if not a DoD-QSM project.

16.3.4.2. DoD-QSM requires that %D for all analytes in the CCV be ≤ 50%. For DoD analyses, immediately analyze two additional consecutive CCVs.

16.3.4.2.1. When both CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.3.4.2.2. If either fails or if two consecutive CCVs cannot be run, perform corrective

actions and repeat the analytical sequence.

16.4. Internal Standards

16.4.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.1.1. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.

16.4.1.2. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.

16.4.1.3. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.4.1.4. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".

16.5. Surrogates

16.5.1. Examine the bench sheet to verify spiking levels are correct.

16.5.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.5.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.6. Method Blanks- Corrective action for a method blank which fails acceptance criteria may involve re-preparation of a secondary method blank and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.7. Blank spikes

16.7.1. Examine the bench sheet to verify spiking levels are correct.

16.7.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8. Matrix Spike/Matrix Spike Duplicates

16.8.1. Examine the bench sheet to verify spiking levels are correct.

16.8.2. Recoveries are advisory and should not necessarily result in re-extraction.

16.8.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.9. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve, a dilution must be performed such that the analyte's quantitated value is within the curve range.

16.9.1. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

16.9.2. When peaks from an analyte saturate the detector:

16.9.2.1. The analyst must flag all affected analytes with an S flag.

16.9.2.2. The analyst should evaluate samples following a saturation or over range hit to determine if carry over has occurred.

16.10. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when initial calibration verification responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.

16.10.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)

16.10.2. All QC limit issues (including initial calibration verification and continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

16.11. Mass Spectrometer Tuning

16.11.1. When the MS does not produce an acceptable mass spectrum when injected with 5 to 50 µg/mL of BFB, re-inject the BFB. If the spectrum again fails to meet the criteria found in Appendix 20.4, the MS should be re-tuned.

16.11.2. If the re-tuned mass spectrum still fails to meet the criteria found in Appendix 20.4, the GC-MS may require maintenance. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.12. Holding blanks should meet the same criteria as the method blanks detailed below.

16.12.1. Corrective action must be taken when holding blank contamination is greater than ½ the method reporting limits for all analytes except for acetone and methylene chloride.

16.12.2. Corrective action must also be taken if Detections of acetone and methylene chloride are > the Method reporting limit.

16.12.3. Holding blanks requiring corrective action must also be submitted to the QA department for further review.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Section 16.2 for guidance on dealing with out-of-control initial calibrations.

17.2. See Section 16.3 for guidance on dealing with out-of-control initial calibration verifications.

17.3. See Section 16.4 for guidance on dealing with internal standard out-of-control events.

17.4. See Section 16.5 for guidance on dealing with surrogate out-of-control events.

17.5. See Section 16.6 for guidance on dealing with method blank related out-of-control events.
17.6. See Section 16.7 for guidance on dealing with BS/BSD related out-of-control events.
17.7. See Section 16.8 for guidance on dealing with MS/MSD related out-of-control events.
17.8. See Section 16.9 for guidance on dealing with over range samples.
17.9. See Section 16.10 for guidance on dealing with project managers.
17.10. See Section 16.11 for guidance on dealing with out-of-control tuning events.
17.11. See Section 16.12 for guidance on holding blanks.

18. Waste Management

18.1. All sample vials, standard vials and extract vials containing Methanol must be disposed of by placing them in the 'Methanol Vials' satellite accumulation hazardous waste drum. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.
18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.
18.3. All spent charcoal must be disposed of by placing it in the 'Solvent Contaminated Solids' hazardous waste drum located in the Central Accumulation Area (Bay).
18.4. Autosampler waste is neutralized in the large neutralization tank in the warehouse.
18.5. All acid preserved spent vials are placed into the 'Autosampler Vials' Satellite Accumulation waste drum for proper disposal after analysis is finished.
18.6. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

19.1. "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)": Method 8260D Revision 4, February 2017.
19.2. EPA Contract Laboratory Program Statement of Work for Organic Superfund Methods -Multi-Media, Multi-Concentration SOM02.2, August, 2014.
19.3. "Determinative Chromatographic Separations": Method 8000D, Test Methods for Evaluating Solid Waste (SW-846), Revision 5, March, 2018.
19.4. Department of Defense (DoD) Quality Systems Manual – Version 5.0 July 2013
19.5. "Sample Preparation for Volatile Organic Compounds" EPA Method 5000, Revision 0, December 1996
19.6. "Method 624.1 – Purgeables", Appendix A to CFR Part 136, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. December 2016
19.7. "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)": Method 8260B Revision 2, December 1996.

20. Appendices

20.1. Appendix 20.1: Quality Control Requirements

20.2. Appendix 20.2: 8260D target analyte list

20.3. Appendix 20.3: BFB ion abundance criteria

20.4. Appendix 20.4: Chromatogram of Typical VOA calibration standard

20.5. Appendix 20.5: Example VOA Sequence Log

20.6. Appendix 20.6: Example Batch Attachment

20.7. Appendix 20.7 Sample Screening

20.8. Appendix 20.8: Dry weight determination

20.9. Appendix 20.9: Tentatively Identified Compounds

20.10. Appendix 20.10: Pea Bubble Chart

20.11. Appendix 20.11: Synchronized SIM scan/full scan analysis

20.12. Appendix 20.12: Modifications Required for Method 624.1

20.13. 624.1 BS and MS/MSD Limits

Appendix 20.1 - Method 8260D Quality Control Requirements

Appendix 20.1 - Method 8260D Quality Control Requirements					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method (see ARI SOP 1017S)	QC acceptance criteria published by DoD, if available; otherwise method specified criteria.	1) Recalculate results 2) Locate and correct the source of the problem and repeat the test for all parameters of interest.	Not applicable (NA)	This is a demonstration of ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., BS or PT sample) as described in ARI SOP 1017S. An analyst must complete a successful demonstration of capability before analyzing client samples
Method detection limit (MDL) study	At initial set-up and subsequently once per 12 month period.	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or reconduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Tuning	Prior to calibration.	Refer to method for specific ion criteria. See appendix 20.3	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units of the daily CCal	Correct problem, then rerun CCal.	Flagging criteria are not appropriate.	
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	Option 1: RSD for each analyte ≤ 20% Option 2: linear least squares regression $r^2 > 0.99$ Option 3: non-linear regression - coefficient of determination (COD) $r^2 \geq 0.99$ (Max 10% of target analytes may fail) (6 points shall be used for second order)	Correct problem then repeat initial calibration.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification	Once after each initial calibration	Value of second source for all analytes within ± 30% of expected value (initial source)	Correct problem, verify second source standard. Rerun verification. If that fails, correct problem and repeat ICal	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Retention time established for all analytes and surrogates	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the ICV run at the beginning of the analytical shift.	Same	NA	NA

Appendix 20.1 - Method 8260D Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Calibration verification (CV)	Daily, before sample analysis, and every 12 hours of analysis time	%Difference/Drift for all target analytes: ≤ 20%D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration.) Up to 20% of analytes may exceed ≤ 20%D	Correct problem, then rerun CV. If that fails, repeat initial calibration.	DoD: Apply Q-flag if no sample material remains and analyte exceeds criteria. ARI: Apply Q-flag to any analytes that exceed ≤ 20%D	.
Internal standards verification	In all field samples and standards	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL EICP area within - 50% to + 100% of ICAL midpoint standard	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for failed standards.	Sample results are not acceptable without a valid IS verification.
Method blank	One per preparatory batch	No analytes detected > ½ RL. For common laboratory contaminants, no analytes detected ≥ 5 X the RL.	Correct problem, if required, reprep then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch	
Blank spike (BS) containing all reported analytes & surrogates	One BS per preparatory batch	QC acceptance criteria specified published in ARI's LQAP.	Correct problem, then reprep and reanalyze the BS and all samples in the associated batch, if sufficient sample material is available	If corrective action fails apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch	
Matrix spike (MS)	One MS/MSD per preparatory batch per matrix when sufficient sample is available	For matrix evaluation, use QC acceptance criteria specified by for BS.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply *-flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are out of control, evaluated data to determine the source of difference and to determine if there is a matrix effect or analytical error.
Surrogate spike	All field and QC samples	QC acceptance criteria specified by DoD, if available; otherwise method-specified criteria or laboratory's own in-house criteria	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	For the specific analyte(s) in all field samples collected from the same site matrix as the parent, apply *-flag if acceptance criteria are not met. For QC samples, apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Results report-ed between LOD & LOQ	NA	NA	NA	Apply J-flag to all results between LOD and LOQ.	

Appendix 20.2
ARI's Routine Method 8260D Target Analytes
Internal Standards, Quantitation Ions, and Calibration Criteria

Internal Standard Associated Analyte[1]	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
Pentafluorobenzene (IS)[1]				--	--	--
Acetone	67-64-1	43	58	0.01	20	20
Acrolein	107-02-8	56	55, 58	0.01	20	20
Acrylonitrile	107-13-1	53	52, 51	0.01	20	20
Bromochloromethane	74-97-5	128	49, 130	0.01	20	20
Bromoethane	74-96-4	108	110		20	20
Bromomethane	74-83-9	94	96	0.01	20	20
2-Butanone	78-93-3	43	57, 72	0.01	20	20
Carbon disulfide	75-15-0	76	78	0.01	20	20
Chloroethane	75-00-3	64	66	0.01	20	20
Chloroform	67-66-3	83	85	0.02	20	20
Chloromethane	74-87-3	50	52	0.01	20	20
Dibromofluoromethane (surrogate)	1868-53-7	111	113	0.01	20	20
Dichlorodifluoromethane	75-71-8	85	87	0.01	20	20
1,1-Dichloroethane	75-34-3	63	65, 83	0.02	20	20
1,1-Dichloroethene	75-35-4	96	61, 98	0.05	20	20
cis-1,2-Dichloroethene	156-59-2	96	61, 98	0.01	20	20
trans-1,2-Dichloroethene	156-60-5	96	61, 98	0.01	20	20
2,2-Dichloropropane	78-87-5	77	97	0.01	20	20
n-Hexane	110-54-3	56	57	0.01	20	20
Methyl tert butyl ether	1634-04-4	73	57	0.01	20	20
Methylene chloride	75-09-2	84	86, 49	0.01	20	20
1,1,1-Trichloroethane	71-55-6	97	--	0.01	20	20
Trichlorofluoromethane	75-69-4	101	103	0.01	20	20
Vinyl acetate	108-05-4	43	86	0.01	20	20
Vinyl chloride	75-01-4	62	64	0.01	20	20
1,2-Dichloroethane -d4 (surrogate)	107-06-2	62	98	0.01	20	20
1,1,2-trichloro -1,2,2-trifluoroethane	76-13-1	101	85, 151	0.01	20	20
Iodomethane	74-88-4	142	127	0.01	20	20
Chlorobenzene-d5 (IS)	108-90-7	117	82	--	--	--
Chlorodibromomethane	124-48-1	129	127	0.02	20	20
Chlorobenzene	108-90-7	112	77, 114	0.05	20	20
1,3-Dichloropropane	142-28-9	76	78	0.01	20	20
Ethylbenzene	100-41-4	91	106	0.01	20	20
2-Hexanone	91-78-6	43	58, 57, 100	0.01	20	20
Styrene	100-42-5	104	78	0.03	20	20

Internal Standard Associated Analyte[1]	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
1-chlorohexane	544-10-5	91	55	0.01	20	20
Methylcyclohexane	108-87-2	83	55	0.01	20	20
Cyclohexane	110-82-7	84	56	0.01	20	20
Cyclohexanone	108-94-1	55	42, 98	0.01	20	20
1,1,1,2-Tetrachloroethane	630-20-6	131	133, 119	0.01	20	20
Tetrachloroethene	127-18-4	166	164, 131, 129	0.02	20	20
M + p-Xylene	108-38-3, 106-42-3	106	91	0.01	20	20
o-Xylene	95-47-6	106	91	0.03	20	20
4-Bromofluorobenzene(surrogate)	400-00-4	95	174	0.01	20	20
1,4-Difluorobenzene (IS)		114	88	0.01	20	20
Benzene	71-43-2	78	52, 77	0.05	20	20
Bromodichloromethane	75-27-4	83	85	0.01	20	20
Toluene-d8(surrogate)	108-88-3	98	100	0.01	20	20
Carbon tetrachloride	56-23-5	117	119	0.01	20	20
2-Chloroethyl vinyl ether	110-75-2	63	65, 106	0.05	20	20
1,2-Dibromoethane	106-93-4	107	109, 188	0.01	20	20
Dibromomethane	74-95-3	93	95, 174	0.01	20	20
1,2-Dichloroethane	107-06-2	62	98	0.01	20	20
1,2-Dichloropropane	78-87-5	63	112	0.01	20	20
1,1-Dichloropropene	563-58-6	75	110, 77	0.01	20	20
cis-1,3-Dichloropropene	10061-01-5	75	77, 110	0.02	20	20
trans-1,3-Dichloropropene	10061-02-6	75	77, 110	0.01	20	20
4-Methyl-2-pentanone	108-10-1	58	43, 100	0.01	20	20
2-Pentanone	107-87-9	86	43	0.01	20	20
Toluene	108-88-3	92	91	0.04	20	20
Trichloroethene	79-01-6	130	132, 95	0.02	20	20
1,1,2-trichloroethane	79-00-5	97	99, 83	0.01	20	20
1,4-Dichlorobenzene-d4 (IS)	106-46-7	150	152	0.01	20	20
Bromobenzene	108-86-1	159	77, 158	0.01	20	20
Bromoform	75-25-2	173	175, 171	0.01	20	20
n-Butylbenzene	104-51-4	91	92, 134	0.01	20	20
trans-1,4-dichloro 2-butene	110-57-6	53	75	0.01	20	20
d4-1,2-Dichlorobenzene(surrogate)	95-50-1	150	152	--	--	--
sec-Butylbenzene	135-98-8	105	134	0.01	20	20
tert-Butylbenzene	98-06-6	119	91, 134	0.01	20	20
2-Chlorotoluene	95-49-8	91	126	0.01	20	20
4-Chlorotoluene	106-43-4	91	126	0.01	20	20

Internal Standard Associated Analyte[1]	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
1,2-Dibromo-3-chloropropane	96-12-8	75	155, 157	0.005	20	20
1,2-Dichlorobenzene	95-50-1	146	111, 148	0.04	20	20
1,3-Dichlorobenzene	541-73-1	146	111, 148	0.06	20	20
1,4-Dichlorobenzene	106-46-7	146	111, 148	0.05	20	20
Hexachlorobutadiene	87-68-3	225	223, 227	0.01	20	20
Isopropyl benzene	98-82-8	105	120	0.01	20	20
p-Isopropyltoluene	98-87-6	119	134, 91	0.01	20	20
Naphthalene	91-20-3	128	129, 127	0.01	20	20
n-Propylbenzene	103-65-1	91	120	0.01	20	20
1,1,2,2-Tetrachloroethane	79-34-5	83	97, 85	0.03	20	20
1,2,3-Trichlorobenzene	87-61-6	180	145	0.01	20	20
1,2,4-Trichlorobenzene	120-82-1	180	97, 85	0.02	20	20
1,2,3-Trichloropropane	98-18-4	110	75, 77	0.01	20	20
1,2,4-Trimethylbenzene	95-63-6	105	120	0.01	20	20
1,3,5-Trimethylbenzene	95-63-6	105	120		20	20

1 – Compound designations: IS = Internal Standard, SS = Surrogate Standard

Appendix: 20.3
BFB ION ABUNDANCE CRITERIA

8260D SUGGESTED ION ABUNDANCE CRITERIA[1]

BFB MASS INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)[2]
95	50-200% of mass 174
96	5.0 to 9.0% of mass 95[3] (5-15% when using H_2 carrier)
173	less than 2.0% of mass 174
174	50.0-200% of mass 95
175	5.0 to 9.0% of mass 174
176	95.0% -105% of mass 174
177	5.0 to 10% of mass 176

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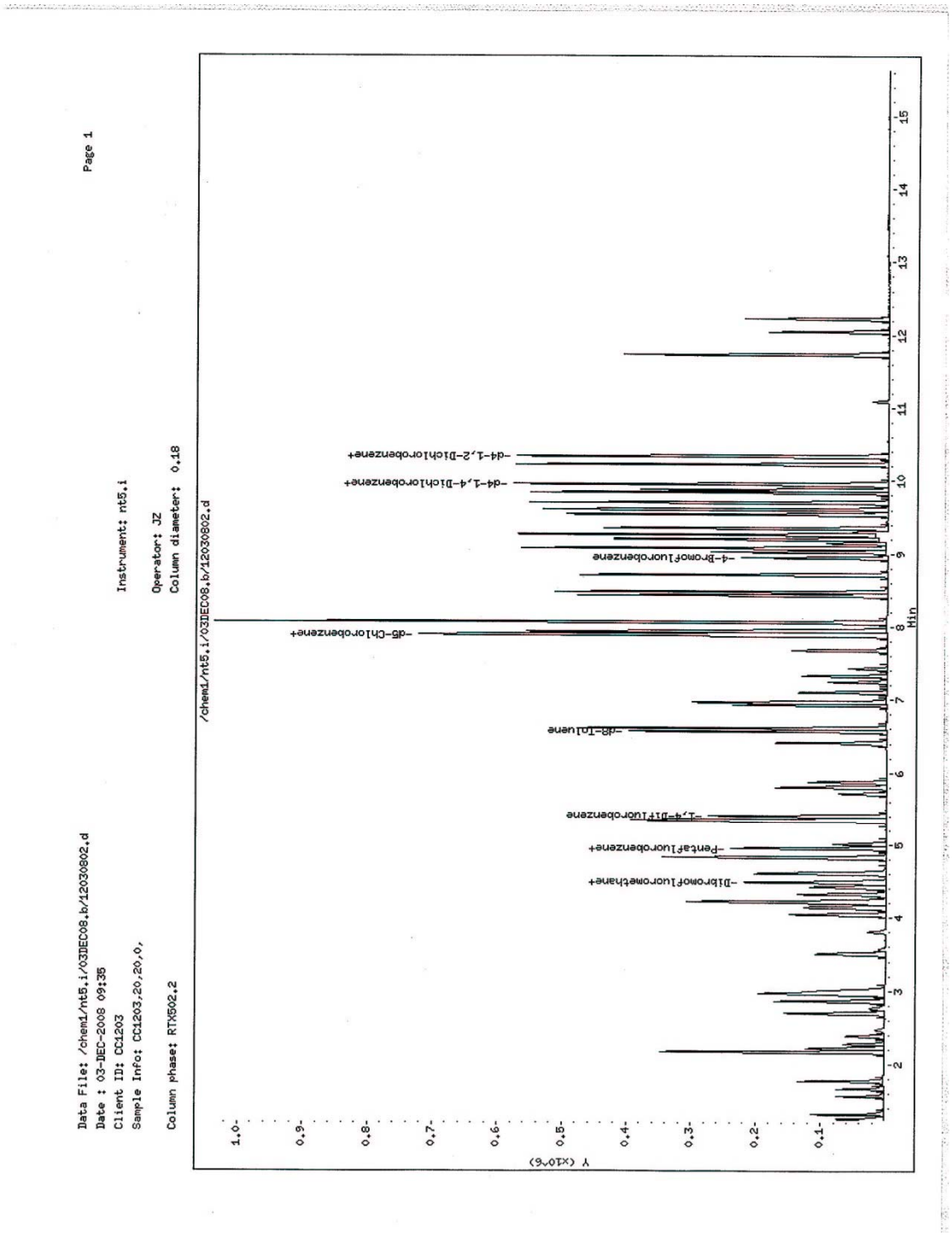
[1] Method 8260D allows the use of alternate abundance criteria, including CLP.
[2] Raw data is rounded to three significant figures and one or less decimal point before comparison to the abundance criteria.
[3] All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundances of m/z 174 may be up to 120% that of m/z 95.

Appendix 20.4
Chromatogram of Calibration Standard



Appendix 20.5
Example VOA Sequence Log

Analytical Resources, Incorporated
Analytical Chemists and Consultants

ANALYSIS SEQUENCE
SGF0182

Printed: 6/21/2018 12:49:03PM

Instrument: NT2 Element Column ID: 1295415 RTXV
Calibration ID: BF00032 Tune File: bfb.u
EM Voltage: 1847

Lab Number	Sample Name	Analysis	Container	Order	STD ID	ISTD ID	Comments
SGF0182-TUN1	MS Tune	QC		1	G003328	G003153	
SGF0182-CAL1	8260C 0.2	QC		2	G005421	G003153	
SGF0182-CAL2	8260C 0.5	QC		3	G005422	G003153	
SGF0182-CAL3	8260C 1.0	QC		4	G005423	G003153	
SGF0182-CAL4	8260C 2.0	QC		5	G005424	G003153	
SGF0182-CAL5	8260C 10	QC		6	G005425	G003153	
SGF0182-CAL6	8260C 20	QC		7	G005426	G003153	
SGF0182-CAL7	8260C 40	QC		8	G005427	G003153	
SGF0182-CAL8	8260C 80	QC		9	G005428	G003153	

seq_ARI_GCMS_Data.rpt

Page 1 of 1

INTERNAL STANDARD SUMMARY FOR DATABATCH - \\target\share\chem1\nt2.i\20180611.b

	Time	Filename	LabID	ClientID	Vial#	pH	DF								
1	0943	V206111801.D	RINSE				1								
2	1003	V206111802.D	TEST				1								
3	1048	V206111803.D	SGF0153-TUN1				1								
4	1123	V206111804.D	0.2TEST				1	5.16	311301	5.55	518059	7.52	468693	9.31	228363
5	1240	V206111805.D	SGF0-ICV1	ICV test			1	5.16	3017301	5.55	507572	7.52	453221	9.31	233310
6	1300	V206111806.D	BGF0-BSD1				1	5.16	290923	5.55	481002	7.52	427671	9.31	223293
7	1349	V206111807.D	RINSE				1	5.56	1849	7.63	4747	9.32	3771		
8	1409	V206111808.D	SGF0153-CAL1	0.2			1	5.16	271749	5.55	454417	7.52	414984	9.31	207952
9	1429	V206111809.D	SGF0153-CAL2	0.5			1	5.16	271899	5.55	457148	7.52	410243	9.31	214686
10	1450	V206111810.D	SGF0153-CAL3	1			1	5.16	276278	5.55	459832	7.52	420977	9.31	210152
11	1510	V206111811.D	SGF0153-CAL4	2			1	5.16	271219	5.55	442009	7.52	405187	9.31	209954
12	1530	V206111812.D	SGF0153-CAL5	10			1	5.16	266998	5.55	445870	7.51	404046	9.30	216598
13	1551	V206111813.D	SGF0153-CAL6	20			1	5.16	279239	5.55	466606	7.52	423545	9.30	223793
14	1611	V206111814.D	SGF0153-CAL7	40			1	5.16	284265	5.55	474676	7.52	418019	9.31	223786
15	1631	V206111815.D	SGF0153-CAL8	80			1	5.15	281556	5.55	472470	7.52	404986	9.31	213127
16	1651	V206111816.D	SGF0153-SCV1				1	5.16	275468	5.55	463596	7.52	422633	9.31	219775

MANUAL INTEGRATION SUMMARY FOR DATABATCH - \\target\share\chem1\nt2.i\20180611.b

Instrument: nt2.i Date: 11-JUN-2018

Time	Filename	LabID	DF	Manually Integrated Compounds
0943	V206111801.D	RINSE	1	NO MANUAL INTEGRATION
1003	V206111802.D	TEST	1	NO MANUAL INTEGRATION
1046	V206111803.D	SGF0153-TUN1	1	NO MANUAL INTEGRATION
1123	V206111804.D	0.2TEST	1	Dichlorodifluoromethane, Trichlorofluoromethane,
1240	V206111805.D	SGF0-ICV1	1	Dichlorodifluoromethane,
1300	V206111806.D	BGF0-BSD1	1	NO MANUAL INTEGRATION
1349	V206111807.D	RINSE	1	NO MANUAL INTEGRATION
1409	V206111808.D	SGF0153-CAL1	1	Dichlorodifluoromethane, Vinyl Chloride, Bromomethane, Chloroethane, Trichlorofluoromethane, 1,1-Dichloroethen Carbon Disulfide, Acrylonitrile, Vinyl Acetate, Cis-1,2-Dichloroethene, Bromochloromethane, 2-Butanone 2-Pentanone, 2-Chloroethyl Vinyl Ether, Styrene, Trans-1,4-Dichloro 2-Butene,
1429	V206111809.D	SGF0153-CAL2	1	Dichlorodifluoromethane, Trichlorofluoromethane, 1,1-Dichloroethene, Carbon Disulfide, Iodomethane, Methylene Cis-1,2-Dichloroethene, 2-Pentanone, Trans-1,4-Dichloro 2-Butene,
1450	V206111810.D	SGF0153-CAL3	1	Dichlorodifluoromethane, Chloroethane, Trichlorofluoromethane, 1,1-Dichloroethene, Carbon Disulfide, Iodometha Bromoethane, Methylene Chloride, Vinyl Acetate, 2-Pentanone, Trans 1,3-Dichloropropene,
1510	V206111811.D	SGF0153-CAL4	1	Dichlorodifluoromethane, Trichlorofluoromethane, 1,1-Dichloroethene, Carbon Disulfide, Iodomethane, Bromoethan Methylene Chloride, Vinyl Acetate, Trans-1,4-Dichloro 2-Butene,
1530	V206111812.D	SGF0153-CAL5	1	Dichlorodifluoromethane, Trichlorofluoromethane, 1,1-Dichloroethene, Iodomethane, Bromoethane, Methylene Chlor
1551	V206111813.D	SGF0153-CAL6	1	Dichlorodifluoromethane, Chloroethane, Trichlorofluoromethane, 1,1-Dichloroethene, 112Trichloro122Trifluoroethane, Methylene Chloride,
1611	V206111814.D	SGF0153-CAL7	1	Dichlorodifluoromethane, Chloroethane, Trichlorofluoromethane, 1,1-Dichloroethene, Carbon Disulfide, Iodometha Bromoethane, Methylene Chloride,
1631	V206111815.D	SGF0153-CAL8	1	Trichlorofluoromethane, 1,1-Dichloroethene, Carbon Disulfide, Iodomethane, Bromoethane, Methylene Chloride, Pentafluorobenzene,
1651	V206111816.D	SGF0153-SCV1	1	Dichlorodifluoromethane, Chloroethane, 1,1-Dichloroethene, Iodomethane, Methylene Chloride,

Security Status Report

Date: 13-Jun-2018 07:16

V206111801.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111802.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111803.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111804.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111805.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111806.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111807.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111808.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111809.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111810.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111811.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111812.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111813.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111814.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111815.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111816.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111817.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111818.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111819.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111820.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111821.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111822.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111823.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111824.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111825.D	Data Locked	lanih, 13-Jun-2018 07:16
V206111826.D	Data Locked	lanih, 13-Jun-2018 07:16

Appendix 20.6
Example Batch Attachment

Analytical Resources, Incorporated
Analytical Chemists and Consultants

PREPARATION BENCH SHEET
BGF0426

Printed: 6/19/2018 8:57:44AM

Matrix: Water **Prepared using: Volatiles - EPA 5030 (Purge and Trap)** **Surrogate used: G003068**

Lab Number	Analysis	Prepared	Initial (mL)	Final (ml)	Spike ID	Source ID	ul Spike	ul Surrogate	pH	Extraction Comments
18F0250-01 D	8260C VOA	18-Jun-2018 11:32	10	10				1	2	
18F0250-01 D	8260C Gas (NWTPH)	18-Jun-2018 11:32	10	10				1	2	
18F0250-02 A	8260C Gas (NWTPH)	18-Jun-2018 11:32	10	10				1	2	
18F0250-02 A	8260C VOA	18-Jun-2018 11:32	10	10				1	2	
18F0250-03 B	8260C Gas (NWTPH)	18-Jun-2018 11:32	10	10				1	2	
18F0250-03 B	8260C VOA	18-Jun-2018 11:32	10	10				1	2	
18F0250-04 D	8260C VOA	18-Jun-2018 11:32	10	10				1	2	PB
18F0250-04 D	8260C Gas (NWTPH)	18-Jun-2018 11:32	10	10				1	2	PB
18F0250-05 A	8260C VOA	18-Jun-2018 11:32	10	10				1	2	PB
18F0263-01 C	8260C VOA	18-Jun-2018 11:32	0.05	10				1	2	Use Go No Go List
BGF0426-BLK1	QC	18-Jun-2018 07:32	10	10				1		
BGF0426-BLK2	QC	18-Jun-2018 07:32	10	10				1		
BGF0426-BS1	QC	18-Jun-2018 07:32	10	10	G004905		5	1		
BGF0426-BS2	QC	18-Jun-2018 07:32	10	10	G004481		2	1		
BGF0426-BSD1	QC	18-Jun-2018 07:32	10	10	G004905		5	1		
BGF0426-BSD2	QC	18-Jun-2018 07:32	10	10	G004481		2	1		

Spiking Witnessed By Date

Preparation Reviewed By Date

Extracts Received By Date

bch_ARI_with_pH.rpt

Page 1 of 1

Appendix 20.7
Sample Screening

1.1. Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary, and will prevent contamination of the purge-and-trap system.

20.13.1. Aqueous Samples

20.13.1.1. Place an appropriate volume of aqueous sample in a 45 mL vial and fill the vial with organic free water (OFW). Analyze the sample as a normal sample and determine the appropriate dilution for final analysis.

20.13.2. Solid Samples (Soil & Sediment)

20.13.2.1. For screening soils, oils, and solid materials, place 1g of sample into a scintillation vial with 5mL VOA grade Methanol and vortex until well mixed. Dilute 100

µL of the methanol solution into 45 mL OFW. Analyze the sample as a normal sample and determine the appropriate dilution for final analysis.

20.13.3. Waste Samples

20.13.3.1. Water-miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.

20.13.3.2. Initial and serial dilutions can be made in a 100mL volumetric flask with organic-free reagent water.

20.13.4. Alternatively, prepare dilutions directly in a 5mL syringe filled with organic-free reagent water by adding at least 180µL, but not more than 900µL, of liquid sample.

20.13.5. OVM may be used to determine approximate dilution levels.

Appendix 20.8
Dry Weight Determination

20.14. Determine the percent dry weight of the soil/sediment sample. Other wastes should be reported on a wet-weight basis.

20.14.1. Weigh 5-10g of the sample into a tared weighing dish.

20.14.2. Place the weighted sample in a 104 ± 2°C oven overnight (12 hour minimum).

20.14.3. Remove the sample from the oven and allow it to equilibrate to ambient temperature.

20.14.4. Calculate the sample per cent dry weight:

$$\% \text{ dry weight} = \frac{\text{sample weight dry (g)}}{\text{sample weight wet (g)}} \times 100$$

Appendix 20.9
Tentatively Identified Compounds

20.15. 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. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

20.15.1. Relative intensities of major ions in the reference spectrum (ions >10 % of the most abundant ion) should be present in the sample spectrum.

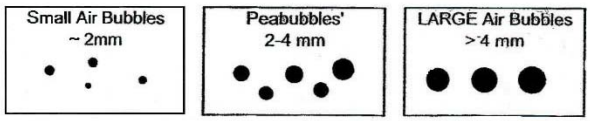
20.15.2. The relative intensities of the major ions should agree within ± 20%.

20.15.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

20.15.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

20.15.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Appendix 20.10
Pea Size Bubble Reference



Appendix 20.11
Synchronous scan

Synchronous scanning may be utilized to produce both SIM scan and full scan data simultaneously during the same acquisition. This methodology requires the use of an Agilent 5975C MSD capable of synchronous scanning. The Agilent Chemstation will generate a .d data file format for each sample acquired. Each .d data file consists of two raw MS data files which are processed separately using both SIM scan and full scan methods. The data.ms file contains the full scan data and the datasim.ms file contains the SIM data. Typically an initial calibration is produced by acquiring all calibration levels for both SIM and full scan ranges and then applying the lowest 6 (or 7) calibration points to the SIM method and the highest 6 (or 7) calibration points to the full scan method. The SIM scan and full scan data are processed and stored in separate directories in Target™ and loaded into ELEMENT individually. Example: 10 different concentration of initial calibration standards are analyzed ranging from .01-80ug/L. The full scan initial calibration is produced by with the highest eight points ranging from .2-80ug/L. The SIM scan initial calibration is produced with the lowest eight calibration points ranging from .01-5ug/L. The total cycle time for the synchronous acquisition is designed to meet the method requirement of 1 second/scan or less using the formulae provided by Agilent:

Total cycle= 1/((1/a+1/b)*1.05)

Where a = total scan cycles per second

Where b = total sim cycles per second

Total cycle time will be optimized to ensure we are collecting between 5-10 scans for every chromatographic peak. Several advantages are realized with synchronous scan including better comparability between SIM and full scan data, fewer sample containers are required, and the requirement for SIM and full scan data is met in a single analysis. Please also see SOP #703S which provides more detail specific to the SIM component of the synchronous scan procedure.

Appendix 20.12

Modifications Required for EPA Method 624.1 (These modifications are only implemented when specifically requested by a client. Otherwise, Method 624.1 is analyzed as described previously in this SOP.)

1. The following BFB key ions and ion abundance criteria for Method 624.1 are substituted for those listed in Appendix 20.3 used for Method 8260D. (The method states that alternative tuning criteria from other published EPA reference methods may be used, provided method performance is not adversely affected.)

EPA 624.1 ION ABUNDANCE CRITERIA

BFB MASS INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
50	15.0 to 40.0% of mass 95
75	30.0 to 60.0% of mass 95
95	base peak, 100% relative abundance
96	5.0 to 9.0% of mass 95
173	less than 2.0% of mass 174
174	>50.0% of mass 95
175	5.0 to 9.0% of mass 174
176	>95.0% but <101% of mass 174
177	5.0 to 9.0% of mass 176

2. Initial calibration RSD for Method 625 must be RSD< 35% or R2 <.920 with no exceptions.
3. QC requirements for 624.1 are as follows: BFB, Blank Spike, and Blank.
4. The 12-hour shift begins after the analysis of the BFB, BS, and the blank and ends 12 hours later. The BFB, BS, and blank are outside of the 12-hour shift. The MS/MSD and samples are treated as samples and are analyzed within the 12-hour shift. The total shift, including BFB, LCS, and the blank is not to exceed 14 hours.
5. Blank Spike Requirements
   5.1. The BS must be from a source different from the source used for calibration.
   5.2. Blank spike and matrix spike recoveries verification for Method 624.1 must fall within the limits shown in appendix 20.12.13. Note that these limits are not in Element and must be evaluated manually.

5.3. A retest is allowed in the event of failure and, per 624.1, it may be prudent to analyze two BSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.

6. Method Blank Requirements

6.1. The method blank passes QC requirements if no analytes of interest are found: 1) at a concentration greater than the MDL for the analyte, 2) at a concentration greater than 1/3 the regulatory compliance limit, or 3) at a concentration greater than 1/10 the concentration in a sample analyzed during the 12-hour shift.

6.2. A blank must also be analyzed after a sample containing a high concentration of an analyte or potentially interfering compound to demonstrate freedom from carry-over.

7. Sample Preservation

7.1. If acrolein is to be determined, analyze the sample within 3 days (for an unpreserved sample) or acidify the sample to pH 4-5 if a 14-day holding time is desired.

Appendix 20.13
624.1 BS and MS/MSD Limits

Table 7 – LCS (Q), DOC (s and $\bar{X}$), and MS/MSD (P and RPD) Acceptance Criteria [1]					
Analyte	Range for Q (%)	Limit for s (%)	Range for $\bar{X}$ (%)	Range for P_1, P_2 (%)	Limit for RPD
Acrolein	60-140	30	50-150	40-160	60
Acrylonitrile	60-140	30	50-150	40-160	60
Benzene	65-135	33	75-125	37-151	61
Benzene-d_6					
Bromodichloromethane	65-135	34	50-140	35-155	56
Bromoform	70-130	25	57-156	45-169	42
Bromomethane	15-185	90	D-206	D-242	61
2-Butanone-d_5					
Carbon tetrachloride	70-130	26	65-125	70-140	41
Chlorobenzene	65-135	29	82-137	37-160	53
Chloroethane	40-160	47	42-202	14-230	78
Chloroethane-d_5					
2-Chloroethylvinyl ether	D-225	130	D-252	D-305	71
Chloroform	70-135	32	68-121	51-138	54
Chloroform-^{13}C					
Chloromethane	D-205	472	D-230	D-273	60
Dibromochloromethane	70-135	30	69-133	53-149	50
1,2-Dichlorobenzene	65-135	31	59-174	18-190	57
1,2-Dichlorobenzene-d_4					
1,3-Dichlorobenzene	70-130	24	75-144	59-156	43
1,4-Dichlorobenzene	65-135	31	59-174	18-190	57
1,1-Dichloroethane	70-130	24	71-143	59-155	40
1,2-Dichloroethane	70-130	29	72-137	49-155	49
1,2-Dichloroethane-d_4					
1,1-Dichloroethene	50-150	40	19-212	D-234	32
1,1-Dichloroethene-d_2					
trans-1,2-Dichloroethene	70-130	27	68-143	54-156	45
1,2-Dichloropropane	35-165	69	19-181	D-210	55
1,2-Dichloropropane-d_6					
cis-1,3-Dichloropropene	25-175	79	5-195	D-227	58
trans-1,3-Dichloropropene	50-150	52	38-162	17-183	86
trans-1,3-Dichloropropene-d_4.					
Ethyl benzene	60-140	34	75-134	37-162	63
2-Hexanone-d_5					
Methylene chloride	60-140	192	D-205	D-221	28
1,1,2,2-Tetrachloroethane	60-140	36	68-136	46-157	61
1,1,2,2-Tetrachloroethane-d_2					
Tetrachloroethene	70-130	23	65-133	64-148	39
Toluene	70-130	22	75-134	47-150	41
Toluene-d_8					
1,1,1-Trichloroethane	70-130	21	69-151	52-162	36
1,1,2-Trichloroethane	70-130	27	75-136	52-150	45
Trichloroethene	65-135	29	75-138	70-157	48
Trichlorofluoromethane	50-150	50	45-158	17-181	84
Vinyl chloride	5-195	100	D-218	D-251	66
Vinyl chloride-d_3					

[1] Criteria were calculated using an LCS concentration of 20 µg/L

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

GC-MS Analysis of PAH/PCP
Method 8270E – Selective Ion Monitoring (SIM)

SOP 801S
Revision 012

Revision Date: 6/25/19
Effective Date: 6/25/19

Prepared by:

Peter Kepler, Van Spohn

Approvals:

Brian N. Bebee, Laboratory Section Manager

Bob Congleton, Quality Assurance Manager

Annual Review

SOP Number: 801S

Title: GC-MS Analysis of PAH/PCP Method 8270E – Selective Ion Monitoring (SIM)

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

GC-MS Analysis of PAH/PCP Method 8270 – Selective Ion Monitoring (SIM)

1. Scope and Application

1.1. This procedure utilizes Method 8270E acquiring in the selected ion mode (8270E sim) to determine the concentration of selected semi volatile organic compounds in extracts prepared from various types of sediments, soils, solid waste matrices, tissues, and waters. See Appendix 20.2 for the compounds that may be determined using this method. EPA Method 8270E will be reported for State of California work.

1.2. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including the EPA SW-846 methods and the Department of Defense Quality Systems Manual (DoD-QSM). Some text is directly from the referenced documents. The table in Appendix 20.1 outlines ARI's routine in-house acceptance criteria. DOD-QSM acceptance criteria are shown in Appendix B of DOD-QSM 5.3. Acceptance criteria for projects requiring modified DOD-QSM criteria are provided by the project manager and are project specific. Analysts are responsible for determining which QA program is applicable to a set of samples prior to beginning analyzes and complying with all project specific analytical requirements.

1.3. The reference methods for this procedure are listed in Section 19.

1.4. Method 8270E sim is used primarily in the analysis of polynuclear aromatic hydrocarbons (PAH), and Pentachlorophenol (PCP). Appendix 20.2 includes a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system. Detailed lists of project-specific compounds may be found in the LQAP for a given project. Other compounds may be analyzed if specifically requested.

1.5. Pentachlorophenol is an active analytes and subject to erratic chromatographic behavior, especially if the GC system is contaminated. Derivatization of PCP with Diazomethane is utilized by this method to reduce activity.

1.6. Estimated Method Reporting Limits (MRL)

Analysis code	Water MRL	Soil MRL
8270D-sim PAH	0.1µg/L	5.0µg/kg
8270D-sim PAH/PCP	0.1µg/L 0.5µg/L for PCP	5.0µg/kg 25µg/kg for PCP
8270D-sim PAH low	0.01µg/L	0.5µg/kg
8270D-sim Alkyl PAH	0.1-1.0µg/L	5.0-50µg/kg

1.7. This method 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. Each analyst must demonstrate the ability to generate acceptable results with this method.
1.8. ARI routinely performs Method Detection Limit (MDL) studies for each extraction and analytical method performed using this SOP. The results of these studies help define the reporting limits of data generated. The results are kept by the QA department, and are distributed to the bench chemists and the ELEMENT administrator. For current MRLs and MDLs, see Element

2. Summary of Procedure

2.1. An aliquot of sample for matrices suitable for analysis by GC/MS SIM) is extracted by a matrix appropriate sample technique. Usually this aliquot will be 500 mL for aqueous samples and 10 grams for solid samples. Sample extraction will typically be by either continuous liquid-liquid extraction or separatory funnel extraction for aqueous samples and microwave for solid samples. The extracted sample is subjected to any appropriate cleanup and then concentrated. Final extract volume will normally be 0.5 mL for aqueous samples and either 0.5 or 1mL for solid samples. The extract is then delivered to Refrigerator 15.
2.2. After the instrument lab has assumed custody of the sample, it is injected onto the column of a properly calibrated GC/MS system for chromatographic determination. If the analyte PCP is to be determined, the extract is derivatized using diazomethane before chromatographic determination. Analyte identification is performed using the relative time of elution (RRT, relative to the appropriate internal standard) and comparison of mass spectra to a spectral library. Quantitation is performed by comparing the detector responses of each analytes' characteristic mass ion and internal standard characteristic mass ion to the responses of these ions in a calibration curve containing those analytes at known concentrations.

3. Definitions

3.1. SIM - Selected Ion Monitoring- a mode of data acquisition wherein the mass spectrometer is programmed to scan for a limited number of specific masses, increasing the amount of time spent searching for each of these masses.
3.2. Initial Calibration Verification (ICV): A process used to verify that the current instrument calibration is acceptable at the beginning of an analytical sequence

3.3. Continuing Calibration Verification (CCV): A process used to verify that the current instrument calibration is acceptable during or at the end of an analytical sequence.
3.4. Decafluorotriphenylphosphine, (DFTTP): used to demonstrate acceptable tuning parameters.

3.5. Method detection Limit (MDL): The lowest result that can reliably be distinguished in a matrix from a blank.

3.6. Extracted Ion Current Profile (EICP): A plot of the abundance of a specific ion as a function of time

3.7. Second Source Verification (SCV): A process used to verify that the current instrument verification is acceptable.

3.8. Internal Standard (IS): Internal standards are compounds added to each standard, sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of these internal standards.

3.9. Blank Spike (BS): A sample matrix, free from the analytes of interest, spiked with verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system.

3.10. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, a BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS.

3.11. Laboratory Information Management System (LIMS): Software used to compile and report final chromatographic data. The use of the term “Element” refers to the LIMS system.

3.12. Limit of Detection (LOD): The lowest result that can be reported while meeting method precision and accuracy requirements.

3.13. Method Reporting Limit (MRL): The lowest result that may be reported unqualified based upon the lowest curve point.

3.14. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method.

3.15. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision.

3.16. Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and interferences. It is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures.

3.17. Organic-free reagent water (OFW): Organic-free reagent water, all references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.

3.18. Method Detection Limit (MDL) spike: A matrix spike prepared at the reporting limit and used to calculate the MDL.

3.19. Reconstructed Ion Current (RIC): A plot of the total instrument response versus time
3.20. Relative Retention Time (RRT): The elution time of an analyte relative to the elution time of its associated internal standard
3.21. Instrument Blank (IB): Clean solvent containing internal standards at the appropriate level for the analysis is analyzed using the same conditions as a regular sample. An instrument blank is analyzed to detect and/or remove sample carryover from one analysis to another.
3.22. Surrogate (SURR): A substance with properties that mimic analytes of interest. It is unlikely to be found in environment samples and is added to them to monitor extraction efficiency.
3.23. Low level calibration verification (LCV): Lowest calibration standard used for an initial calibration.
3.24. Target software (TARGET): Chromatographic analysis software from Thermo Thru-Put version 4.14.

4. Interferences

4.1. Extraction Interferences: Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem. Most commonly this will involve contamination with the phthalate esters.
4.2. Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride followed by baking the glassware at 500 degrees centigrade overnight.
4.3. High purity reagents must be used to minimize interference problems.
4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, or the detector shows saturation due to analytes present in a sample, subsequent samples should be scrutinized for cross contamination.
4.5. Matrix interferences may be removed using sample clean-ups depending on the list of target analytes, these may include (but are not limited to) the use of solid phase extraction clean-up, silica gel, absorption chromatography or gel permeation chromatography. See the appropriate extractions SOPs for clean-up applicability to matrices or target analytes.
4.6. Deactivated glassware must be used when extracting samples for the lower level PAH analysis due the activity of these Targets at trace levels.

5. Safety

5.1. The toxicity and carcinogenicity of each reagent used in this method is not precisely defined. However, all compounds and solutions should be treated as health hazards, and exposure of these chemicals to skin and clothing should be minimized to the lowest possible level by whatever means available.

5.2. Contact with all chemicals should be minimized by the used of nitrile gloves, safety glasses, and laboratory coats.

5.3. All materials should be handled in the fume hoods to avoid exposure to fumes.

5.4. All GC split vents and vacuum exhaust are connected to an exhaust vent or charcoal filter.

5.5. Special care should be taken when derivitizing samples for PAH/PCP analysis. The Diazomethane gas produced by the reaction of Diazald, sodium hydroxide, and methanol is both toxic and explosive. The derivatization MUST take place within a fume hood, and the analyst should work with the sash down and full protective wear.

5.6. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult with SDS sheets for all chemicals handled. SDS are available on-line at www.msdshazcon.com.

6. Equipment and Supplies

6.1. Gas chromatograph/mass spectrometer system

6.1.1. Gas chromatograph - An analytical system with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, autosampler, and gases. The capillary column should be directly coupled to the source of the mass spectrometer.

6.1.2. Fused-silica capillary column - 30 m x 0.25 mm ID (or 0.32 mm ID) 0.25 -0.5 µm film thickness. (Restek Rxi-17SIL MS or equivalent).

6.1.3. Mass spectrometer - Capable of scanning from 35 to 500 AMU every 1 second or less. The mass spectrometer must can produce a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all the criteria in Appendix 20.3 when 1-2 µL of the GC/MS tuning standard is injected through the GC (50 ng or less of DFTPP).

6.1.4. GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration for each compound of interest and achieves acceptable tuning performance criteria. For a capillary column, the interface is usually capillary-direct into the mass spectrometer source.

6.2. Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on electronic media of all mass spectra obtained throughout the duration of the chromatographic program.

6.2.1. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits.

6.2.2. The data system should be equipped with the most recent version of the EPA/NIST Mass Spectral Library.

6.2.3. The data must be securely stored for at least seven years from date of acquisition in Target.

7. Reagents and Standards

7.1. Stock standard solutions (1000 - 10,000 µg/L) - Standard solutions can be prepared from neat standards or purchased as certified solutions. Certificates of analysis for all purchased neats and solutions are kept electronically in Element.

7.2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2.1. All Components and reagents used for any standard preparation are entered in Element

7.2.2. The laboratory should have high purity acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, methanol and other appropriate solvents for preparing standards.

7.2.3. Organic-free reagent water - All references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.

7.2.4. Neat standards are not assigned an expiration day and are considered never expired regardless of what is shown on the standard certificate.

7.2.5. Stock Standard Preparation

7.2.6. Prepare stock standard solutions by accurately weighing about 0.2500 g of pure material. Dissolve the material in pesticide quality methylene chloride or other suitable solvent and dilute to volume in a 25 mL volumetric flask. Larger or smaller volumes can be used at the convenience of the analyst. When compound purity is assayed to be 97% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

7.2.7. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.2.8. Transfer the stock standard solutions into amber bottles with Teflon lined screw-caps. Store at >0 to 6°C and protect from light.

7.2.9. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.2.10. Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

7.2.11. Stock standard solutions must be replaced 1 year after being de-ampullated.

7.2.12. A PDF record of analysis must be attached to the standard in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.

7.3. Internal Standard Stock Solution - The internal standards employed are naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12. Other compounds may be used as internal standards if the method requirements are met. Dissolve 0.250 g of each compound with a small volume of methylene chloride or appropriate solvent. Transfer to a 250mL volumetric flask and dilute to volume with methylene chloride. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d12. The resulting solution will contain each standard at a concentration of 1,000µg/ml.

7.3.1. Each 0.1 mL aliquot of the sample extract undergoing analysis should be spiked with 2µL of the internal standard solution, resulting in a concentration of 2ng/µL of each internal standard (for example, when preparing a sample aliquot of 0.3ml, spike the extract with 6µl of the internal standard stock). Low PAH internal standard is at 0.2µg/mL final concentration

7.4. Surrogate Stock Standards - The surrogate standards employed are 2,4,6-tribromophenol, 2-Methylnaphthalene-d10, Fluoranthene-d10, and Dibenzo(a,h)anthracene-d14.

7.5. Prepare a stock solution containing all the PAH base surrogates 2-Methylnaphthalene-d10, Fluoranthene-d10, and Dibenzo(a,h)anthracene-d14 by dissolving 250mg of each into a 50 mL volumetric flask. Bring the solution up to volume with methylene chloride. The resulting solution will contain the surrogates at 5000µg/ml.

7.6. Prepare a stock solution containing 2,4,6-tribromophenol
by dissolving 250mg of each into a 50mL volumetric flask. Bring the solution up to volume with methylene chloride. The resulting solution will contain the surrogate at 5000µg/ml.

7.7. Working solutions- working standards are prepared from stock standards or purchased as commercially certified mixtures.

7.7.1. Working standards expire on the date of expiration of the stock solutions they are made from, on the manufacturer's certified expiration date or within one year from date of preparation, whichever comes first. They must be replaced now.

7.7.2. Working standard solutions must be replaced 1 year after being de-ampullated.

7.7.3. Working standards must be stored at >0 to 6°C and protected from light.

7.7.4. Working standards should be checked frequently for signs of concentration or degradation.

7.7.5. A PDF record of analysis must be attached to the standard (non-virtual only) in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.

7.8. Surrogate working standards

7.8.1. Surrogate calibration standard- the surrogate calibration standard is prepared by diluting the surrogate stock in methylene chloride such that the concentration of each analyte is 50µg/ml (5µg/mL for low PAH) This solution is used to calibrate the instrument to quantitate surrogate concentrations.

7.8.2. Surrogate spiking standard- the surrogate spiking standard is prepared by diluting the surrogate stock such the concentrations of the surrogates are 15-75µg/mL (1.5-7.5 for low PAH) prepared in acetone. This solution is used to spike all extracted samples and QC samples with surrogates.

7.9. Matrix spike working standards- the matrix spiking standards are used to prepare MS/MSD sets as well as BS/BSDs.

7.9.1. The matrix spiking solution is purchased commercially and contains all the analytes in acetone. The concentration of each analyte is 15µg/mL (1.5µg/ml for low PAH)

7.9.2. If alternative matrix spiking solutions are required (for example, a matrix spike containing an extra analyte not contained in the full spike) an appropriate concentration should be determined, and the solution prepared in a water-soluble solvent (usually methanol or acetone) at that concentration.

7.9.3. Calibration working standards- the standards used to prepare calibration curves are usually purchased as commercially certified mixtures. Working calibration solutions are prepared by diluting these standards in methylene chloride such that the concentration of each analyte is 50

7.9.4. Calibration working standards for PCP/PAH analysis are prepared in Hexane saturated with Diazomethane gas to derivatize the PCP to a methyl ester.

7.9.5. GC/MS working tuning standard- a tuning standard should be prepared containing 500µg/mL each of DFTPP (Decafluorotriphenylphosphine); p,p'-DDT, Pentachlorophenol, and Benzidine. This should be used to prepare the 25µg/mL or less standard used to tune the instrument in cases where the mid-level calibration standard is acquired in selected ion mode.

7.9.6. Derivatization apparatus and reagents for Diazomethane gas (PCP analyses only)

7.9.6.1. A 60 mL VOA vial, with cap and Teflon lined septum.

7.9.6.2. A Teflon tube pushed through the septum of the 60ml vial

7.9.6.3. Diazald

7.9.6.4. 3M NaOH in Methanol

8. Sample Collection, Preservation, Shipment, Storage, Holding Times and Disposal.

8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 ºC.

8.2. Samples must be stored at ARI, at >0 to 6 ºC until final disposal.

8.3. Samples must be extracted within holding times determined from the day of sampling. The standard holding time for water samples is seven days. The standard holding time for solid samples is 14 days.

8.4. Solid and sediment samples may be stored at -10 to -20 ºC to extend the holding time to one year.

8.5. Extracts are delivered to Refrigerator 15 in the instrument laboratory by extractions technicians.

8.5.1. Analysts in the instrument lab assume custody of the sample extracts and then move them into Refrigerator 18 in a bin assigned in Element

8.5.2. Extracts must be stored at >0 to 6 °C and protected from light.

8.5.3. Extracts must be analyzed within 40 days of extraction.

8.5.4. Extracts must be stored in their assigned Element bin.

8.5.5. Extracts may be deposed 40 days after the analysis has been completed and the Element bin will be recycled for future use.

8.5.6. Extract will be disposed in the large blue barrel in the satellite accumulation area designated for extract vials. Disposed extracts are now marked in Element as disposed.

9. Quality Control

9.1. Quality control requirements related to tuning, initial and continuing calibration are detailed in Section 10 of this document.

9.2. Surrogates

9.2.1. Surrogate standards are added to every sample and associated QA (MB, BS, MS etc.) prior to extraction to monitor extraction efficiency.

9.3. Method Blanks and Instrument Blanks

9.3.1. A method blank is a volume of a clean reference matrix (OFW or sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

9.3.2. Method blank extraction and analysis are performed as follows:

9.3.2.1. MBs must be processed with every batch of 20 or fewer samples of similar matrix

9.3.2.2. Method blanks should be analyzed on each GC/MS system used to analyze associated samples. When a method blank shows contamination the blank should be re-vialed and reanalyzed to confirm the contamination.

9.3.2.3. A method blank for water samples consists of 0.5-1L volume of reagent water. For medium and low-level soil/sediment samples, a method blank consists of 1g to 10g of sodium sulfate. Extract, concentrate, cleanup and analyze the method blank according to procedures used for water; tissue; or solid (soil or sediment) samples.

9.3.2.4. An instrument blank consisting of internal standard and clean solvent is analyzed prior to sample analysis after the ICV when a method blank is not analyzed.

9.4. Blank Spikes (BS)

9.4.1. To evaluate the accuracy of the analytical method independent of matrix-related effects, a matrix-specific blank spike (BS) must be included in each preparation batch. The BS must contain all surrogates and target analytes required by the method.

9.4.2. In instances where insufficient sample volumes exist to perform an MS/MSD analysis, an BS/BSD may be performed upon client request to assess the precision of the analytical method. A BSD, when required, is prepared and analyzed identically to the BS.

9.4.2.1. The recovery of each blank spike target must be evaluated and reported

9.4.2.2. The RPDs between the BS/BSD samples must be measured and reported.

9.4.2.3. Evaluate the BS/BSD RPD and note any deviation >30% in the reviewer checklist.

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

9.5.1. To evaluate the effects of the sample matrix on the methods used for ABN analyses, a mixture of all target compounds is spiked into two aliquots of a sample and analyzed using the same method as all other samples.

9.5.2. A matrix spike and matrix spike duplicate should be extracted and analyzed for every 20 field samples of a similar matrix or whenever samples are extracted by the same procedure.

9.5.2.1. The recovery of each matrix spike must be evaluated and reported.

9.5.2.2. The RPDs between the MS/MSD samples must be measured and reported.

9.5.2.3. Evaluate the MS/MSD RPD and note any deviation >30% in the reviewer checklist.

9.5.3. As part of a client's QA/QC program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to the laboratory for analysis. The laboratory will not perform MS/MSD analysis on any of the field QC samples.

9.5.4. If a client designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the laboratory shall choose

another sample on which to perform an MS/MSD analysis. At the time the selection is made, the laboratory shall notify the client that insufficient sample was received and identify the sample selected for the MS/MSD analysis. The rationale for the choice of another sample other than the one designated by the client shall be documented in the narrative.

9.5.5. If there is insufficient sample to perform a requested MS/MSD, the laboratory should contact the client to inform them of the situation. The client will either approve that no MS/MSD is required, require that a reduced sample aliquot be used for the MS/MSD analysis or request that a BS/BSD (See Section 9.4.2) analysis be performed. The laboratory shall document the client's decision in the narrative.

9.5.6. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.5.7. Duplicate Analysis

9.5.8. When mandated by project-specific requirements, a duplicate analysis of a given sample may be performed as an independent assessment of method precision. A duplicate consists of an independently prepared second aliquot of a given sample carried through the entire analytical process.

9.5.9. The RPDs between the Sample and Sample duplicate must be measured and reported.

9.5.10. Evaluate the Sample and Sample duplicate RPD and note any deviation >30% in the reviewer checklist.

9.5.11. When mandated by project-specific requirements, an SRM (Standard Reference Material) sample will be analyzed as an independent assessment of method performance.

9.5.12. The recovery of each target in the SRM must be compared to the true value provided by the SRM provider to be evaluated and reported. Any targets not meeting the recovery limits will require corrective action.

9.6. Internal Standard Response (EICP) area and retention time data must be evaluated during and/or immediately after the analysis. The response for the ICV internal standards must be within the inclusive range of -50.0 to +100.0 percent of the response of the internal standards in the most recent mid-point of the initial calibration analysis. The response for each sample, associated batch QC, and the CCV internal standards must be within the inclusive range of -50.0 to +100.0 percent of the response of the internal standards in the most recent ICV. The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the ICV and the last CCV run or from the middle point of the initial calibration. The retention time shift for each of the internal standards must be within ±0.166 minutes (10 seconds) between samples/associated batch QC and the ICV.

9.7. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for BS/BSD are statistically generated on a periodic basis. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. All analysts using this SOP must use it in conjunction with Control Limit documentation to assess data quality and any possible need for corrective actions. Current control limits may be found in the Element.

9.8. Initial Demonstration of Proficiency- Each analyst must demonstrate initial proficiency with each sample preparation and determinative method combination performed, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat these procedures whenever new staff is trained or significant changes in instrumentation or procedure are made. See EPA Methods 8000 and 3500 for information on how to accomplish this demonstration.

10. Calibration and Standardization

10.1. Calibration standards

10.1.1. A minimum of six calibration standards should be prepared.

10.1.2. One of the calibration standards must be at the reporting limit, while the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. The lowest calibration point of each individual target analyte becomes the reporting limit for that target. All target analytes quantitated below the lowest calibration point for any target analyte must be qualified with a “J” flag to show the quantitation is below the working range of the curve and therefore is an estimate.

10.1.3. Calibration standards are prepared from the working calibration solutions at concentrations of 0.1, 0.5, 1.0, 2.5, 5.0 and 10µg/ml.

10.1.4. Low PAH calibration standards are prepared from the working calibration solutions at concentrations of 0.01, 0.05, 0.1, 0.25, 0.5 and 1.0µg/ml.

10.1.5. PAH/PCP standard Concentrations standards are prepared from the working calibration solutions at concentrations of 0.1, 0.5, 1.0, 2.5, 5.0 and 10µg/mL with PCP and Tribromophenol at 0.5, 2.5, 5.0, 12.5, 25.0 and 50µg/ml.

10.1.6. The calibration curve standards are made as needed and the internal standard solution is added prior to analysis.

10.1.7. Each standard must contain all analytes requested for a specific project, and no target analyte may be quantitated without first being calibrated.

10.1.8. All standards should be stored at >0 to 6°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The ICV/CCV standard should be prepared weekly with the preparatory date on the label and stored at >0 to 6°C. If the analyst suspects degradation the standard should be replaced.

10.1.9. The calibration standards are analyzed, and a minimum of six curve points are used to calibrate each analyte as follows:

Compounds that are routinely calibrated at 10, 5, 2.5, 1.0, 0.5, and 0.1µg/ml		
Naphthalene	Benzo(b)thiophene	2-methylnaphthalene
1-methylnaphthalene	2-Chloronaphthalene	Biphenyl
2,6-Dimethylnaphthalene	Acenaphthylene	Acenaphthene
Dibenzofuran	2,3,5-Trimethylnaphthalene	Fluorene
Dibenzothiophene	Phenanthrene	Anthracene
Carbazole	1-methylphenanthrene	Fluoranthene
Pyrene	Benzo(a)anthracene	Chrysene
Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(j)fluoranthene
Benzo(e)pyrene	Benzo(a)pyrene	Perylene
Dibenzo(a,h)anthracene	Indeno(1,2,3-cd) pyrene	Benzo(g,h,i)perylene
2-methylnaphthalene-d10 (SS)	Fluorene-d10 (SS)	Dibenzo(a,h)anthracene-d14 (SS)

Compounds that are routinely calibrated (Low PAH) at 1.0, 0.5, 0.25, 0.10, .05, and .01µg/ml		
Naphthalene	Benzo(b)thiophene	2-methylnaphthalene
1-methylnaphthalene	2-Chloronaphthalene	Biphenyl
2,6-Dimethylnaphthalene	Acenaphthylene	Acenaphthene
Dibenzofuran	2,3,5-Trimethylnaphthalene	Fluorene
Dibenzothiophene	Phenanthrene	Anthracene
Carbazole	1-methylphenanthrene	Fluoranthene
Pyrene	Benzo(a)anthracene	Chrysene
Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(j)fluoranthene
Benzo(e)pyrene	Benzo(a)pyrene	Perylene
Dibenzo(a,h)anthracene	Indeno(1,2,3-cd) pyrene	Benzo(g,h,i)perylene
2-methylnaphthalene-d10 (SS)	Fluorene-d10 (SS)	Dibenzo(a,h)anthracene-D14 (SS)

Compounds that are routinely calibrated (PCP/PAH) at 50, 25, 12.5, 5.0, 2.5, and 0.5µg/ml

Pentachlorophenol	Tribromophenol (SS)	

10.2. MS tuning- prior to initial calibration, each GC/MS system must be hardware-tuned to meet the criteria in Appendix 20.3 for a 50ng total or less injection of DFTPP. Analyses must not begin until all these criteria are met. Evaluate the ion abundance by using any of the following three scenarios: Use a single spectrum at the apex of the DFTPP peak, use the mean of the apex and the preceding and following scans (the mean of a symmetric pattern of scans about the apex), or use the average across the entire peak. The tune must satisfy the ion abundance acceptance criteria listed in Appendix 20.3. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. Do not subtract part of the DFTPP peak.

10.2.1. The GC/MS tuning standard is also used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD must not exceed 20%. DDT percent breakdown is calculated by dividing the sum of the DDD and DDE areas by the sum of the areas of DDT, DDE and DDD and then multiplying this result by 100. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. Peak tailing factors will be calculated using the procedure detailed in Appendix 20.6 using a Target macro to calculate the tailing factor.

10.2.2. Tailing factors must be <2.0 for benzidine and pentachlorophenol. See Section 16.3 for procedures on how to bring the instrument into compliance for tuning, DDT breakdown, or peak tailing factors.

10.2.3. The tune standard is run in the full scan mode separate from the calibration standards and must meet all ion abundance criteria shown in Appendix 20.3 before the initial calibration may continue.

10.2.4. All analyses performed in the sequence following the tune standard must use the same instrument parameters (GC program, MS parameters, etc.)

10.3. Calculate Relative Response Factors (RFs)

10.3.1. Evaluation of the initial calibration begins by calculating response factors (RRFs) for each analyte in each calibration standard. The formula for calculating each response factor involves the areas of the quantitation ion of the analyte and its associated internal standard as well as the concentration of the analyte and internal standard in the calibration standard according to the formula:

RRF = (As * Cis)/(Ais * Cis)
Where
As = The peak area of the analyte or surrogate

Cis = The concentration of the internal standard in µg/L
Ais = The peak area of the internal standard
Cs = The concentration of the analyte or surrogate in µg/L

10.3.2. The RRF for each analyte should meet the advisory RRF listed for the analyte in Appendix 20.2 for each of the calibration levels. Special care should be taken to monitoring the RRF in the lowest calibration standard to ensure adequate sensitivity at the reporting limit. The minimum RRF for any target for all calibration levels is 0.01

10.3.3. Analytes which fail the minimum RRF guidance listed in Section 10.3.2 should be noted in the reviewer checklist.

10.4. Analyte Linearity.

10.4.1. After measuring the relative response factors for each analyte in each of the calibration standards, the linearity of the analyte must be measured.

10.4.2. The average RRF should be calculated for each compound using the formula

$\mathbf{RRFav = \frac{\sum RRFi}{n}}$
Where
RRFi = the RRF of the analyte in each calibration level
n = the number of calibration levels (usually six or five)

10.4.3. The percent relative standard deviation (% RSD) should also be calculated for each compound using the formula

$\mathbf{RSD = \frac{100 * SD}{RFav}}$	$\mathbf{= 100* ((\sum(RRFi- RRFav)^{2)}/(n-1))^{1/2}/RRFav}$
Where	
RRFi = the RRF of the analyte in each calibration level	
RRFav = the average RRF of the analyte over the entire calibration range	
n = the number of calibration levels (usually six or five)	

10.4.4. The % RSD should be less than 15% for each compound, in which case the average response factor will be used for quantitation as it is considered constant over the calibration range. Target analytes that exceed 15% RSD will attempt to utilize an alternative calibration option.

10.4.4.1. Before attempting an alternative calibration model, the analyst should ensure that the RSD failure is not due to detector or chromatographic system saturation and that the chromatographic system is functioning properly. Should saturation or chromatographic activity

be evident, the analyst should correct the problem and reanalyze the affected calibration standards.

10.4.4.2. A linear fit calibration that does not include the origin and generates a coefficient of determination (R^2) that is greater than or equal to 0.99 is acceptable. ARI will primarily attempt to force calibration curve through zero. Forcing the curve through zero is not the same as including the origin as a point in the calibration. When the curve is forced through zero, the intercept is set to 0 before the regression is calculated, thereby setting the bias to favor the low end of the calibration range by "pivoting" the function around the origin to find the best fit and resulting in one less degree of freedom.

10.4.4.3. Next the analyst may attempt a quadratic non-linear calibration which may be used with target analytes that have six or more calibration points only. An additional initial calibration point may be considered for target analytes that require non-linear calibration if only five calibration points are available.

10.4.4.4. An analyte is determined to meet the calibration criteria found in Section 10.4.4, even if its RSD exceeds 15% if the analyte has an acceptable linear or quadratic fit curve with a coefficient of determination (R^2) greater than 0.99.

10.4.4.5. See EPA Method 8000C Section 11 for reference to linear fit and non-linear (quadratic) calibration.

10.4.5. Targets requiring either a linear or quadratic fit will be documented in the reviewer checklist.

10.4.6. Individual targets that are unable to meet the above requirements in Section 10.4.4.4 must be documented in the reviewer checklist

10.4.7. Special care should be taken to monitor the RRF in the lowest calibration standard to ensure adequate sensitivity at the method reporting limit. In addition, the lowest calibration point should be recalculated (not reanalyzed) using the final calibration curve in which the standard is used. The recalculated concentration, especially where linear and quadratic fits are used, should be within ±50% of the standard's true concentration. The recalculated concentration of the standards above the low point should be ±30%. If a failure occurs in the lowest calibration point and it is equivalent to the method reporting limit (MRL), the analyte should be reported as estimated near that concentration or the MRL should be reestablished at a higher concentration. Following examination of the ICAL and any corrective action, all compounds not meeting the calibration acceptance criteria must be documented on the reviewer's checklist.

10.5. Calibration Acceptance

10.5.1. A calibration for an analyte is deemed valid when it meets the RSD criteria found in 10.4.4 and 10.4.4.4

10.5.2. Due to the large number of analytes that may be assayed using this SOP, some analytes may fail to meet the calibration acceptance criteria. The method allows some flexibility in dealing with such cases.

10.5.2.1. A calibration curve may be considered valid even with some analytes failing the criteria so long as the number of analytes failing the acceptance criteria found in Section 10.5.1 is equal to or less than 10% of the total number of analytes calibrated including surrogates (e.g. a calibration with sixty analytes may have up to six analytes exceed the acceptance criteria.)

10.5.2.2. Quantitated values for analytes which fail calibration acceptance criteria must be flagged with a “Q” qualifier for all detected analytes and noted on the Reviewer checklist.

10.6. Evaluation of retention times - The relative retention time (RRT) of each target analyte in the calibration standard should agree within 0.05 RRT units. Late-eluting target analytes usually have much better agreement. The RRT is calculated by dividing the retention time of the target analyte/surrogate by the retention time of its assigned internal standard.

10.6.1. The internal standards selected should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards.

10.7. Calibration curve verification - Prior to use for sample analysis, the acceptability of a calibration curve must be verified through analysis of a second source calibration verification (SCV) obtained from a second source. The SCV must be derived from a different manufacturer than the stock standard used to prepare the calibration curve when available. The SCV should show 70 - 130% (80 – 120% for DOD-QSM analyses) recovery for all compounds when compared to the initial calibration curve. Due to the large number of analytes that may be assayed using this SOP, some analytes may fail to meet the calibration acceptance criteria. Up to 10% of analytes may exceed the SCV criteria if they show a recovery within 50-150% of the true value for in-house analyses. No exceptions for DOD-QSM are allowed.

10.8. The reference mass spectrum used to verify the identity of analytes should be updated from the mid-point of the initial calibration.

10.9. Daily GC/MS calibration verification - Performed at the beginning of each 12-hour analytical shift.

10.9.1. The GC/MS tuning standard is not required for GC/MS calibration verification.

10.9.2. Analysis of an initial calibration verification (ICV) at mid-concentration (2.5 or 0.25µg/mL), containing each compound of interest, including all required surrogates, must be performed daily before analysis. Next, a continuing calibration verification (CCV) must be run after every 12 hours of analysis time and at the end of the analytical sequence, using the introduction technique used for the initial calibration. The results from the ICV analysis must meet the acceptance criteria detailed below. See section 10.9.2.7 and 10.9.2.8 for CCV acceptance criteria.

10.9.2.1. Calculate Relative Response Factors- A system performance check must be made at the start of every 12-hour shift. This is the same check that is applied during the initial calibration. Calculate the RRF for each analyte. Each compound should meet the advisory minimum relative response factor found in Appendix 20.2 If the minimum relative response factors are not met, the system should be evaluated, and corrective action may be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the guard column/analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins. See Section 16.5 for procedures for dealing with RRF failures.

10.9.2.2. Analyte linearity- The response factors calculated in Section 10.9.2.1 are used to measure the validity of the initial calibration by using them to calculate the percent difference (for average RRF calibrations) or percent drift (for linear fit or quadratic fit calibrations.)

10.9.2.2.1. Calculate the percent difference using:

$\%\ \text{Difference} = \frac{RRF_i - RRF_c}{RRF_i} * (100)$
Where:
RRFi = Average relative response factor from initial calibration.
RRFc = Relative response factor from current verification check standard.

10.9.2.3. If the percent difference for each analyte is less than or equal to 20% the initial calibration verification (ICV) is valid. Problems like those listed under the minimum response factors could affect this criterion. See Section 16.6 for procedures for dealing with %D failure.

10.9.2.4. The responses and retention times in the calibration check standard must be evaluated immediately after data acquisition. Chromatography system maintenance (shortening the column, etc.) may change retention times. Corrective action is required when:

10.9.2.5. Relative retention times change.

10.9.2.6. The response (EICP) of any internal standard (IS) is in the acceptable range of -50% to +200% using the IS in the mid-point standard level (25ng/ul) from the most recent initial calibration as the reference.

10.9.2.7. Much in the manner that a certain number of analytes may fail the initial calibration criteria, the method allows a certain number of analytes to fail the criteria set above for initial calibration verification. In the case of the initial calibration verification (ICV), many analytes less than or equal to 20% of the total number of calibrated analytes (including surrogates) may exceed the criteria set in Sections 10.9.2.1 and 10.9.2.2.

10.9.2.8. Reported values for the analytes failing the acceptance criteria must be flagged with a "Q" qualifier and noted in the Reviewer checklist.

10.9.2.9. A continuing calibration verification may be used as an initial calibration verification to extend the analytical sequence if the CCV meets all requirements as required for the ICV

10.9.2.10. (CCV criteria) If the percent difference for each analyte is less than or equal to 50% the continuing calibration verification (CCV) is valid. Problems like those listed under the minimum response factors could affect this criterion. See Section 16.6 for procedures for dealing with %D failure.

10.9.2.11. (CCV criteria) The response (EICP) of any internal standard (IS) is in the acceptable range of -50% to +200% using the IS reference from the ICV.

10.10. Additional guidance for selected ion monitoring (SIM) analysis.

10.10.1. The exact mass acquired (i.e. mass 188.1 not 188) should include the mass defect.

10.10.2. The dwell time must be adjusted for each ion descriptor such that a minimum of five scans per chromatographic peak are acquired.

10.10.3. Two ions should be monitored for each target and their spectra should be updated from the calibration mid-point

11. Procedure

11.1. Prior to using this method, the samples must be extracted using the appropriate sample preparation and cleanup methods.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561, 3565
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

11.2. Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Polynuclear aromatic hydrocarbons	3630, 3660, 3640

11.3. Derivatization- When Pentachlorophenol (PCP) is a requested analyte, the extracts must be derivatized with diazomethane prior to GC/MS analysis. All derivatization MUST take place within the fume hood.

11.3.1. Add one pipette of Hexane saturated with Diazomethane gas to the extract reduced to a volume of 2-3ml. The solution should turn light yellow indicating the diazomethane is saturated in the solution. This procedure is done in the extraction lab prior to final blowdown.

11.3.2. Do not perform any cleanups on the extracts for the PCP/PAH analysis.

11.4. The recommended GC/MS operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration).

Quantitation Mass range:	Discrete ion
Tuning Mass Range	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	60°C, hold for 2 minutes
Temperature program:	60-130°C at 30C°/min 130-330°C at 20C°/min
Final temperature:	330°C, hold for 5 minutes
Injector temperature:	270°C
Transfer line temperature:	300°C
Source temperature:	According to manufacturer's specifications (230°C for Agilient 5973 MSD)
Injector:	Grob-type, splitless/split
Sample volume:	1-2 µL
Carrier gas:	Helium at 30 cm/sec.

11.5. Prior to sample analysis the GC/MS system must be tuned as described in Section 10.2 and must have an acceptable initial calibration curve (the requirements for the calibration curve are found in Section 10.3 and 10.4.

11.6. Prior to sample analysis an initial calibration verification (ICV) standard must be analyzed, and this ICV must meet the criteria found in Section 10.9. If time remains in the 12-hour QC period begun with the initial calibration, the midpoint calibration standard from the initial calibration may be used as the CCV provided it meets the requirements found in Section 10.9.

11.7. Next, a method blank or an instrument blank must be analyzed after the ICV and prior to sample analysis to ensure the system is free of contaminants. If the method blank shows contamination, then it may be appropriate to analyze an instrument blank to demonstrate the source of contamination is not the result of carryover from standards or samples.

11.8. GC/MS analysis

11.8.1. It is highly recommended that the extract be screened on a GC/FID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high

concentrations of organic compounds and may show high background samples that should be analyzed using a medium/high level extraction.

11.8.2. Spike a 0.3ml aliquot of the 0.5-1ml extract obtained from sample preparation with 6µL of the internal standard solution just prior to analysis. This is the equivalent internal standard concentration of 2µg/mL (low 0.2µg/mL) of each standard in the sample. This aliquot should be prepared in an amber glass autosampler vial and sealed with a PFTE crimp cap.

11.8.3. Analyze the 0.3 ml aliquot by GC/MS. The injection volume must be the same volume used for the calibration standards. The recommended GC/MS operating conditions to be used are specified in Section 11.4.

11.8.4. If the response for any target analyte exceeds 10/50µg/mL (high point of the initial calibration curve for PAHs or PCP respectively), the extract must be diluted and re-analyzed. See Section 16.12 for guidance on dilutions. In the case of low sim PAH if the response for any target analyte exceeds 1µg/mL, then extract dilution must take place. See section 16.12 for guidance on dilutions.

11.8.5. Perform all qualitative and quantitative measurements as described in Section 11. Store the extracts at >0 to 6°C, protected from light in screw-cap vials equipped with un-pierced PFTE lined septa.

12. Data Analysis and Calculations

12.1. An analyte is identified by comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this SOP. These standard reference spectra may be obtained through analysis of the calibration standards and should be updated with every initial calibration. The characteristic ions are defined as the three ions of greatest intensity, or any ions over 30% intensity relative to the base ion, if less than three such ions occur in the reference spectrum. Two criteria must be satisfied to verify identification: (1) elution of sample component at or near the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component mass spectrum/ion abundances and the standard component mass spectrum/ion abundances.

12.2. The intensities of the characteristic ions must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where 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 will be accepted as meeting this criterion.

12.3. The sample component RRT must compare within 0.05 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12-hour QC period as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT

from the total ion chromatogram, the RRT should be assigned by using extracted ion-current profiles for ions unique to the component of interest.

12.4. All ions present in the standard mass spectra at a relative intensity greater than 10% (the most abundant ion in the spectrum is equal to 100% intensity) should be present in the sample spectrum. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Spectral enhancement can sometimes create these discrepancies.

12.4.1. The relative intensities of ions specified in Section 12.1 must agree within plus or minus 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample abundance must be between 20 and 80 percent.) If not, the compound may be flagged with an "M" if the analyst determines that the identification is valid (favors false positive).

12.4.2. Structural isomers that produce very similar mass spectra should be 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 and reported as the average of both compounds by the analyst.

12.4.3. 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 co-elute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

12.5. Quantitative analysis

12.5.1. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of a given analyte. If secondary ion quantitation is necessary due to interference, then a short quantitation report list is generated. This quantitation contains the integrated areas of the affected compounds, based on the secondary ion(s) for that compound, and of the relevant internal standards. Identical reports must be generated for the sample with

interference and for the relevant initial calibration. The report for the initial calibration is used to generate a relative response factor for the affected compound based on its secondary ion. This relative response factor is then used in the calculations for that compound in the affected sample. Note that the source of the relative response factor for the aforementioned situation differs from the quantitation using the primary characteristic ion (when free of interference). All quantitation using the primary characteristic ion use the average relative response factor from the initial calibration. The short quantitation report may be hand calculated by the analyst if it is signed and dated by the analyst. The report must be included with the data file PDF in Element.

12.5.2. Calculate the concentration of each identified analyte in the sample as follows:

Concentration (µg/L) = $\frac{(Ax)(Is)(Vt)}{(Ais)(RRF)(Vo)(Vi)}$
where:
A_X = Area of characteristic ion for compound being measured
Is = Amount of internal standard injected (ng).
Vt = Volume of total extract
A_{IS} = Area of characteristic ion for the internal standard
RRF = Relative response factor for compound being measured
Vo = Volume of water extracted (ml)
Vi = Volume of extract injected (µL)

12.5.3. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)

Concentration (µg/kg) =	**$\frac{(Ax)(Is)(Vt)}{(Ais)(RRF)(Vi)(Ws)(D)}$**
where:	
A_X = Area of characteristic ion for compound being measured	
Is = Amount of internal standard injected (ng).	
Vt = Volume of total extract	
A_{IS} = Area of characteristic ion for the internal standard	
RRF = Relative response factor for compound being measured	
Vi = Volume of extract injected (µL)	
Ws = Weight of sample extracted or diluted in grams	
D = % Dry weight of sample = 1.0 on an as received basis	

13. Method Performance

13.1. The QA department measures method performance using a combination of continuing MDL studies, quarterly LOD verifications, performance evaluation samples, standard reference materials, and the monitoring of surrogate and spike recoveries.

13.1.1. Detection limits- the LOD for all analytes quantitated using this SOP are set using the MDL studies. The detection limit indicates the lowest result that can reliably be distinguished in a matrix from a blank.

13.1.2. LOD verifications are performed each quarter for each analyte by each preparatory and analytical method.

13.1.3. MDL, LOD and MRL values may be found for each analyte in Element

13.2. Laboratory precision and bias measurements are performed by monitoring surrogate and spike recoveries in samples and quality control samples.

13.2.1. Control limits are calculated from these recoveries.

13.2.2. These control limits are disseminated to the bench chemists and ELEMENT administrator for use in monitoring method performance in real time.

13.2.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found in Element

13.3. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in Section 12.3 and Appendix 2.2 of ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC is kept on record in SharePoint

13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.

13.5. The experience of the analyst must weigh heavily in the interpretation of the chromatogram.

14. Pollution Prevention

14.1. All syringe rinsing must be performed over charcoal to minimize the exposure of the environment to solvent or extract.

14.2. Charcoal containers must be covered when not in use to prevent fugitive vapors from escaping.

14.3. All GC split vents will be connected to an exhaust vent or charcoal filter.

14.4. All MS vacuum pumps will have a charcoal exhaust filter.

14.5. All spent vials are placed into the blue waste drum for proper disposal after analysis is finished.

14.6. Open solvent containers should only be present when actively preparing samples.

14.7. Wherever possible the final sample extract volume should be as small as possible to minimize the generation of waste.

15. Data Assessment and Acceptance Criteria for QC Measure

15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 of this document.

15.2. Method Blanks and Instrument Blanks- The method blank must contain less than 1/2 the reporting limit (MRL)of the targeted analytes or corrective action is required.

15.3. Internal Standards- All samples and associated QC internal standard EICP areas following the ICV must meet the technical acceptance criteria listed in Section 9.6.

15.4. Surrogate Recoveries

15.4.1. All method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates, SRMs or other samples must have acceptable surrogate recoveries. See Element for the most recent control limits.

15.4.2. Recoveries outside of the in-house QC limits should not necessarily be used to reject batch data, but will require corrective action.

15.4.3. Any surrogate recovery less than 10% will require corrective action.

15.4.4. These requirements do not apply to subsequent dilutions of samples where a prior analysis of the diluted sample extract shows acceptable surrogate recovery.

15.4.5. Certain methods or clients may specify project specific surrogate recovery acceptance windows.

15.4.6. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet project specific surrogate acceptance criteria, even when the criteria are labeled as advisory in the reference method.

15.4.7. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.

15.5. Blank Spikes (BS)/Blank Spike Duplicates (BSD)

15.5.1. The BS recovery values should fall within the specified recovery acceptance limits. If an BSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.

15.5.2. BS recovery acceptance windows are determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Project or method specific limits may supersede laboratory acceptance criteria.

15.5.2.1. The RPDs between the BS/BSD samples must be measured and reported

15.5.2.2. Evaluate the BS/BSD RPD and note any deviation >30% in the reviewer checklist.

15.5.3. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.

15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.6.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified recovery acceptance limits.

15.6.2. MS/MSD recovery and RPD acceptance windows are ideally determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Certain methods or clients may require project specific MS/MSD recovery and RPD acceptance windows.

15.6.2.1. The RPDs between the MS/MSD samples must be measured and reported.

15.6.2.2. Evaluate the MS/MSD RPD and note any deviation >30% in the reviewer checklist.

15.6.3. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.

15.7. Holding Times

15.7.1. Samples must be extracted within holding times (7 days for water samples and 14 days for solid samples).

15.7.2. Extracts must be analyzed within the extract holding time (40 days from the initial date of extraction).

15.7.3. In the event that re-extraction due to an out of control event requires that samples be re-extracted after their extraction holding time has elapsed (7 days for water and 14 days for tissues/solids) the analyst should analyze and report both extraction sets, whenever practical, distinguishing between the initial extraction and re-extraction on all deliverables. This will document that the samples were originally extracted within holding times and may allow for comparisons that will determine whether any of the more volatile analytes were lost in the interval between extractions.

15.7.4. If any extracts are analyzed after the 40-day extract holding time has elapsed, the analyst must document this in the reviewer checklist.

16. Corrective Actions for Out of Control of Unacceptable Data

16.1. Corrective actions may include any, but are not limited to, the following:

16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the reviewer checklist.

16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.3. Repreparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.4. Reanalysis – the extract aliquot that was originally prepared is reinjected and run on the gas chromatograph again.

16.1.5. Re-extraction – a re-extraction request is filled out (Form 0030F). Copies of the form are provided to the extractions department, the project manager, the QA manager and the lab manager. The remaining sample is extracted.

16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in ELEMENT.

16.1.7. Recalibration – a new initial calibration is evaluated, and the associated samples reanalyzed.

16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.

16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.

16.2. Mass Spectrometer Tuning

16.2.1. When the MS does not produce an acceptable mass spectrum when injected with 25 µg/mL of DFTPP, re-inject the DFTPP. If the spectrum again fails to meet the criteria found in Appendix 20.3, the MS may need to be re-tuned.

16.2.2. If the re-tuned mass spectrum still fails to meet the criteria found in Appendix 20.3, the MS may require maintenance. The MS should be vented, and maintenance may include replacing the filaments, cleaning the MS source, cleaning the MS lenses, cleaning the MS mass selective filter, or replacing the electron multiplier. All maintenance must be documented in Element.

16.3. If Peak tailing factors and or DDT breakdown exceed the limits found in Section 10, the chromatographic system may need maintenance. Inspect and perform maintenance on the chromatographic system. This maintenance may include, but is not limited to: replacing the inlet liner and liner packing, cleaning the inlet liner, cleaning or replacing the inlet seal, cleaning or replacing the inlet body, replacing the split line, cleaning the split arm, clipping a length from the front of the column, or replacing the column. All maintenance must be documented in Element.

16.4. When an Initial Calibration RSD for an analyte exceeds 15%

16.4.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

16.5. RRF failure- If the minimum RRF of 0.01 is not met for all analytes and calibration points perform any appropriate corrective action found in section 16.1

16.6. When an Initial Verification (ICV) fails:

16.6.1. At the discretion of the analysts, a second ICV may be immediately run after the failing ICV. If the second ICV meets all ICV criteria, then the sequence may begin.

16.6.2. If the second injection of the ICV fails, perform the appropriate corrective action(s) from Section 16.1 and re-calibrate the instrument.

16.6.3. DoD-QSM requires that %D for all analytes in the ICV is ≤ 20%. For DoD analyses, immediately analyze two additional consecutive ICVs.

16.6.3.1. When both ICVs meet acceptance criteria the analytical sequence may be continued.

16.6.3.2. If either fails or if two consecutive ICVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.6.4. If a CCV is used both as an ICV and CCV (in the middle of an analytical sequence) then the ICV requirements must be applied.

16.7. When a Continuing Calibration Verification (CCV) fails:

16.7.1. Perform any appropriate corrective action(s) from Section 16.1 if not a D0D-QSM project.

16.7.2. DoD-QSM requires that %D for all analytes in the CCV be ≤ 50%. For DoD analyses, immediately analyze two additional consecutive CCVs.

16.7.2.1. When both CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.7.2.2. If either fails or if two consecutive CCVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.8. Internal Standards

16.8.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8.1.1. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.

16.8.1.2. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.

16.8.1.3. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.8.1.4. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".

16.9. Surrogates

16.9.1. Examine the bench sheet to verify spiking levels are correct.

16.9.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.9.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.10. Method Blanks and Instrument Blanks-

16.10.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.10.2. Corrective action for a method blank which fails acceptance criteria may involve re-extraction and reanalysis of all associated samples and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager.

16.10.3. Corrective action for an instrument blank which fails acceptance criteria may involve re-preparation of the instrument blank and re-analyzing the instrument sequence.

16.11. Blank Spikes (BS)/Blank Spike Duplicates (BSD)

16.11.1. Examine the bench sheet to verify spiking levels are correct.

16.11.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.12. Matrix Spike (MS)/Matrix Spike Duplicates (MSD)

16.12.1. Examine the bench sheet to verify spiking levels are correct.

16.12.2. Recoveries are advisory and should not necessarily result in re-extraction.

16.12.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.13. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve; a dilution must be performed such that the analyte's quantitated value is within the curve range.

16.13.1. Additional internal standard must be added to the diluted extract to maintain the required 2µg/mL (0.2µg/mL for low sim) of each internal standard in the extracted volume.

16.13.2. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

16.13.3. When peaks from an analyte saturate the detector

16.13.3.1. The analyst must note the saturation in the reviewer checklist.

16.13.3.2. The analyst should analyze an Instrument Blank consisting of clean solvent until the system has been decontaminated

16.14. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.

16.14.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)

16.14.1.1. All QC limit issues (including continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Section 16.2 for guidance on dealing with out-of-control tuning events.

17.2. See section 16.3, 16.4 and 16.5 for guidance on dealing with out-of-control events related to initial calibrations (RRF or RSD), peak tailing factors, or DDT breakdown.

17.3. See section 16.6 for guidance on dealing with ICV out-of-control events.

17.4. See section 16.7 for guidance on dealing with CCV out-of-control events.

17.5. See Section 16.8 for guidance on dealing with internal standard out-of-control events.

17.6. See Section 16.9 for guidance on dealing with surrogate out-of-control events.

17.7. See Section 16.10 for guidance on dealing with method blank and instrument blank related out-of-control events.

17.8. See Section 16.11 for guidance on dealing with BS/BSD related out-of-control events.

17.9. See Section 16.12 for guidance on dealing with MS/MSD related out-of-control events.
17.10. See Section 16.13 for guidance on dealing with over range value related out-of-control events.
17.11. See Section 16.14 for guidance on dealing with particular circumstances out-of-control events.

18. Waste Management

18.1. All extract vials and standard vials must be disposed of by placing them in the blue hazardous waste drum in the station set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.
18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.
18.3. All spent charcoal must be disposed of by placing it in the charcoal disposal bin located in the hazardous waste storage area.
18.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

19.1. "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Method 8270E, Test Methods for Evaluating Solid Waste (SW-846), Revision 6, June 2018.
19.2. “EPA Method 625.1-Base/neutrals and acids”, Appendix A to CFR Part 136, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. December 2016.
19.3. “Determinative Chromatographic Separations”: Method 8000D, (SW-846), Revision 5, March 2018.
19.4. “Department of Defense (DOD) Department of Energy (DOE) Consolidated Quality Systems Manual for Environmental Laboratories”, Final Version 5.3 2019.

20. Appendices

20.1. Appendix 20,1: ARI Acceptance Criteria
20.2. Appendix 20. 2: PAH Target analyte List
20.3. Appendix 20.3: DFTPP key ions and ion abundance criteria.
20.4. Appendix 20.4: Example Chromatogram of Calibration standard
20.5. Appendix 20.5: Example pages from GC/MS PAH organics virtual logbook
20.6. Appendix 20.6: Peak Tailing Factor Calculation
20.7. Appendix 20.7: Selected PCB congeners by GC/MS
20.8. Appendix 20.8: Method 625.1 requirements

Appendix 20.1

ARI ACCEPTANCE CRITERIA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method (see ARI SOP 1017S)	QC acceptance criteria published by DoD, if available; otherwise method specified criteria.	1) Recalculate results 2) Locate and correct the source of the problem and repeat the test for all parameters of interest.	Not applicable (NA)	This is a demonstration of ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., LCS or PT sample) as described in ARI SOP 1017S. Analysis is not allowed by analyst until she/he has completed a successful demonstration of capability.
Method detection limit (MDL) study	At initial set-up and subsequently once per 12-month period; otherwise quarterly MDL verification checks shall be performed (see box D-18)	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or reconduct MDL study	NA	Samples should not be analyzed without a valid MDL.
Tuning	Prior to the initial calibration	Refer to method for specific ion criteria.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
DDT breakdown check	Prior to the initial calibration	Degradation < 20% for DDT. Benzidine and PCP peak tailing must be <2.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
Retention time (RT) window calculated for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	RT width is ± 3 times standard deviation for each analyte RT from 72-hour study.	NA	NA	
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.	

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	1)Analytes' RRFs must meet 0.01 across calibration range. 2) Analytes' RSDs must be less than or equal to 15%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (R^2) greater than 0.99. 3)Up to 10% of the total analytes may fail 1 and 2 above.	Correct problem then repeat initial calibration.	Analytes which fail the RRF or RSD/R^2limits must have their values flagged with Q qualifiers to mark the values as estimates.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification	Once after each initial calibration	Value of second source for all analytes within ± 30% of expected value (initial source) Up to 10% of analytes may exceed SCV criteria if they show a recovery within 50-150% of the true value	Correct problem, verify second source standard. Rerun verification. If that fails, correct problem and repeat ICAL	Flagging criteria are not appropriate.	Historic data shows that some analytes will very seldom meet ±20% when purchased from different vendors. Second sources may not be available for all analytes.
Retention time established for all analytes and surrogates	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	NA	NA	
Initial and Continuing Calibration verification (ICV/CCV)	Daily, before sample analysis (ICV); after every 12 hours of analysis time; and at the end of the analytical batch run (CCV).	1. Analytes RRF must meet 0.01 2. ICV %Difference/Drift for analytes ≤ 20%D Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the ICVS are Q flagged. 3: CCV %Difference/Drift for analytes ≤ 50%.	ICV FAILURE: Correct problem, then rerun ICV. If that fails, repeat initial calibration. CCV FAILURE: Perform corrective action from section 16.1	Apply Q-flag to reported target analytes exceeding criteria.	.
Internal standards verification	All ICV	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or most recent ICV. EICP area within - 50% to + 100% of ICAL midpoint standard	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	Flagging criteria are not appropriate.	Sample results are not acceptable without a valid IS verification.
Internal standards verification for samples, batch QC, and CCV	All samples, batch QC, and the CCV	Retention time ± 10 seconds from retention time of the ICV. EICP area within -50% to +100% of ICV	Rerun affected samples	If corrective action fails in field samples, associated batch QC, or the CCV apply *-flag to the non-compliant IS.	

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank and instrument blank	One per preparatory batch	No analytes detected > ½ MRL. For common laboratory contaminants, no analytes detected ≥ MRL.	Correct problem, if required, re-prep then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) reported above the MRL to all samples in the associated preparatory batch for method blanks exceeding criteria. Flagging criteria are not appropriate for instrument blanks.	
Blank spike control sample (BS) containing all reported analytes & surrogates	One BS per preparatory batch	QC acceptance criteria specified by ARI LQAP.	Correct problem, then re-prep and reanalyze the BS. Perform corrective action from section 16.1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to BS results.	
Blank Spike Duplicate (BSD)	Project specific	RPD ≤30% between BS and BSD	Perform corrective action from section 16,1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to BSD results.	The data shall be evaluated to determine the source of difference.
Matrix spike (MS)	One MS per preparatory batch per matrix	For matrix evaluation, use QC acceptance criteria specified by ARI LQAP for MS. MS recoveries are advisory.	Perform corrective action from section 16.1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to MS results.	For matrix evaluation only. If MS results are out of control, data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	RPD ≤ 30% (between MS and MSD or sample and sample duplicate) Limits are advisory.	Perform corrective action from section 16.1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to MSD results.	The data shall be evaluated to determine the source of difference.
Surrogate spike	All field and QC samples	Method-specified criteria or laboratory's own in-house criteria; all surrogate recoveries must be > 10%.)	For QC and field samples, correct problem then re-prep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Apply * flag to the specific analyte(s) if acceptance criteria are not met to surrogate results.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Results reported between LOD and LOQ	When requested	Peak integration should meet signal to noise ratio of 3:1	NA	Apply J-flag to all results between MDL and MRL.	

Appendix 20.2
PAH Target Analytes, Quantitation Ions, Calibration Criteria and Associated Internal Standards

Internal Standard Associated Analyte	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD [1]	Max %D [1]
D8-Naphthalene (IS) [2]		136	--			
Naphthalene	91-20-3	128	--	0.70	15.0	20.0
D10-2-Methylnapthalene (SS) [3]	7297-45-2	152	150, 153	0.70	15.0	20.0
2-Methylnaphthalene	91-57-6	142	141, 143	0.70	15.0	20.0
1-Methylnaphthalene	90-12-0	142	141, 143	0.70	15.0	20.0
Benzo(b)Thiophene	95-15-8	134	89	0.01	15.0	20.0
D10-Acenaphthene (IS)		164	--			
2-Chloronaththalene	00091-58-7	162	162	0.01	15.0	20.0
Biphenyl	92-52-4	154	153	0.01	15.0	20.0
2,6-Dimethylnaphthalene	581-42-0	156	155	0.01	15.0	20.0
Acenaphthylene	208-96-8	152	150, 151	0.90	15.0	20.0
Acenaphthene	83-32-9	153	152, 154	0.90	15.0	20.0
Dibenzofuran	132-64-9	168	139, 169	0.80	15.0	20.0
2,3,5-Trimethylnaphthalene	2245-38-7	170	155	0.01	15.0	20.0
Fluorene	86-73-7	166	165, 167	0.90	15.0	20.0
D10-Phenanthrene (IS)		188	--			
Dibenzothiophene	132-65-0	184	185	0.01	15.0	20.0
Pentachlorophenol [4]	87-86-5	280	278	0.05	15.0	20.0
2,4,6-Tribromophenol (SS) [5]	118-79-6	141	143	0.05	15.0	20.0
Phenanthrene	85-01-8	178	176, 179	0.70	15.0	20.0
Anthracene	120-12-7	178	176, 179	0.70	15.0	20.0
Carbazole	86-74-8	167	166	0.01	15.0	20.0
1-methylphenanthrene	832-69-9	192	191	0.01	15.0	20.0
Fluoranthene-d10 (SS)	93951-69-0	212	208	0.60	15.0	20.0
Fluoranthene	206-44-0	202	200, 201	0.60	15.0	20.0
Pyrene	129-00-0	202	200, 201	0.60	15.0	20.0
D12-Chrysene (IS)		240	--			
Benzo(a)anthracene	56-55-3	228	226, 229	0.80	15.0	20.0
Chrysene	218-01-9	228	226, 229	0.70	15.0	20.0
D12-Perylene (IS)		264	--		15.0	
Benzo(b)fluoranthene	205-99-2	252	250, 253	0.70	15.0	20.0
Benzo(k)fluoranthene	207-08-9	252	250, 253	0.70	15.0	20.0
Benzo(j)fluoranthene	205-82-3	252	250, 253	0.70	15.0	20.0
Benzo(e)pyrene	192-97-2	252	250, 253	0.70	15.0	20.0
Benzo(a)pyrene	50-32-8	252	250, 253	0.70	15.0	20.0

Perylene	198-55-0	252	250, 253	0.01	15.0	20.0
Indeno(1,2,3-cd) pyrene	193-39-5	276	274, 277	0.50	15.0	20.0
D14-Dibenz(a,h)anthracene (SS)	D-53-70-3	292	291	0.40	15.0	20.0
Dibenz(a,h)anthracene	53-70-3	278	139, 279	0.40	15.0	20.0
Benzo(g,h,i)perylene	191-24-2	276	274, 277	0.50	15.0	20.0

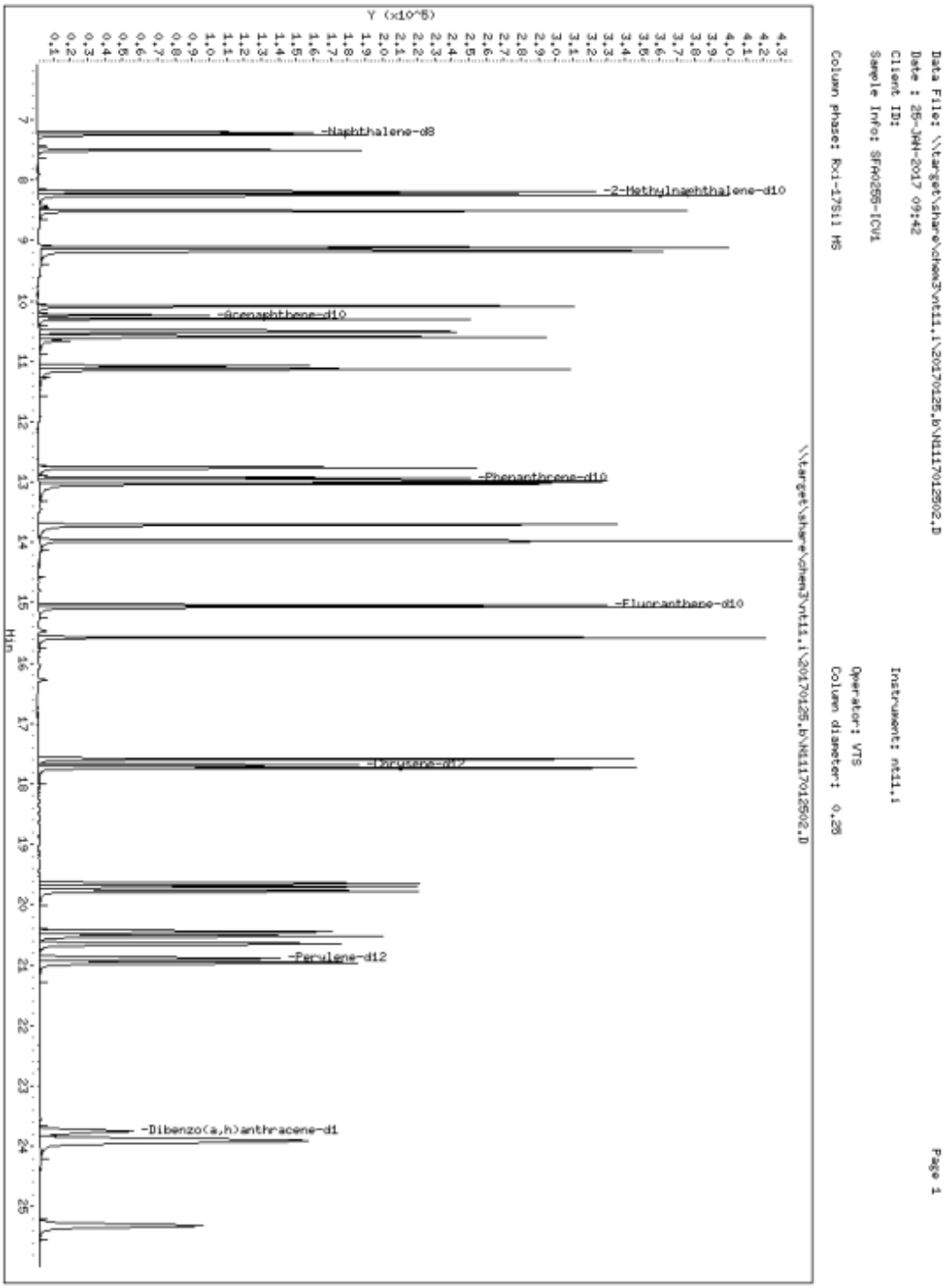
1 – A maximum of 2 compounds are allowed > 20%RSD .
2 – Compounds followed by (IS) are internal standards
3 – Compounds followed by (SS) are surrogate standards
4 – Optional Analyte
5 – This surrogate added only when Pentachlorophenol is a targeted analyte

Appendix: 20.3
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[1]

Mass	Ion Abundance Criteria
68	< 2% of mass 69
69	Present
70	< 2% of mass 69
197	< 2% of mass 198
198	Base peak or Present
199	5-9% of mass 198
365	> 1% of base peak
441	< 150% of mass 443
442	Base peak or Present
443	15-24% of mass 442

1. Raw data is rounded to three significant figures and one or less decimal point before comparison to the abundance criteria.

Appendix: 20.4
EXAMPLE CHROMATOGRAM OF CALIBRATION STANDARD



Appendix: 20.5
EXAMPLE PAGES OF VIRTUAL LOGBOOK

Analytical Resources, Incorporated
Analytical Chemists and Consultants

ANALYSIS SEQUENCE
SFA0255

Printed: 1/26/2017 8:12:55AM

Instrument: NT11 Element Column ID: E006480
Calibration ID: ZL00083 Tune File: 161216.U
EM Voltage: 2353

Lab Number	Sample Name	Analysis	Container	Order	STD ID	ISTD ID	Comments
SFA0255-TUN1	DFTPP	QC		1	E007446		
SFA0255-ICV1	Initial Cal Check	QC		2	E006577	E002870	
BFA0320-BLK1	Blank	QC		3		E002870	
BFA0320-BS1	LCS	QC		4		E002870	
17A0190-02	DA2 (Basin 3) 8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		5		E002870	
17A0190-03	DA3 (Basin 4) 8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		6		E002870	
17A0190-04	DA4 (Basin 5) 8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		7		E002870	
17A0195-01	KSC - MH-20.237 -8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		8		E002870	
17A0195-02	KSC - MH-20.235 -8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		9		E002870	
17A0195-03	KSC - MH-16.12 -8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		10		E002870	
17A0195-04	KSC - MH-15.10 -8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		11		E002870	
BFA0320-MS1	Matrix Spike	QC		12		E002870	
BFA0320-MSD1	Matrix Spike Dup	QC		13		E002870	
17A0195-05	KSC - OF-16 - W8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		14		E002870	
17A0195-06	KSC - OF-NDP - W8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		15		E002870	
17A0190-01	DA1 (Rx System)8270D-	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		16		E002870	
SFA0255-CCV1	SIM PAH 250	QC		17	E006577	E002870	

Page 1 of 1

INTERNAL STANDARD SUMMARY FOR DATABATCH - \\target\share\chem3\nt11.i\20170125.b

	Time	Filename	LabID	ClientId	DF									
1	0926	N1117012501.D	SFA0255-TUN1		1	NO ISTDS FOUND								
2	0942	N1117012502.D	SFA0255-ICV1		1	7.21	221638	10.23	145546	12.92	286458	17.69	270379	20.89	263628
3	1013	N1117012503.D	SFA0255-LCV1		1	7.21	236521	10.23	149706	12.94	296790	17.69	297882	20.89	286171
4	1046	N1117012504.D	BFA0320-BLK1		1	7.21	209823	10.24	127178	12.92	240475	17.69	261459	20.89	268502
5	1118	N1117012505.D	BFA0320-BS1		1	7.21	224643	10.23	146324	12.92	287697	17.68	288037	20.89	287256
6	1149	N1117012506.D	17A0190-D1		5	7.21	237737	10.23	144735	12.92	252088	17.69	245938	20.89	282243
7	1220	N1117012507.D	17A0190-D2		3	7.21	220793	10.23	142050	12.92	276263	17.69	236409	20.89	259123
8	1252	N1117012508.D	17A0190-D3		1	7.21	234838	10.23	150579	12.92	290487	17.68	261735	20.89	269272
9	1324	N1117012509.D	17A0190-D4		1	7.22	211399	10.24	127012	12.92	218356	17.69	210439	20.90	260632
10	1356	N1117012510.D	17A0195-D1		1	7.21	224142	10.23	148934	12.92	285573	17.69	239906	20.89	263386
11	1427	N1117012511.D	17A0195-D2		1	7.21	230494	10.23	152661	12.92	293341	17.69	251162	20.89	271337
12	1458	N1117012512.D	17A0195-D3		1	7.21	223053	10.23	147219	12.92	290845	17.69	248371	20.89	270876
13	1530	N1117012513.D	17A0195-D4		1	7.21	238864	10.23	154039	12.92	297532	17.69	244430	20.89	275138
14	1601	N1117012514.D	BFA0320-MS1		1	7.21	253564	10.23	168800	12.92	322809	17.69	291355	20.89	307409
15	1632	N1117012515.D	BFA0320-MSD1		1	7.21	244945	10.23	162638	12.92	307675	17.69	263454	20.89	287731
16	1704	N1117012516.D	17A0195-D5		1	7.21	224053	10.23	130718	12.92	235703	17.69	229616	20.89	262068
17	1735	N1117012517.D	17A0195-D6		1	7.21	220375	10.23	150175	12.92	297429	17.69	264403	20.89	292951
18	1806	N1117012518.D	17A0190-D1		1	7.21	225836	10.23	129678	12.93	230786	17.69	290847	20.91	316538
19	1838	N1117012519.D	SFA0255-DCV1		1	7.21	213677	10.24	152986	12.94	294771	17.69	251512	20.89	304195

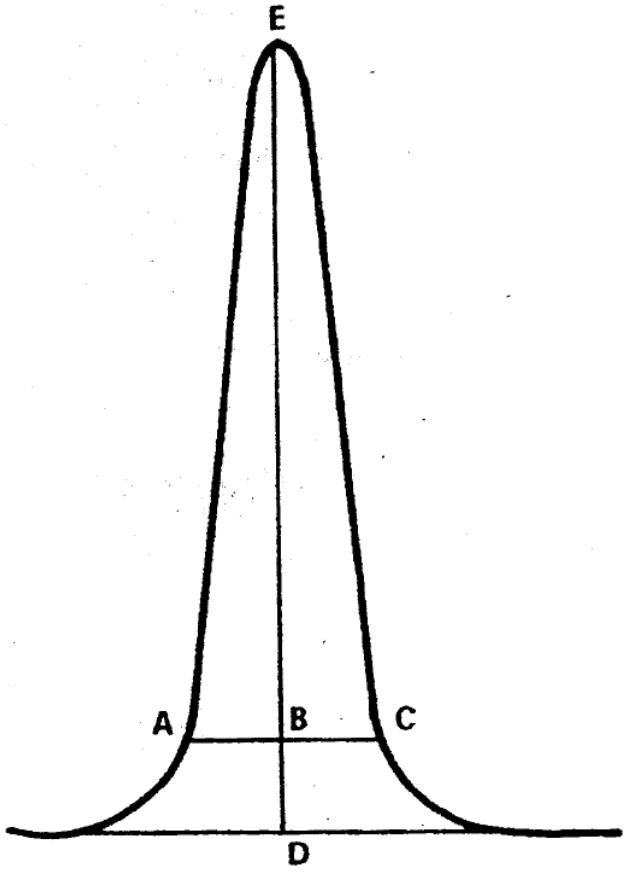
MANUAL INTEGRATION SUMMARY FOR DATABATCH - \\target\share\chem3\nt11.i\20170125.b

ARI Job No.: SFA0 Method: DFTPP.m Instrument: nt11.i Date: 25-JAN-2017

Time	Filename	LabID	ClientId	DF	Manually Integrated Compounds
0926	N1117012501.D	SFA0255-TUN1		1	NO MANUAL INTEGRATION
0942	N1117012502.D	SFA0255-ICV1		1	NO MANUAL INTEGRATION
1013	N1117012503.D	SFA0255-LCV1		1	NO MANUAL INTEGRATION
1046	N1117012504.D	BFA0320-BLK1		1	NO MANUAL INTEGRATION
1118	N1117012505.D	BFA0320-BS1		1	NO MANUAL INTEGRATION
1149	N1117012506.D	17A0190-01		S	NO MANUAL INTEGRATION
1220	N1117012507.D	17A0190-02		1	Acenaphthene,
1252	N1117012508.D	17A0190-03		1	NO MANUAL INTEGRATION
1324	N1117012509.D	17A0190-04		1	NO MANUAL INTEGRATION
1356	N1117012510.D	17A0195-01		1	1-Methylnaphthalene,
1427	N1117012511.D	17A0195-02		1	1-Methylnaphthalene,
1458	N1117012512.D	17A0195-03		1	NO MANUAL INTEGRATION
1530	N1117012513.D	17A0195-04		1	NO MANUAL INTEGRATION
1601	N1117012514.D	BFA0320-MS1		1	NO MANUAL INTEGRATION
1632	N1117012515.D	BFA0320-MSD1		1	NO MANUAL INTEGRATION
1704	N1117012516.D	17A0195-05		1	1-Methylnaphthalene,
1735	N1117012517.D	17A0195-06		1	1-Methylnaphthalene,

Appendix 20.6: Peak Tailing Factor Calculations

$$RF = \frac{(A_s)\,(C_{is})}{(A_{is})\,(C_s)}$$



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Appendix 20.7: Selected PCB congeners by GC/MS

Selected PCB congeners may also be analyzed under the guidance of this SOP. The selected PCB method utilizes a unique scan descriptor tailored for the characteristic PCB ions. The SOP pertains to all aspects of the selected PCB congener analysis with modifications made to the scan descriptor and a specific PCB congener calibration. The target congeners for this procedure are PCB-8, PCB-18, PCB-28, PCB-44, PCB-52, PCB-66, PCB-101, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138, PCB-153, PCB-169, PCB-170, PCB-180, PCB-187, PCB-195, PCB-206, PCB-209. Two internal standards used for quantitation are d10-Phenanthrene and d12-Chrysene. The target analytes and associated internal standards are shown below in table 1. The calibration is a six-point calibration from 5ng/ml to 1000ng/ml. The six calibration points used are 5, 10, 25, 50, 75, and 100ng/ml. The second source calibration verification is not run with the calibration as one is not readily available. Eight discrete sim scan descriptors are employed: one for each native/c13 congener pair and one for each internal standard. The internal standard concentration is static at 200ng/ml for all calibration levels.

See table 1 below which outlines the ions acquired during acquisition and the calibration requirements.

Table 1
PCB Target Analytes, Quantitation Ions, Calibration Criteria and Associated Internal Standards

Internal Standard Associated Analyte	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
D10-Phenanthrene (IS)	1517-22-2	188	184			
PCB-8	34883-43-7	222	152, 186	0.2	15.0	20.0
PCB-18	37680-65-2	186	256, 221	0.2	15.0	20.0
PCB-28	7012-37-5	258	186, 150	0.2	15.0	20.0
PCB-44	41464-39-5	222	292, 257	0.2	15.0	20.0
PCB-52	35693-99-3	292	222, 184	0.2	15.0	20.0
PCB-66	32598-10-0	292	220, 184	0.2	15.0	20.0

PCB-101	37680-73-2	326	254, 291	0.2	15.0	20.0
PCB-105	32598-14-4	326	256, 292	0.2	15.0	20.0
PCB-118	31508-00-6	326	256, 207	0.2	15.0	20.0
PCB-153	35065-27-1	360	290, 207	0.2	15.0	20.0
c13-PCB-37	208263-79-0	270	268, 198	0.2	15.0	20.0
c13-PCB-47	NA	304	302, 232	0.2	15.0	20.0
c13-PCB-54	234432-88-3	304	302, 232	0.2	15.0	20.0
c13-PCB-111	235416-29-2	338	336, 266	0.2	15.0	20.0
D12-Chrysene (IS)	1719-03-5	240	241			
PCB-126	57465-28-8	326	254, 207	0.2	15.0	20
PCB-128	38380-07-3	362	290, 325	0.2	15.0	20
PCB-138	35065-28-2	360	325, 290	0.2	15.0	20
PCB-169	32774-16-6	207	362, 290	0.2	15.0	20
PCB-170	35065-30-6	396	324, 281	0.2	15.0	20
PCB-180	35065-29-3	207	394, 324	0.2	15.0	20
PCB-187	52663-68-0	394	324, 361	0.2	15.0	20
PCB-195	52663-78-2	281	358, 430	0.2	15.0	20
PCB-206	40186-72-9	207	281, 464	0.2	15.0	20
PCB-209	2051-24-3	498	428, 356	0.2	15.0	20
c13-PCB-138	208263-66-5	372	370, 302	0.2	15.0	20.0
c13-PCB-178	232919-67-4	406	408, 336	0.2	15.0	20.0

This procedure is being developed to access the validity of polymeric sampling procedures in aquatic environments and must meet all method requirements for DFTPP tuning, peak tailing, and DDT breakdown as detailed in the main section of this SOP.

Appendix 20.8: Modifications Required for EPA Method 625.1(These modifications are only implemented when specifically requested by a client, otherwise method 625.1 is analyzed as 8270E described previously in this SOP)

Please refer to SOP 804S section 20.7 for guidance.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Polychlorinated Biphenyls (Aroclor) Analysis

SOP 403S
Revision 24

Revision Date: 7/19/18
Effective Date: 7/19/18

Prepared by:

Josh Rains, Van Spohn

Approvals:

Brian N. Bebee, Laboratory Section Manager

David R. Mitchell, Quality Assurance Mgr.

Annual Review

SOP Number: _____

Title: _____

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This procedure summarizes ARI's protocol for identifying and quantifying mixtures of Polychlorinated Biphenyls (PCBs), known as Aroclors, in a variety of matrices including sediments, soils, solids, tissues, waters, and waste products (oils, etc.) The procedures described meet the requirements of EPA Method 8082A (Reference 19.1) and EPA Method 608 for PCB Aroclors only (Reference 19.2). The following Aroclors may be determined using this protocol:

Table 01: Aroclor Analytes	
PCB Mixture	**CAS Number**
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5
Aroclor-1262	37324-23-5
Aroclor-1268	11100-14-4

1.2. Detection limits- depending on the volume of sample extracted, the detection limits range from 0.01 to 10ug/L for aqueous samples and from 4 to 800ug/kg (based on dry weight) for solid samples.

Table 02: Aroclor Reporting Limits			
Sample Matrix	**Extract Volume or Weight**	**Final Volume**	**Reporting Limit**
Aqueous	500 mL	5 mL	1 ppb
	500 mL	1 mL	0.1 ppb
	1000 mL	0.5 mL	0.01 ppb
(TCLP)	100 mL	10 mL	10 ppb
Solids	12 g	4 mL	33 ppb
	12.5 g	2.5 mL	20 ppb
	12.5 g	2.5 mL	10 ppb
	12.5 g	2.5 mL	4 ppb
	1 g	40 mL	800 ppb
	5 g	40 mL	800 ppb

Tissue	10 g	5 mL	50 ppb
	25 g	5 mL	20 ppb
	25 g	1 mL	4 ppb

1.3. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including the EPA SW-846 methods, EPA Contract Laboratory Program (CLP), NELAP and the Department of Defense Quality Systems Manual (DoD-QSM). The table in Appendix 20.1 outlines ARI's routine procedure. Please refer directly to DOD-QSM 5.1 for guidance on the special requirements of the DoD-QSM. Analysts are responsible for determining which QA program is applicable to a set of samples prior to beginning analyzes and complying with all project specific analytical requirements.

1.4. The reference methods for this procedure are listed in Section 19.

2. Summary of the Procedure

2.1. Surrogate standards are added to a measured volume or weight of sample which is extracted using an appropriate organic solvent and extraction technique. The resulting extract is concentrated to a specified final volume. Project or Protocol required Quality Assurance Samples are prepared and analyzed using identical techniques.

2.1.1. A variety of cleanup steps may be applied to the extracts, depending on the nature of any co-extracted matrix interferences and the requested target analytes. All cleanup techniques must be applied to all sample extracts including QC samples (MB, BS, MS, MRL, and DUP).

2.1.1.1. Following any cleanup, the extract is concentrated to a designated final effective volume and delivered to ARI's Gas Chromatography Laboratory for identification and quantification of polychlorinated biphenyls.

2.1.1.1.1. Following addition of internal standards 1-2 µL of the extract is injected onto a GC using an auto-sampler and splitless injection technique.

2.1.1.1.1.1. The injected sample is split onto two columns by passing through a glass Y connector. Analytes are detected and quantified using ECD detectors.

2.1.1.1.1.2. Identified Target analytes are quantified using an internal standard procedure as described in Sections 10 and 11

3. Definitions

3.1. Aroclors- mixtures of polychlorinated biphenyl congeners

3.2. BNB (1-Bromo-2-Nitrobenzene): Internal standard.

3.3. Initial Calibration Verification (ICV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable.

3.4. Continuing Calibration Verification (CCV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable.

3.5. Continuing Calibration Verification Standard (CCVS): The standard prepared at the mid-point concentration of the initial calibration, and prepared from the same source as the initial calibration used to perform the ICV and CCV.

3.6. DCBP (Decachlorobiphenyl): Surrogate standard.

3.7. ECD (Electron Capture Detector): A detector with a high specificity and sensitivity to organic molecules with highly electronegative functional groups. An ECD is especially suitable for identifying and quantifying organochlorine compounds including Aroclors and selected pesticides and herbicides.

3.8. HBBP (2,2',4,4',5,5'-Hexabromobiphenyl): Internal standard.

3.9. Second source Calibration Verification (SCV): An instrument calibration standard purchased from a secondary vendor is used to verify that the current instrument calibration is acceptable.

3.10. Instrument Blank (IB): A QC sample made by adding surrogates to clean solvent used to measure instrument background.

3.11. Internal Standard (IS): internal standards are compounds added to each standard, sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of these internal standards.

3.12. Blank Spike (BS) – A sample matrix, free from the analytes of interest, spiked with verified amounts of analytes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system. Aroclor 1660 (Section 7.1) is the routine BS analyte.

3.13. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, an BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS. Aroclor 1660 (Section 7.1) is the routine BSD analyte.

3.14. ELEMENT (Laboratory Information Management System): Software used to compile and report final chromatographic data.

3.15. MDL (Method detection Limit): The lowest result that can reliably be distinguished in a matrix from a blank. Also referred to as the limit of Detection (LOD)

3.16. MRL (Method Reporting Limit)–The lowest result that may be reported unqualified based on the lowest curve point.

3.17. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a

specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method. Aroclor 1660 (Section 7.1) is the routine MS analyte.

3.18. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision. Aroclor 1660 (Section 7.1) is the routine MSD analyte.

3.19. Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

3.20. PCBs - polychlorinated biphenyls- biphenyl molecules with varying degrees of chlorination

3.21. MRL (Method Reporting Limit): A matrix spike prepared at reporting limit, used to determine MDL(LOD) and MRL.

3.22. Solvent Blank (SB) – Clean solvent is analyzed using the same conditions as a regular sample. A solvent blank is analyzed to detect and/or remove sample carryover from one analysis to another.

3.23. Surrogate – A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

3.24. Target Software: Software used to integrate and reduce raw chromatographic data.

3.25. TCMX (Tetra chloro-m-Xylene): Surrogate standard

4. Interferences

4.1. Extraction Interferences: Data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

4.1.1. Method interferences are reduced by washing all glassware with hot soapy water, a weak HCL acid bath, and finally OFW before being baked at 500 degrees centigrade overnight.

4.1.2. Recycled glassware method interferences are reduced by washing all glassware with hot soapy water, a weak HCL acid bath, OFW, acetone, and methylene chloride in the order listed.

4.1.3. High purity reagents must be used to minimize interference problems.

4.2. Co-extraction of analytes which respond to the ECD detector may cause interferences. These co-extracted contaminants may be removed by an appropriate clean-up technique.

4.2.1. Typical clean-up procedures include silica gel clean-up, removal of elemental sulfur, and sulfuric acid treatment as described in SOP 3327S.

4.3. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a solvent blank to check for cross contamination (if needed).

4.4. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to assure proper qualitative and quantitative analysis. In these cases, PCB congener analysis may be more appropriate.

5. Safety

5.1. The toxicity and carcinogenicity of each reagent used in this method is not precisely defined. However, all compounds and solutions should be treated as health hazards, and exposure of these chemicals to skin and clothing should be minimized to the lowest possible level by whatever means available.

5.2. Wear nitrile gloves, safety glasses, and laboratory coats when working with reagents, standards and sample extracts to minimize exposure to chemicals.

5.3. Standard solutions should be handled in the fume hoods to avoid exposure to fumes.

5.4. All GC split vents are connected to an exhaust vent

5.5. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult with SDS website for all chemicals handled. www.msdshazcom.com

6. Equipment and Supplies

6.1. Gas chromatograph

6.1.1. Gas chromatograph - An analytical system with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including:

6.1.2. ECD detectors

6.1.3. Autosampler

6.1.4. Analytical columns Fused-silica capillary columns - Columns used may vary depending on currently available technology (other column pairs may be used so long as they generate equivalent data):

6.1.4.1. Standard pair - Column 1: ZB-5, 30m, 0.53mm ID, 0.5µm film. Column 2: ZB-35, 30m, 0.53mm ID, 0.5µm film.

6.1.4.1.1. Alternate pair - Column 1: Rtx CLP1 30m, 0.32mm ID, 0.5µm film. Column 2:

Rtx CLP2, 30m, 0.32mm ID, 0.25µm film.

6.1.4.2. Guard Column 5m IP deactivated.

6.1.4.3. Y-connectors

6.1.5. High Purity Gases

6.2. Chemstation Data system - A computer system capable of collecting chromatographic data must be connected to the GC. The system must allow the recording of instrument response as a function of time

6.3. Syringes - 10µL, 25µL, 50µL, 100µL,250µL, 500µL, and 1000µL

6.4. Volumetric flasks, Class A - 5mL to 1000mL.

6.5. Bottles – 5, 10, 25, 50, and 100 mL glass with Teflon-lined screw caps or crimp tops.

6.6. Balance - Analytical, readable to 0.0001 g

6.7. Autosampler vials- clear 2 ml autosampler vials with PTFE crimp caps.

7. Reagents and Standards

7.1. Stock standard solutions (100 - 10,000µg/L) - Standard solutions can be prepared from neat standards or purchased as certified solutions. Certificates of analysis for all purchased neat and solutions are kept in PDF format in Element

7.2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2.1. The laboratory should have acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, methanol and other appropriate solvents for preparing standards.

7.2.2. Organic-free reagent water - All references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.

7.2.3. Neat chemicals do not have an expiration date regardless of what is shown on the certificate of analysis.

7.2.4. All reagents and chemicals used in any preparation must be documented in Element.

7.3. Stock Standard Preparation

7.3.1. Prepare stock standard solutions by accurately weighing about 0.2500g of pure material. Dissolve the material in pesticide quality methylene chloride or other suitable solvent and dilute to volume in a 25mL volumetric flask. Larger or smaller volumes can be used at the convenience of the analyst. When compound purity is assayed to be 97% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

7.3.2. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.3.3. Transfer the stock standard solutions into amber bottles with Teflon lined screw-caps. Store at >0 to 6°C and protect from light.

7.3.4. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.3.5. Stock standard solutions must be re-assayed or replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

7.4. Aroclor 1660- is a mixture of Aroclors 1016 and 1260 used to prepare the instrument calibration curve and as the spike in blank spikes and matrix QC - Purchased commercially as a 1000 µg/mL in Hexane stock solution.

7.4.1. Prepare an BS and MS spike solution by diluting 2.0 mL of the Aroclor 1660 stock to 100 mL using Acetone.

7.5. Standardized solutions (100 to 1000 µg/mL in Hexane) of Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268 are purchased from a commercial vendor.

7.6. Aroclor 2162 – A mixture of Aroclors 1221 and 1262 used for instrument calibration and as a non-routine BS or MS spike. The mixture is prepared by mixing equal volumes of the purchased Aroclor 1221 and 1262 standard solutions and therefore has each Aroclor at 500 µg/mL.

7.7. Aroclor 3268 – is a mixture of Aroclors 1232 and 1268 used for instrument calibration and as a non-routine BS or MS spike. The mixture is prepared by mixing equal volumes of the purchased Aroclor 1232 and 1268 standard solutions and therefore has each Aroclor at 500µg/mL.

7.8. 1-Bromonitrobenzene (BNB) the first eluting internal standard, Aroclors 1016, 1221, 1232, 1242, 1248, and 1254 are quantified using its response.

7.9. 2,2',4,4',5,5'-Hexabromobiphenyl (HBBP) the second eluting internal standard. Aroclors 1260, 1262, and1268 are quantitated using its response.

7.10. Tetrachloro-m-xylene (TMCX) - the surrogate (CAS # 877-09-8) purchased as a neat compound.

7.11. 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl (DCBP) - the surrogate (CAS # 2051-24-3) purchased as a neat compound.

7.12. Internal Standard Stock Solution – Prepared by diluting the commercially prepared stocks 1000 µg/mL solutions of the internal standards BNB and HBBP in hexane.

7.13. Internal Standard Working Solution- Prepare an internal standard working standard (IS)with 8 µg/mL BNB and HBBP in hexane.

7.13.1. Each 0.1 mL aliquot of the sample extract undergoing analysis should be spiked with 1 µL of the IS Working Solution, resulting in a concentration of 80ng/mL BNB and HBBP (for example, when preparing a sample aliquot of 0.3ml, spike the extract with 3µL of the internal standard stock).

7.14. Surrogate Stock Standards- Prepared Stock 1000µg/mL solution of the surrogate standards TCMX and DCBP by dissolving 0.10g of each in a small amount of hexane in a 100mL volumetric flask and diluting to volume with hexane.

7.15. Surrogate spiking standard- Prepare a surrogate working standard with 2ug/mL TCMX and DCBP by diluting 0.08mL of the surrogate stock solutions with acetone.

7.16. Blank Spike (BS) Stock Standards – Typically, a 1000 µL/mL solution of Aroclor 1660 in Hexane is used to spike BS and MS samples. The spike is purchased as a commercially certified working solution and diluted to volume with acetone.

7.17. BS Spike Working Standard contains Aroclor 1660 at 80µg/mL. Prepare the standard by adding 0.8mL of the BS Spike Stock Standard and dilute to volume with hexane.

7.18. MRL spike working standards made from certified solutions are used to prepare MRL spikes. Aroclor 1660 is used in the preparation of the MRL spike.

7.19. Calibration working standards Prepared as outlined in Section 10.

7.20. The SCV must be derived from a different manufacturer than the stock standard used to prepare the calibration curve.

7.20.1. Two sources from different manufacturers are obtained when feasible or at least two different lot numbers from the same manufacturer.

7.20.2. Standards produced by two different manufacturers may be purchased from the same vendor.

8. Sample Collection, Preservation, Shipment, Storage, Holding times and Disposal.

8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 ºC.

8.2. Samples must be stored at ARI, at >0 to 6 ºC until final disposal.

8.2.1. Samples must be extracted with holding times determined from the day of sampling. The standard holding time for water samples is 7 days. The standard holding time for solid samples is 14 days.

8.2.2. A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

8.2.3. Solid and sediment samples may be stored frozen at -10 to -20 ºC to extend the holding

time to one year.

8.2.4. Water samples being analyzed under the MTCA program stored at >0 to 6 ºC have an extended holding time of one year

8.3. Extracts

8.3.1. Extracts are delivered to Refrigerator 15 in the instrument laboratory by extractions technicians.

8.3.2. Analysts in the instrument lab assume custody of the sample extracts and then move them into Refrigerator 17 and place them in a bin assigned in Element.

8.3.3. Extracts must be stored at >0 to 6 °C and protected from light.

8.3.4. Extracts must be analyzed within 40 days of extraction except for MTCA waters which have an extract holding time of one year.

8.3.5. Extracts must be stored in their assigned Element bin.

8.3.6. Extracts may be disposed 40 days after the analysis has been completed and the Element bin will be recycled for future use.

8.3.7. Extracts will be disposed in the large blue barrel in the satellite accumulation area designed for extract vials.

9. Quality Control

9.1. Quality control requirements are available in the table in Appendix 20.1.

9.1.1. Criteria for ARI's routine analyses are listed in Appendix 20.1

9.1.2. When DoD-QSM acceptance criteria are required, please refer to DoD-QSM 5.1 for further guidance.

9.2. ARI routinely checks the effect of the matrix on both method precision and bias. At a minimum, this check should include the analysis of at least one matrix spike and one duplicate unspiked sample, or one MS/MSD pair with each preparation batch of up to 20 samples of the same matrix.

9.2.1. ARI will not perform MS/MSD analysis on any of the field QC samples delivered as part of a client's QA/QC program (water rinsate samples, field/trip blanks etc.)

9.2.2. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.3. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for matrix spike and matrix spike duplicates are statistically generated on a periodic basis.

9.3.1. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation.

9.3.2. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. Current control limits are listed in Element.

9.3.3. All analysts using this SOP must use it in conjunction with the Control Limit documentation in Element to assess data quality and any possible need for corrective actions.

9.4. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC must be documented in SharePoint.

9.5. Each reagent and standard preparation is recorded in Element standard registry and assigned a unique identification for traceability to the certificate of analysis of the source chemical. See ARI SOP 1013S for details.

10. Calibration and Standardization (Calibration criteria and verification apply to both chromatographic columns)

10.1. ARI uses single injection dual column GC-ECD systems for analysis of Aroclors. Analysis must not proceed until both columns meet initial calibration criteria.

10.2. The Aroclor 1660 mixture contains many of the congeners present in other Aroclors, an acceptable calibration performed with this Aroclor mixture serves to demonstrate the linearity of the detector for the other Aroclors.

10.3. Prepare six calibration solutions by diluting the stock of the 1660 calibration solution described in Sections 7.1 through 7.4 as outlined in Table 03.

Table 03 - Calibration Standard Concentration

Stock Calibration Dilution		1X	2X	4X	10X	20X	50X
Used for:		ICAL	ICAL	ICAL ICV CCV	ICAL	ICAL	ICAL
Aroclor	Component	Calibration Standard Concentration (ng/mL)					
1660	1016	1000	500	250	100	50	20
	1260	1000	500	250	100	50	20
2162	1221	-	-	250[1]	-	-	-
	1262	-	-	250[1]	-	-	-
3268	1232	-	-	250[1]	-	-	-
	1268	-	-	250[1]	-	-	-
1242	1242	-	-	250[1]	-	-	-
1248	1248	-	-	250[1]	-	-	-

Table 03 - Calibration Standard Concentration							
Stock Calibration Dilution		1X	2X	4X	10X	20X	50X
Used for:		ICAL	ICAL	ICAL ICV CCV	ICAL	ICAL	ICAL
Aroclor	Component	Calibration Standard Concentration (ng/mL)					
1254	1254	-	-	250[1]	-	-	-

1) Working standards prepared at 250ng/ml do not require dilution.

10.4. Add surrogate standards to the calibration working solutions so that the final concentration of each surrogate is 40ng/mL.

10.5. Spike each calibration solution with 1µL Internal Standard solution per 100µL of each standard.

10.6. Analyze each calibration solution using the same conditions and instrument setting to be used for sample extract analyzes.

10.7. For each Aroclor, select 3 or more characteristic peaks on each column to represent that Aroclor. The area of selected peaks should be ≥ 25% of the area of the largest Aroclor peak. An effort should be made to make sure that the peaks selected for quantitation in one Aroclor are not used for quantitation in other Aroclors.

10.8. Calculate the Relative Response Factor (RRF) for each Aroclor peak selected in Section 10.7 using the following formula:

$RRF = (A_X C_{IS}) / (A_{IS} C_X)$
where:
A_X = Peak area for the quantitation peak being measured
A_{IS} = Peak area of the internal standard
C_{IS} = Concentration of the IS associated with the peak
C_X = Concentration of the analyte

10.9. Calculate the Average RRF for each peak.

$\text{Average RRF} = \Sigma RRF_i / n$
where:
RRF_i = the peak response factor for each quantitation peak in the calibration standard
N = the total number of standards (usually 5)

10.10. Calculate the Relative Standard Deviation (RSD) for each peak. (These calculations are

normally performed by the chromatographic data system).

$$\textbf{RSD = SD / (Ave RRF) = } \left(\left(\Sigma \left(RRF_i - \text{Ave RRF}\right)^2\right) / (n-1)\right)^{1/2}$$

10.11. When the average RSD for each compound is ≤ 20%, the calibration is acceptable and the average RRF is used to calculate analyte concentration.

10.12. When the %RSD for any Aroclor peak is not ≤ 20% the analyst will:

10.12.1. Determine that there is no detector or chromatographic peak saturation and that the chromatographic system is functioning properly, then:

10.12.2. Use a linear or quadratic regression to calibrate for the Aroclor.

10.12.2.1. The analyst will first attempt to use a linear fit requiring at least five calibration points.

10.12.2.2. Next, a Quadratic non-linear calibration requires six calibration points may be used.

10.12.3. See EPA Method 8000C Section 11 for reference to linear or quadratic regression calibration.

10.12.4. When specifically required by a project or QAP, the other Aroclors may be curved along with or in lieu of Aroclor 1660.

10.12.5. The DoD-QSM requires that all Aroclors be quantified using a five-point calibration curve for each specific Aroclor quantified in a sample.

10.13. The average RSD for the quantitation peaks for each Aroclor must be less than or equal to 20% for the initial calibration to be valid. Quantitation is performed using the average RRF from the initial calibration. Surrogates may use the linear calibration model discussed in Section 11.5 of Method 8000C so long as the coefficient of determination is greater than 0.99.

10.14. Retention time windows- Retention times for each analytical batch are established by the first calibration verification in each analytical sequence.

10.14.1. ARI uses a default retention time window width of ± 0.05 minutes. Retention time studies suggested by the method often result in windows of 0.01 minutes or less.

10.14.2. ARI's experience indicates that allowing the chromatographic data system to identify analytes based on narrow statistically derived retention times may lead to false negative results. This happens often when analyzing extracts from difficult matrices that contained oily material or high background contamination. For this reason, ARI sets retention time windows to ±0.05 minutes and requires the analyst to manually screen for and eliminate resulting false positives.

10.14.3. Retention time criteria may change during an analytical sequence if the RT shift is

explainable (a column was shortened and all RT shift equally) and CCVs confirm that the calibration is valid. All such deviations must be explained on the Analyst Notes form.

10.15. The instrument initial calibration (ICAL) must be verified prior to use by analysis of a second source calibration verification standard (SCV).

10.15.1. The SCV standard is prepared at the same concentration as the mid-point ICAL standard as noted in Table 3.

10.15.2. Analyze the SCV using the same conditions as the initial calibration.

10.15.3. The SCV must be derived from a different manufacturer than the stock standard used to prepare the calibration curve.

10.15.3.1. Two sources from different manufacturers are obtained when feasible or at the very least two different lot numbers from the same manufacturer.

10.15.3.2. Standards produced by two different manufacturers may be purchased from the same vendor.

10.15.4. Calculate the percent difference using the formula:

%D = 100(Conc – Concmp) / Concmp
where:
Concc = the quantitated concentration in the CVS
Concmp = the concentration of the midpoint in the ICal (500)

10.16. Initial and Continuing Calibration Verification (ICV/CCV): The performance of the instrument over time is monitored by analyzing initial and continuing calibration verifications.

10.16.1. The ICV/CCV standards are prepared from the same source as the ICAL standards. ICV/CCV standards are analyzed at the concentration of the mid-point ICAL standard (250ng/ml).

10.16.2. Each set of ICV/CCV analyses should include an Aroclor 1660 standard and one other Aroclor standard (1242, 1248 or 1254) on a rotating basis. When requested, ARI may vary the concentration of ICV/CCVs to include several standards from the calibration range or use different Aroclor pairs in the ICV/CCV sets.

10.16.3. The ICV/CCV standards are prepared from the same source as the ICAL standards. CCV standards are analyzed at the midpoint ICAL concentration as noted in Table 3.

10.16.4. An ICV is analyzed at the beginning of the analytical bracket and CCVs must be analyzed at the end of an analytical bracket.

10.16.5. A CCV pair must be analyzed after every 10 field samples.

10.16.6. No more than 12 hours may pass between ICV/CCVs.

10.16.7. The retention times of all analytes in all daily ICV/CCVs must fall within the retention time windows established during initial calibration.

10.16.8. The Aroclors in the ICV/CCVs are quantified using the average response of 3 to 5 representative PCB congener peaks.

10.16.9. Calculate the RRF for each group of peaks in the ICV/CCV using the formulae used for the ICAL.

10.16.10. Calculate the %D between the CCV RRF and the average ICAL RRF.

10.16.11. Each ICV/CCV must have an average concentration of these peaks within ±20% of the true value when quantified using the ICAL.

10.16.12. All peaks used for quantitation should be at least 25% in height when compared to the height of the largest aroclor peak.

10.16.13. A minimum of three quantitated peaks need to be included to average an Aroclor and determine its percent difference from the ICAL.

11. Procedure

11.1. Prior to using this method, the samples must be prepared for chromatography using the appropriate sample preparation and cleanup methods.

11.2. Examine the project requirements in Element for each Work order.

11.2.1. Work order documents and the project version may contain information affecting the analysis such as unusual analytes, control limits, project specific MRL standard requests, and project required data quality objectives.

11.2.2. Organic extraction documents may contain useful sample or extract specific information and may include screening to which may be used to adjust extract concentration prior to analysis.

11.3. The recommended GC operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration.)

Initial temperature:	160°C, hold for 1 minute
Temperature program:	160-310°C at 15C°/min
Final temperature:	310°C, hold for 4 minutes
Injector temperature:	220°C
Detector temperatures:	330°C
Detector make-up gas flows	40 mL/min (front) and 35 mL/min (back)
Column initial flow	3.6 mL/min (hold for 12 minutes)

Column flow ramp	3.6-5 mL/min at 1 mL/min
Column flow final hold	5 minutes at 5 mL/min
Injector:	Grob-type, splitless/split
Injector Pulse	20 psi at 0.45 minutes
Split flow	20 mL/min at 0.5 minutes
Sample volume:	2 µL
Carrier gas:	Helium at 30cm/sec.

11.4. Prior to sample analysis the GC system must have an acceptable initial calibration curve (the requirements for the calibration curve are found in Section 10)

11.5. Prior to sample analysis an initial calibration verification must be analyzed and this ICV must meet the criteria found in Section 10.11. If time remains in the 12-hour QC period begun with the initial calibration, the mid-point calibration standard from the initial calibration may be used as the CCV provided it meets the requirements found in Section 10.11.

11.5.1. Rinses before CCVs are not allowed unless rinses are placed before all injections in the analytical sequence.

11.6. Screen extracts as necessary

11.6.1. It is highly recommended that the extract be screened on a GC/ECD using the same type of capillary column. This will minimize contamination of the GC system from unexpectedly high concentrations of organic compounds and may show high background samples that should be analyzed using a medium/high level extraction. If the screening chromatograms indicate the presence of elemental sulfur, remove the sulfur using elemental Mercury as described in Appendix 20.3.

11.7. Remove sample extracts from refrigerator 15 and change the location to refrigerator 17 in Element under batch or sequence.

11.8. GC analysis

11.8.1. Measure a 0.3-0.5ml aliquot of the sample extract obtained from sample preparation. Use a 10µL syringe to add 1µL of Internal Standard spiking solution for each 0.1mL of extract. This results in a concentration of 80ng/µL of each internal standard in the extract. This aliquot should be prepared in a clear glass auto-sampler vial and sealed with a crimp cap. Store the remaining extract volume at >0 to 6°C, protected from light in screw-cap vials equipped with unpierced Teflon lined septa.

11.8.2. Load autosampler with the aliquots prepared in Section 11.8.1.

11.8.3. Enter the analytical sequence into the chromatography data system.

11.8.4. Begin the analytical sequence.

11.8.5. The injection volume must be the same volume used for the calibration standards. Recommended GC operating conditions are specified in Section 11.3.

11.8.6. The computer system will collect and process the chromatography data and export it to "Target" software.

11.8.7. The "Target" software assigns the chromatographic baseline and integrates the electronic signal producing a chromatogram.

11.8.8. Examine the chromatogram for the presence of elemental sulfur.

11.8.8.1. If the presence of sulfur is suspected a Mercury cleanup must be performed on the affected extract and all associated QA sample extracts. The clean-up procedure is outlined in Appendix 20.3. Following clean-up, the sample extracts must be re-analyzed starting at Section 11.8.2.

11.8.9. Verify that the computer has correctly identified the chromatographic baseline and integrated all peaks correctly.

11.8.9.1. If corrections are required, manually re-integrate the data file following guidelines in SOP 1021S "Manual Integration of Chromatographic Peaks".

11.8.9.2. Manual integrations must be identified and explained in the reviewer checklist associated with each analytical sequence loaded into Element.

11.8.9.3. The final raw data report includes a before manual integration chromatogram and an after manual integration chromatogram for all manual integrations performed. This manual integration report is attached to the data file .PDF.

11.8.10. Perform all qualitative and quantitative measurements as described in Section 12.

11.8.11. Replace the punctured septum on the auto-sampler vial with a new one.

11.8.12. Store the extracts at >0 to 6°C, protected from light in Refrigerator 17.

11.8.13. Following the data analysis, upload the data into Element using data tool.

11.8.14. Attach PDF's of all bracketing CCVs, raw data for all the samples and associated QC, the ELEMENT report, and an analyst's note form in the project folder.

11.8.15. Attach a .pdf of the virtual logbook to the sequence associated with the data.

11.8.15.1. Make sure the Reviewer Checklist(s) include all deviations from standard procedure and any other noteworthy information concerning the project analyzes.

12. Data Analysis and Calculations

12.1. Aroclor Identification- A sample is tentatively determined to have Aroclor content when the Aroclor peaks fall within the retention time windows for the Aroclor peaks that are used to

calibrate the Aroclor and the pattern ratios are consistent with one or more of the Aroclor standards.

12.1.1. The Aroclor detection must be confirmed by examining the data from the second analytical column. Should the second column also show detection of Aroclor peaks within the RT windows, the hit has been confirmed.

12.1.2. Choose the Aroclor standard whose pattern most closely resembles that of the sample chromatogram. Carefully examine the patterns on both columns.

12.1.3. When samples appear to contain weathered PCBs, treated PCBs, or mixtures of various Aroclors, use of Aroclor standards may not be straightforward (or technically appropriate). In such cases, the analyst must decide which Aroclor or Aroclors most closely represent the range of PCBs present and will quantify total PCBs by quantifying and averaging those congener peaks with the most consistent ratios based on the analyst's opinion. When samples appear to contain multiple Aroclors, the analyst should attempt to quantify the individual Aroclors using peaks that are unique to each Aroclor or are significantly larger in one of the Aroclors. Weathered patterns and difficult mixtures should be noted in the Analyst Notes report. The analyst should also attempt to report the total PCB content as accurately as possible and avoid "double counting" of Aroclors.

12.1.4. All Aroclor peaks should show consistent RT shifting in comparison to the initial calibration (i.e. all peaks should elute earlier or later compared to the initial calibration, and by the same amount.) Large chromatographic interferences may cause inconsistent shifting by moving some of the peaks more than others. The chromatographs of samples should be examined to ensure that false negatives aren't created by this manner of chromatographic overload.

12.2. All peaks for each Aroclor should show quantitative agreement. Again, interferences can elevate the quantitation number for some of the peaks. Analysts are expected to average the peaks that best represent a given Aroclor in a specific chromatogram. Should some of the quantitation peaks be interfered with, these peaks may be removed from the average Aroclor concentration calculation, so long as at least three peaks remain for averaging. The peaks removed from the calculation, as well as the corrected average concentration need to be noted on the raw data.

12.3. Sample Quantitiation (Calculation performed by Target and verified with Element software)

12.3.1. Water

Concentration (µg/L) =	$\frac{(Ax)(Is)(Vt)(DF)}{(Ais)(RRF)(Vo)(Vi)}$
where:	

A_X = Peak of the quantitation peak for the compound being measured
Is = Amount of internal standard injected (ng).
Vt = Volume of total extract
A_{IS} = Peak area of the internal standard
RRF = Relative response factor for compound being measured
C_X = Concentration of the analyte
Vo = Volume of water extracted (ml)
Vi = Volume of extract injected (ul)
DF = Sample Dilution Factor (1 for undiluted samples)

12.3.2. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)

Concentration (µg/kg) =	$\frac{(Ax)(Is)(Vt)(DF)}{(Ais)(RRF)(Vi)(Ws)(D)}$
where:	
A_X = Peak of the quantitation peak for the compound being measured	
Is = Amount of internal standard injected (ng).	
Vt = Volume of total extract	
DF = Sample Dilution Factor (1 for undiluted samples)	
A_{IS} = Peak area of the internal standard	
RRF = Relative response factor for compound being measured	
Vi = Volume of extract injected (ul)	
Ws = Weight of sample extracted or diluted in grams	
D = % Dry weight of sample = 1.0 on an as received basis	

12.4. ARI will report the higher of the Aroclor results as per Method 8000B. This approach is conservative relative to protection of the environment. In certain instances, or for project specific requirements, it may be appropriate to report the lower result as per Method 8000C. This approach is only valid under the discretion of an experienced analyst and must be noted in the analyst's notes and in the project narrative.

13. Method Performance

13.1. The QA department measures method performance using a combination of quarterly MRL studies, performance evaluation samples, and the monitoring of surrogate and spike recoveries.

13.1.1. Detection limits- the LOD for all analytes quantitated using this SOP are set using the low point of the initial calibration curve and validated by MRL studies.

13.1.2. MRL studies are performed each quarter for each analyte by each preparatory and analytical method.

13.1.3. LOD and MRL values may be found for each analyte on the ARI's Web Site

13.2. Laboratory precision and bias measurements are performed by monitoring surrogate and spike recoveries in samples and quality control samples.

13.2.1. Control limits are calculated from these recoveries.

13.2.2. These control limits are disseminated to the bench chemists and Element administrator for use in monitoring method performance in real time.

13.2.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found on the ARI's Web Site.

13.3. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. See ARI SOP 1017S.

13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.

13.5. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to assure proper qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation (weathering) or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards. In these cases, PCB peak analysis may be more appropriate.

13.6. **The experience of the analyst must weigh heavily in the interpretation of the chromatogram**. In the case of multi-component analytes such as Aroclors the analyst should rely primarily on pattern recognition.

14. Pollution Prevention

14.1. All syringe rinses are discharged into activated charcoal. Spent charcoal is properly disposed of as "Solvent Contaminated Solids" by ARI's designated Treatment, Storage and Disposal Facility.

14.2. Charcoal containers must remain covered when not attended to prevent fugitive vapors.

14.3. Disposed expired standards into the designated barrel in the hazardous waste room.

14.4. Auto-sampler vials containing sample extracts are placed in the satellite accumulation station in the GC store room for eventual removal by an EPA approved Treatment, Storage and Disposal Facility.

14.5. All GC split vents are connected to an exhaust vent and the filter is changed biannually.

14.6. Open solvent containers should only be present when actively preparing samples.

14.7. Wherever possible the final sample extract volume should be as small as possible to minimize the generation of waste.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 and Appendix 20.1 of this document.

15.2. Requirements for Method Blanks are tabulated in Appendix 20.1.

15.3. Internal Standards- All samples' internal standard peak areas must meet the technical acceptance criteria listed in Appendix 20.1 of this SOP.

15.4. Surrogate Recoveries

15.4.1. All method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates, or other samples must have acceptable surrogate standard recoveries. Surrogate recoveries are acceptable when they are within ARI's statistically generated control limits or limits set by ARI's client or a specific quality systems protocol such as the DoD-QSM.

15.4.2. Any surrogate recovery that is "out-of-control" required that a corrective action be initiated.

15.4.2.1. These requirements do not apply to subsequent dilutions of samples where a prior analysis of the diluted sample extract shows acceptable surrogate recovery.

15.4.2.2. When mandated by contract-specific requirements, corrective actions must be performed for unacceptable surrogate recovery even when the criteria are labeled as advisory in the reference method.

15.4.3. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.

15.5. Blank spikes (BS)

15.5.1. Blank Spike recovery must fall within specified recovery acceptance limits or corrective action is required.

15.5.1.1. Blank Spike recovery acceptance criteria are determined statistically from historic laboratory data. Criteria specified by a method, ARI's client or a particular quality system (i.e. DoD-QSM) may supersede ARI's historic values.

15.5.1.2. When mandated by a particular quality system or contract-specific requirements, corrective actions is required in response to unacceptable BS criteria, even when the criteria are labeled as advisory in the reference method.

15.5.1.3. Spike acceptance criteria are method, matrix and concentration level specific

(e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no specific acceptance criteria are available, the closest approximation of available acceptance criteria may be used for advisory purposes only.

15.5.2. When an BSD is analyzed, relative percent difference (RPD) acceptance limits also apply, if specified by contract or quality system.

15.5.3. The RPD between spiked Aroclor concentrations in an BS and an BSD should be ≤ 30%. If the RPD exceed 30%, examine the surrogate recovery of the BS/BSD. Since the surrogate is a measure of extraction efficiency, if the RPD between the surrogate recoveries of the BS/BSD is ≤ 30% then no corrective action is necessary. If the surrogate RPD also exceeds 30%, submit the BS and all associated samples for re-extraction and reanalysis.

15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.6.1.1. MS spike recovery must fall within specified recovery acceptance limits or corrective action is required.

15.6.1.2. MS recovery acceptance criteria are determined statistically from historic laboratory data. Criteria specified by a method, ARI's client or a particular quality system (i.e. DoD-QSM) may supersede ARI's historic values.

15.6.1.3. When mandated by a particular quality system or contract-specific requirements, corrective actions is required in response to unacceptable MS criteria, even when the criteria are labeled as advisory in the reference method.

15.6.1.4. Spike acceptance criteria are method, matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no specific acceptance criteria are available, the closest approximation of available acceptance criteria may be used for advisory purposes only.

15.6.2. When an MSD is analyzed, relative percent difference (RPD) acceptance limits also apply, if specified by contract or quality system.

15.6.2.1. The RPD between spiked Aroclor concentrations in an MS / MSD must be ≤ 30%. If the RPD exceed 30%, examine the surrogate recovery of the MS/MSD. Since the surrogate is a measure of extraction efficiency, if the RPD between the surrogate recoveries of the MS/MSD is ≤ 30% then no corrective action is necessary. If the surrogate RPD also exceeds 30%, submit the BS and all associated samples for re-extraction and reanalysis.

15.7. Holding Times

15.7.1. Extracts should be analyzed within the extract holding time (40 days from the date of extraction.)

15.7.2. If re-extraction due to an out of control event requires that samples be re-extracted after

their extraction holding time has elapsed (seven days for water and fourteen days for tissues/solids) the analyst should analyze and report both extraction sets, whenever practical, distinguishing between the initial extraction and re-extraction on all deliverables. This will document that the samples were originally extracted within holding times and may allow for comparisons that will determine whether data quality was affected by the samples being analyzed out of holding.

15.7.3. If any extracts are analyzed after the 40-day extract holding time has elapsed, the analyst shall document this in the analytical notes accompanying the data so that it may be included in the narrative.

15.8. Analytical sequences

15.8.1. For GC and GCMS analysis; Analysts should not intersperse instrument blanks between samples and closing calibrations or method blanks. If instrument blanks are run between samples and QC samples or standards, then every sample in the job or the bracket must be preceded by an instrument blank. Also, QC samples should be run with their associated samples and; specifically, running all method and spike blanks at the beginning of an analytical queue prior to samples is strongly discouraged.

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16. Corrective Actions for Out of Control Events

16.1. Corrective actions may include any, but are not limited to, the following:

16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the analyst notes.

16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.3. Repreparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.4. Reanalysis – the extract aliquot that was originally prepared is reinjected and run on the gas chromatograph again.

16.1.5. Reextraction – a reextraction request is filled out (Form 0030F). PDF Copies of the form are provided to the extractions department, the project manager, the QA manager and the lab manager. The remaining sample is extracted.

16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in Element.

16.1.7. Recalibration – a new initial calibration is evaluated, and the associated samples

reanalyzed.

16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.

16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.

16.2. When an Initial Calibration (ICAL) RSD for an analyte exceeds 20%

16.2.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.

16.2.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option, and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all the data.

16.3. When an Initial or Continuing Calibration Verification (ICV/CCV) %D exceeds 20%

16.3.1. At the discretion of the analyst, a second ICV may be run after the failing ICV. If the second ICV meets all ICV criteria, then the sequence may begin.

16.3.2. If the second injection of the ICV fails, perform the appropriate corrective action(s) from section 16.1 and re-calibrate the instrument

16.3.3. DoD-QSM requires that %D for all analytes in both the ICV and CCV be ≤ 20%. For DoD analyses immediately analyze two consecutive ICVs or CCVs. This is not required; the analyst may default to Section 16.3.1.

16.3.3.1. When both ICVs/CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued

16.3.3.2. If either fails or two consecutive ICVs/CCVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.4. Internal Standards

16.4.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.2. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.

16.4.3. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.

16.4.4. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.4.5. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".

16.5. Surrogates

16.5.1. Examine the bench sheet to verify spiking levels are correct.

16.5.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.5.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.6. Method Blanks- Corrective action for a method blank which fails acceptance criteria may involve re-extraction and reanalysis of all associated samples and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.7. Blank spike/Blank spike duplicate Samples

16.7.1. Control limits for this method and defined in Element for all PCB analysis. Verify that the correct and appropriate control limits have been applied. Blank spikes and blank spike duplicates that do not meet the control limits must not be used solely to reject data.

16.7.2. Examine the bench sheet to verify spiking levels are correct.

16.7.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8. Matrix Spike/Matrix Spike Duplicates

16.8.1. Examine the bench sheet to verify spiking levels are correct.

16.8.2. Recoveries are advisory and should not necessarily result in re-extraction.

16.8.3. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.

16.9. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve; a dilution must be performed such that the analyte’s quantitated value is within the curve range.

16.9.1. Additional internal standard must be added to the diluted extract to maintain the

required 80 ng/mL of each internal standard in the extracted volume.

16.9.2. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

16.9.3. When peaks from an analyte saturate the detector:

16.9.3.1. The analyst should analyze an Instrument Blank consisting of clean solvent until the system has been decontaminated.

16.10. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.

16.10.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)

16.10.2. All QC limit issues (including continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

16.11. If contaminants (including target and non-target compounds) continue to cause significant interference, even after all relevant cleanups have been performed; the sample should be re-extracted at a level appropriate to the amount of contamination. The particular re-extraction level should be based on the initial analysis or pre-analysis GC-ECD screen. The experience and discretion of the analyst and section supervisor will be relied upon for re-extraction decisions. The PM will be notified if re-extraction at a different level is required.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Section 16.2 for guidance on dealing with initial calibration out-of-control events.

17.2. See Section 16.3 for guidance on dealing with initial and continuing calibration verification out-of-control events.

17.3. See Section 16.4 for guidance on dealing with internal standard out-of-control events.

17.4. See Section 16.5 for guidance on dealing with surrogate out-of-control events.

17.5. See Section 16.6 for guidance on dealing with method blank related out-of-control events.

17.6. See Section 16.7 for guidance on dealing with blank spike and blank spike duplicate related out-of-control events.

17.7. See Section 16.8 for guidance on dealing with MS/MSD related out-of-control events.

17.8. See Section 16.9 for guidance on dealing with over range related out-of-control events.

17.9. See Section 16.10 for dealing with particular circumstances out-of-control events.

17.10. See Section 16.11 for dealing with out-of-control events concerning contamination.

18. Waste Management

18.1. All extract and standard vials must be disposed of by placing them in the blue hazardous waste drum in the lab set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.

18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.

18.3. All spent charcoal must be disposed of by placing it in the charcoal disposal bin located in the hazardous waste room.

18.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

19.1. “Polychlorinated Biphenyls by Gas Chromatography”: Method 8082A, Test Methods for Evaluating Solid Waste (SW846), Revision 1, February 2007

19.2. EPA Method 608—Organochlorine Pesticides and PCBs

19.3. USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration Revision OLM03.1, August, 1994.

19.4. “Determinative Chromatographic Separations”: Method 8000C, Test Methods For Evaluating Solid Waste (SW-846), Revision 3, March, 2003.

19.5. Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 5.1, 2017

20. Appendices

20.1. Appendix 20.1: In-house PCB Quality Control Requirements

20.2. Appendix 20.2: Sulfur cleanup procedure

20.3. Appendix 20.3: Congener analysis by ECD

20.4. Appendix 20.4: Method 608 modifications

Appendix 20.1: PCB Quality Control Requirements

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	Corrective Action (see Section 17)	Flagging Criteria
Demonstration of capability (DOC). DOC requirements are outlined in ARI SOP 1017S.	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method.	ARI spike recovery QA limits	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria.	Not applicable (NA)
Method detection limit (MDL) study	At initial set-up and subsequently once per 12-month period; otherwise quarterly MDL verification checks shall be performed.	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study.	NA
Retention time (RT) window width for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	ARI uses a default retention time window of 0.05 minutes	NA	NA
Breakdown check (Endrin and DDT)	Run DDT's to check for possible DDT's in samples	NA	NA	Note possible DDT's in reviewer checklist
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	One of the options below: Option 1: RSD for each analyte ≤ 20% Option 2: non-linear regression: coefficient of determination (COD) r2 ≥ 0.99 (6 points required)	Correct problem then repeat initial calibration.	Flagging criteria are not appropriate.
Second source initial calibration verification	Once after each initial calibration	Value of second source for all analytes within ± 20% of expected value (initial source)	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat initial calibration.	Flagging criteria are not appropriate.
Retention time window position established for each analyte and surrogate	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	NA	NA
Retention time Window verification for each analyte and surrogate	Each calibration verification standard	Analyte within established window	Correct problem, then reanalyze all samples analyzed since the last acceptable retention time check. If they fail, redo ICAL and reset retention time window.	Flagging criteria are not appropriate for initial verification.

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	Corrective Action (see Section 17)	Flagging Criteria
Calibration verification (initial [ICV] and continuing [CCV])	ICV: Daily, before sample analysis CCV: After every 10 field samples and at the end of the analysis sequence	All analytes within ± 20% of expected value from the ICAL	ICV: Correct problem, rerun ICV. If that fails, repeat initial calibration. See section 5.5.10 and box 55. CCV: Correct problem then repeat CCV and reanalyze all samples since last successful calibration verification.	ICV: Flagging criteria are not appropriate. CCV: Flagging criteria are not appropriate.
Method blank	One per preparatory batch	No analytes detected	Correct problem, if required re-prep then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-qualifier to all results for the specific analyte(s) in all samples in the associated preparatory batch
Blank Spike (BS) containing all analytes and surrogates to be reported	One BS per preparatory batch	ARI BS control limits	Correct problem, then re-prep and reanalyze the BS and all samples in the associated preparatory batch, if sufficient sample material is available.	If corrective action fails and there is insufficient sample material; report and discuss in the case narrative.
Matrix spike (MS)	One MS per preparatory batch per matrix.	ARI MS control limits	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the MS sample, apply *-qualifier if acceptance criteria are not met.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	ARI MS and %RPD control limits	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the MSD, apply *-qualifier if acceptance criteria are not met.
Surrogate spike	All field and QC samples	ARI control limits	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	For the specific analyte(s) in all field samples collected from the same site matrix as the parent, apply *-qualifier if acceptance criteria are not met.
Confirmation of positive results (second column or second detector)	All positive results must be confirmed.		NA	Apply p1-qualifier if RPD > 40%. Discuss in the case narrative.
Results reported between LOD and MRL	NA		NA	Apply J-qualifier to all results between LOD and MRL.

20.5. Mercury Clean-up

20.5.1. Elemental Sulfur is precipitated from the sample extract using elemental Mercury which forms the insoluble salt HgS.

20.5.2. This procedure is performed only when the presence of elemental sulfur is indicated in initial sample analyzes and is performed by GC analysts in addition to the Sulfur removal using TBAS performed in the Organic Extractions Laboratory following ARI SOP 334S “Sulfur Removal”.

20.5.3. Using a syringe insert a drop (~0.05 mL) of elemental Mercury into the autosampler vials containing the sulfur contaminated extract(s) and all associated QA sample extracts.

20.5.4. Shake the vials for approximately 30 seconds each using a “Vortex” type shaker.

20.5.5. Let the vial stand for 15 to 20 minutes to allow the precipitate to settle.

20.5.6. Repeat steps 20.2.3 through 20.2.5 until no additional dark precipitate is produced.

20.5.7. When the precipitate has settled, the vial may be placed in the autosampler tray for re-analysis.

20.5.8. Following analysis, dispose of the Mercury contaminated vial in the designated container in Fume Hood 34.

20.6. Appendix 20.3 - PCB Congeners by GC/ECD - ARI Method based on 8082A

20.6.1. This procedure summarizes ARI's protocol for identifying and quantifying specific Polychlorinated biphenyl congeners that in technical mixture compose PCB Aroclors. A variety of matrices may be analyzed including soils, solids, waters, tissues, and waste products (oils, sludges)

20.6.2. Congener analysis is recommended for samples containing multiple Aroclors that are indistinguishable from the patterns used in method 8082A

20.6.3. Detection limits-will depend on the amount of sample extracted and the final effective volume.

20.6.4. η

η

20.6.5.

20.6.6. Compound identification is based on a dual column analysis.

20.6.7. The columns used are Restek STX CLP1 0.32mm ID x 30m x 0.32µm and STX CLP2 0.32mm ID x 30m x 0.25µm.

Appendix: 20.4 Modifications Required for EPA Method 608

20.4 Modification Required for EPA Method 608 (These modifications are only implemented when specifically requested by a client, otherwise Method 608 is analyzed as described in previously in this SOP)

20.4.1 The Initial Calibration for Method 608 is a minimum of 3 points instead of 5 the 5 required in
Method 8082A.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

ICP Analysis
Perkin Elmer DV
EPA SW-846 6010C
EPA 200.7

SOP 540S
Version 010.1

Revision Date: 2/23/17
Effective Date: 2/23/17

Prepared by:

Jenifer L. Bouldron/Jay Kuhn

Approvals:

Eric Larson, Inorganics Division Manager

David R. Mitchell, Quality Assurance Manager

Annual Review

SOP Number: 540S

Title: ICP Analysis Perkin Elmer DV EPA SW-846 6010 or EPA 200.7

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This SOP will cover the analysis of trace metals by inductively coupled plasma spectroscopy (ICP). This method is applicable to all matrix types including drinking water, groundwater, aqueous samples, TCLP and other extracts, industrial and solid wastes, sludges, sediments, and soils.

1.2. All samples, except filtered acid preserved groundwater and extracts plus drinking waters with a turbidity of <1 NTU, will be digested prior to analysis. See appropriate digestion and prep SOPs.

1.3. The procedures, with some modification, follow those given in SW-846 6010C, EPA 200.7, and EPA CLP 200.7M.

1.4. Table 8 lists all applicable elements with their corresponding wavelengths, linear concentration range, reporting limits, and if the element is viewed axial or radial.

1.5. The instruments used for this procedure will be a Perkin Elmer Optima 4300 dual view simultaneous ICP and a Perkin Elmer Optima 7300 dual view simultaneous ICP.

2. Summary of the Procedure

2.1. The Optima 4300DV and 7300DV are simultaneous ICPs with 2 segmented array charge coupled devices (SCD) detectors allowing the detection of numerous wavelengths. An autosampler allows for unattended operation of the ICP and for automated shutdown of the ICP. For each analytical run, the ICP is first calibrated, then QC solutions are checked. After the calibration and QC solutions are verified to be in control, samples are analyzed. Periodic maintenance, optimization of the ICP torch and optics will be described in detail. The biannual procedures for linear limit checks and IEC updates, and the quarterly MDL checks are also described.

2.2. Inductively coupled argon plasma spectrometry (ICP) is an analytical technique based on the measurement of atomic and ionic emission of trace elements by optical spectrometry. By employing a high energy excitation source, a radio-frequency inductively coupled argon plasma, efficient atomization and ionization are achieved. A peristaltic pump evens the flow of sample to the nebulizer, which forms an aerosol that is partially transported to the plasma where desolvation and excitation occur. Characteristic atomic and ionic line spectra are produced by this process. The spectra enter the spectrometer through an entrance slit, then are dispersed by a diffraction grating into separate lines directed to specific locations on the appropriate SCD. 2 SCDs cover wavelengths from 165 to 782nm. The Optima Dual View ICP is designed so that the plasma can be viewed in both axial and radial orientations, which improves detection limits (using axial view) while preserving the extensive linear range (using radial view) for which the ICP technique is known. This wide dynamic range allows for the measurement of concentrations

ranging from 1 ppb to 5000 ppm. Two analytical lines are used for sodium, allowing both a low detection limit and a higher linear limit, which would not be possible using a single analytical line. Background correction and inter-element correction factors are applied, as required, for each analytical line before the reading for each element is displayed and printed. The complexity of the emission spectra and background spectra requires extensive characterization research during the initial methods development period. Scandium is used as an internal standard to compensate for physical interferences: viscosity and surface tension effects in the uptake system, and plasma effects. The element chosen for the internal standard should be a non-analyte element and one which will not be present in the samples. The internal standard is added to all blanks, standards and samples using an on-line mixing block or a "T" between the peristaltic pump and nebulizer.

3. Definitions

3.1. ICP-OES: Inductively Coupled Argon Plasma - Optical Emission Spectrometry

3.2. ICP: ICP-OES abbreviated to ICP for this document.

3.3. IDL: Instrument Detection Limit. Three times the standard deviation of ten replicate measurements of a blank solution.

3.4. RL: Reporting Limit. The RL is the lowest value at which a given analyte is reported. The RL is based on the IDL, MDL, method efficiency, and analyst's judgment. The RL will, at minimum, equal the statistical MDL.

3.5. MDL: Method Detection Limit. As defined in CFR Appendix E Part 136; 3.14 times the standard deviation of seven replicate measurements of a low level standard or sample that has been digested.

3.6. CRDL: Contract Required Detection Limit. Contract specified minimum levels of detection.

3.7. ICV: Initial Calibration Verification. A second source standard analyzed immediately after calibration to verify the accuracy of the calibration.

3.8. CCV: Continuing Calibration Verification. A second source standard analyzed after every group of 10 samples and at the end of the day to verify calibration accuracy during the analytical run.

3.9. ICB: Initial Calibration Blank. A calibration blank analyzed immediately after the ICV to verify the baseline of the calibration.

3.10. CCB: Continuing Calibration Blank. A calibration blank analyzed immediately after every CCV to verify the baseline of the calibration.

3.11. Analytical Batch: An analytical batch will consist of no more than 20 samples.

3.12. MB: Method Blank. An aliquot of deionized water (Type I) taken through the sample

preparation procedure with each analytical batch.

3.13. MBSPK/LCS: Laboratory Control Sample. A reference sample of known concentration processed along with the analytical batch to test the digestion procedure for accuracy.

3.14. MS: Matrix Spike. A sample prepared by adding a known amount of analyte to a specified amount of sample matrix. Matrix spikes are used to determine the effect of the sample matrix on the method's recovery efficiency.

3.15. MSD: Matrix Spike Duplicate. A second replicate matrix spike sample prepared and analyzed as above (Sec.3.14) to measure precision with respect to a given matrix.

3.16. Duplicate: Matrix Duplicate. A second replicate matrix sample prepared and analyzed with a sample batch to measure the precision with respect to a given matrix.

3.17. ICSA, ICSAB: Interference Check Solutions. The ICSA solution contains interference elements, at levels often found in samples, to test the interelement correction factors (IEC). The ICSAB solution contains the same elements as the ICSA at the same concentrations plus analytes at moderate levels, to test the accuracy of analyte measurement in the presence of interferents.

3.18. CRI: Low Level Check Standard. This low level standard is at the RL.

3.19. Internal Standard. A non-analyte element added to all samples, blanks and standards, which is used to compensate for physical interferences, both in the uptake system and in the plasma.

3.20. SD: Standard Deviation

3.21. RSD: Relative Percent Standard Deviation. The SD divided by the mean, multiplied by 100.

3.22. RPD: Relative Percent Difference. The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.

3.23. %R: Percent Spike Recovery. The difference between the matrix spike concentration and the background sample concentration, divided by the concentration of the spike added, multiplied by 100.

3.24. Carryover: The effect of a high level sample on a lower level sample which follows. Residual analyte from the high level sample may be remaining in the uptake lines, in the nebulizer, in the spray chamber or in the injector. A lower level sample which follows may show successively decreasing replicates (high SD or RSD). Carryover may also be referred to as a memory effect.

3.25. IEC: Inter-element Correction Factor. An empirically determined correction factor based on the spectral interference of another element at each analytical line.

3.26. Analysis Protocols:

3.26.1. Routine or Package: - Follows SW-846 6010C and EPA 200.7 If the analysis comment is Package (PKG), a data package will be generated from the Routine analytical run and the Routine QC samples. Other modifications that are necessary for certain quality

assurance plans and/or agencies will be detailed in individual sections.

3.26.2. CLP-Q - Follows Routine protocol with CLP-type and DOD QC standards analyzed at CLP QC frequency, in order to generate a CLP-type data package.

4. Interferences

4.1. Spectral Interferences:

4.1.1. Overlap of a spectral line from another element or molecular band spectra. This can be compensated for by using computer correction of raw data. This requires the monitoring and measurement of the interfering element(s). These corrections are set up using the IEC (Inter Element Correction) routine.

4.1.2. Background contributions from continuous or recombinant phenomena, and/or background contribution from stray light from the line emission of high concentration elements. This may require the selection of an alternative wavelength or selection of background correction adjacent to the analytical line.

4.1.3. Physical Interferences: Effects generally associated with sample nebulization and transport processes especially in samples which contain high dissolved solids and/or acid concentrations. The use of a peristaltic sample pump and a mass flow controller helps to minimize these effects. Internal Standard addition is used to monitor and compensate for moderate physical interferences.

5. Safety

5.1. The toxicity or carcinogenicity of each reagent used in this SOP is not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.

5.2. Always wear appropriate PPE (personal protective equipment) when working in the Metals Preparation Laboratory. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, etc. are provided for your protection

5.3. DO NOT attempt to cleanup acid spills in the laboratory. Immediately evacuate the area and contact a member of the Emergency Response Team (ERT).

5.4. Material Safety Data Sheets (MSDS) that outline hazards, exposure treatments and regulatory guidelines are available for all chemicals used in this procedure and should be consulted as the need may arise. The MSDS file is located in the central project management area. MSDS are also available online, at http//hazard.com/MSDS/.

5.5. Environmental Samples may contain hazardous waste; treat them as potential health hazards.

5.6. Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use glassware that is chipped, cracked, etched, or scratched.

Glassware with minor damage should be set aside for repair.

5.7. Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

5.8. All acid and sample waste must be disposed following the ARI Waste Management Plan.

6. Equipment and Supplies

6.1. Instrument – There are two Perkin Elmer Dual View ICP instruments an Optima 4300 and an Optima 7300. Both consists of a eschelle-based polychromator with a resolution of 0.006nm at 200nm, a solid state RF power generator, an axial and radial (dual view) inductively coupled argon plasma with shear gas, 2 SCD detectors, and a 190 or 200 position autosampler. The optical system is purged and thermostatted to minimize calibration drift. The main difference between the two instruments is that the Optima 7300 is equipped with and ESI Fast autosampler whereas the Optima 4300 has a standard XY Perkin Elmer AS93 autosampler.

6.2. Software – Optima 7300 WinLab 32 for ICP Version 5.1 with ESI SC Version 2.2.11.27. Optima 4300 WinLab 32 for ICP Version 4.02.0380.

6.3. Argon Supply - Argon is supplied from a liquid argon system of high purity argon (99.997% pure) with an110 psi operating pressure set at the regulator behind the instrument.

6.4. Consumables - Spare ICP parts are stocked in the lab to minimize downtime. Lab consumables include 13 X 100 mm polystyrene sample test tubes, Kimwipes, pipette tips, plastic beakers, Gelman IC syringe filters, polyethylene-only syringes (no rubber seals), 50 mL polyethylene centrifuge tubes, peristaltic pump tubing, tubing, tubing connectors and autosampler probes.

6.5. Labware

6.5.1. Glass volumetric flasks, class A

6.5.2. Glass volumetric pipettes, class A

6.5.3. Polypropylene volumetric flasks, class B

6.5.4. Adjustable pipettes covering the range: 5 µL to 10 mL

6.5.5. 5 mL reagent pipette

7. Reagents and Standards

7.1. Reagents

7.1.1. Trace grade concentrated nitric acid

7.1.2. Trace grade concentrated hydrochloric acid

7.1.3. Deionized water produced ARI's deionized water system. The deionized water system produces ASTM Type I reagent water (>18.3 megaohm). Monitoring of the deionized water quality is performed daily by conductivity, weekly on the ICP and approximately bimonthly

on the ICP-MS.

7.2. Standards: All standards must be labeled with the analyst's initials, preparation date, expiration date, and standard identification number (from the standard section of Element). The preparation of all standards and analytic solutions must be documented in the standard section of Element.

7.2.1. Calibration Standard Stocks: The four multiple element stocks are prepared based on chemical stability and on spectral compatibility. They are prepared from Inorganic Ventures ICP grade (at least 99.9% purity, ideally 99.999% purity) single element 10,000 mg/L stocks. Class A glass volumetric flasks and glass volumetric pipettes are used. Prepare each stock, as needed, using the volumes listed in Table 1. Note: for the Standard 4 stock, use a polypropylene volumetric flask and a Pipetman pipet.

7.2.2. Calibration Standards: The calibration stocks are diluted to working levels (Table 2) for the elements and the concentrations of each calibration standard on the first day of the work week. Polypropylene volumetric flasks are used for the calibration standards preparation. Four multiple element standards are prepared in a 5% hydrochloric acid and 5% nitric acid matrix. For standards 2, 3, and 4, use 2.0 mL of the appropriate stock in 100 mL final volume. For standard 5 use 4.0 mL of standard 5 stock in 100 mL final volume.

7.2.3. Calibration Blank: The ICP calibration blank is a solution of 5% hydrochloric acid and 5% nitric acid in DI water. The solution should be prepared as necessary and the flask should be labeled with the analyst's initials, preparation date and the standard identification number. This standard is also used as the ICB and CCB and for diluting samples.

7.2.4. CRI Solutions: The CRI Stock is prepared using the volumes and matrix listed in Table 3. The CRI solution (each analyte at the RL, except Na330) is a 1/2000 dilution of the CRI Stock.

7.2.5. Calibration Verification (CV) Solution: The Optima CV solution is prepared as needed using 2 multiple element, second source stocks: AR-ICPCV-2 and AR-ICPCV-5. These are diluted 1/100 in a 5% hydrochloric acid and 5% nitric acid matrix (see Table 5). The same solution is used for both the ICV and the CCV.

7.2.6. ICSA and ICSAB Solutions: The ICSAB stock and the ICSA solution are prepared using the volumes and matrix listed in Table 6. The ICSAB solution is prepared as the ICSA, with the addition of ICSAB stock and Sb 1000 mg/L using the volumes and matrix listed in Table 6.

7.2.7. Internal Standard Solution: The internal standard solution for the Optima 4300 is a 20 mg/L scandium standard, for the Optima 7300 it is a 10mg/L scandium standard. Use 2.0 or 1.0 mL of 10,000 mg/L scandium stock in a 1000 mL volumetric flask, in a 5% hydrochloric acid and 5% nitric acid matrix.

8. Sample Collection, Preservation, Shipment and Storage

8.1. All samples should be received in appropriate collection containers and have been properly preserved by the clients.

8.2. Samples are checked for proper preservative and stored refrigerated for a maximum of 180 days prior to sample preparation.

8.3. All samples received for dissolved metals analysis should be unpreserved at the time of receipt. They should be filtered through a 0.45µm filter prior to preservation.

8.4. All samples requiring preservation in the lab will be allowed to stand with refrigeration for a minimum of 24 hours after preservation before preparation and analysis is performed. In some instances, this may not be possible and the project manager and client will need to be notified.

8.5. Some samples are shared with the organic extractions and or conventionals laboratories. Sample receiving places these samples in a share bin in Refrigerator 5. SOP 1019S includes procedures for handling shared samples

9. Quality Control

9.1. Documentation

9.1.1. Instrument logbooks

9.1.1.1. ICP Sample logbook is used as a daily run sequence log and includes all solutions in an analytical run whether the data is reported or not. It also includes specific notes made by the analyst for that run. For example: notes on samples for dilutions or other issues, notes on QC samples and limits, and notes pertaining to instrument performance.

9.1.1.2. ICP Maintenance logbook contains notes on periodic checks of instrument performance (i.e. low intensities, high Internal Standard levels etc.) as well as all maintenance procedures.

9.1.2. ICP Files

9.1.2.1. Calibration. The daily calibration slopes printout is filed along with the Hg Profile results done prior to calibration (includes Hg line intensity, Drift, peak offset, and adjustment).

9.1.2.2. Interelement corrections/Linear limits. Contains the raw data and calculations for IEC adjustments and Linear Range checks.

9.1.2.3. IDL File. Contains raw and tabulated data for instrument detection limit determinations.

9.1.2.4. MDL File. Contains raw and tabulated data for Method detection limit determinations.

9.1.2.5. Standard Certificates. Contains current and previous Certifications for all Inorganic

Venture Standards as well QC Standards obtained from other sources.

9.1.2.6. Methods File. Contains all methods and method updates. (Also archived on the server computer.

9.2. Internal Standard. Scandium is used as an internal standard to compensate for physical interferences including viscosity and surface tension effects in the uptake system and plasma-loading effects due to high dissolved solids. The internal standard is added to all standards, blanks, and samples using an on-line mixing device (a mixing block or "T") between the peristaltic pump and nebulizer.

9.3. Calibration Standards. All standards are prepared weekly by dilution from known intermediates and verified by the analysis of certified QC standards obtained from an independent source (Section 9.3.3).

9.3.1. Calibration verification must be performed immediately after calibration with an Initial Calibration Verification Standard (ICV) and after every 10 samples and at the end of the analytical run with a Continuing Calibration Verification Standard (CCV). The ICV and CCV must be made from a source other than that used for the preparation of the standard curve and at a concentration different from the calibration standards.

9.3.2. Calibration Verification Blanks are analyzed to confirm the absence of blank contamination, baseline drift and/or carryover. Immediately after the ICV and after every CCV a Calibration Verification Blank (ICB/CCB) must be analyzed.

9.3.3. Independent QC Solutions. This standard is not required by the methodology but is used to check the calibration stock standard stability, concentrations and preparation. Typically, the elements are divided between two solutions for chemical stability. They are analyzed weekly, on the day new calibration standards are prepared.

9.4. A reporting limit standard (CRI) is analyzed following calibration verification for each element. The standard is used to verify the analytical performance of the instrument at the low end of the calibration or reporting limit.

9.5. Interference Check Solutions (ICSA/ICSAB). The interference check solutions, ICSA and ICSAB (see table 6), are analyzed to check the accuracy of commonly applied IECs. The ICSA solution contains aluminum, calcium, iron and magnesium (the common interfering elements) at high levels. The ICSAB contains these interfering elements at the same levels and 16 analytes at 1.0 mg/L. These solutions check the spectral interferences that are commonly present in environmental samples. These standards are analyzed after calibration verification.

9.6. Serial Dilution. A five-fold serial dilution (1/5 if the sample could be analyzed undiluted, 1/25 if the sample required 1/5 dilution) should be performed on any new or an unusual sample matrix. This dilution test will help identify if matrix interference is present. The dilution is

performed on a sample, typically the sample used for matrix QC, from each group of samples of a similar prep code for each sample digestion batch. The serial dilution should not be performed on a field blank or equipment blank. Some projects, including DOD, require a serial dilution be performed on at least one sample in their batch.

9.7. Post Digestion Spike. A post digestion spike should be performed on a new or an unusual sample matrix, along with the serial dilution (Section 9.6). This sample is intended to help identify matrix interference problems. Some projects, including DOD, require that a post-digestion spike be performed on at least one sample in their batch. The spike should be done on the same sample used for matrix QC within the batch. For CLP type samples this spike is required only for elements that are out of control in the Matrix Spike sample. For DOD type samples all requested elements must be spiked. For a post-digestion spike, an 8 mL aliquot of the background sample is pipetted into an acid and DI water rinsed centrifuge tube and 0.08 mL of the ICP routine spiking solution is added. Check the requested elements list for the specific elements to be spiked; some elements (antimony, boron, molybdenum, silicon, tin and titanium) are not included in the ICP spiking solution and require separate spiking. For most of these single element spiking solutions, 0.008mL or 0.016 mL of spiking solution is added to an 8 mL aliquot of sample. The spiking levels are the ICP spike levels unless the sample background level requires a higher spiking level. Fill out an “Unusual Instrument Spike” form if the spike sample requires higher spiking levels.

9.8. Matrix QC samples. With each preparation batch various matrix QC samples must be analyzed. At a minimum, a matrix spike, laboratory duplicate, method blank and a laboratory control sample should be prepared and analyzed. For some projects matrix spike duplicates, laboratory control sample duplicates, and/or certified reference materials may also be required. The analyst must check all paper work to make sure all necessary QC samples have been prepared and analyzed.

9.9. All logbooks are reviewed monthly for completeness and accuracy by the laboratory personnel.

9.10. The QA section will periodically review the standard preparation process, including standard bottles, logbooks and standard certificates and traceability to standardized sources.

10. Calibration and Standardization

10.1. Calibration is the process of establishing a linear relationship between emission intensity and concentration by analyzing a blank and four multiple element standards with a single concentration for each analytical line. As specified in EPA methods 200.7, 200.7CLP-M and SW-846 6010C, ARI uses a blank and a single standard concentration for each analytical line.

10.2. Calibration standards are prepared as described in Section 7.2.2 on the first day of the work week or more frequently if required.

10.3. Calibration Procedure

10.3.1. In the Automated Analysis Control window click on the Setup Tab, change the Results Data Set name by clicking [OPEN], then type in the filename using the format I#yymmdd (yy=year, mm=month, dd=day where I1yymmdd specifies the Optima 4300 and I2yymmdd specifies the Optima 7300). The Sample Information File should be set to CRISET.

10.3.2. Click on the Analyze tab. Put the internal standard uptake line into a full, well-mixed bottle of scandium Internal standard (20mg/L for the 4300 or 10mg/L for the 7300). Click on [Calibrate] to start the calibration. Review the Calibration Blank for adequate Sc sensitivity (compare to a previous calibration), good RSDs (<3%) and low intensities. After the calibration has been run, review the standards for both scandium %R (axial and radial) and good RSDs. Rerun any standards with RSDs >3% and scandium %R outside 90-110%.

10.3.2.1. To reanalyze a standard or the blank, close the Automated Analysis Control window, then open the Manual Analysis Control window. If the calibration blank is going to be reanalyzed, first rinse as described in section 10.3.2.2. Move the probe to the correct standard or blank tube, then with the correct standard number selected, click on [Analyze Standard] or [Analyze Blank]. After each solution has been analyzed, return to the rinse station. Review the slopes against the previous calibration's slopes in the file drawer; if the slopes are <70% of these slopes, notify the supervisor.

10.3.2.2. Move the probe to the mixed 10% nitric acid and 10% hydrochloric acid rinse solution and allow it to rinse for 15 minutes for the 4300 with AS91 autosampler or up to 5 minutes for the 7300 with ESI FAST autosampler.

11. Procedure

11.1. Initial Methods Development. Before any samples can be analyzed an analytic method must be developed which will include the determination and setting of all necessary background correction points, determination of inter-element correction factors plus linear calibration ranges, and the determination of instrument and method detection limits.

11.1.1. Background correction is required for many elements due to background interference. Single element and multiple element solutions at or near the top of the linear range are scanned during the methods development period. Various sample matrices are also scanned. The resulting intensity vs. wavelength plots show that background varies

depending on the elements present or matrix of the sample. Overlays of the plots reveal where background correction points can be set with minimal interference. One effect other elements have on a given analyte is a constant elevation of the background continuum emission spectrum. It is virtually impossible to set background correction positions free from line interference. The best compromise is to choose background correction positions that are optimized for the common major elements' interference: aluminum, calcium, chromium, cobalt, iron, magnesium, manganese, molybdenum, titanium and vanadium.

11.2. Inter-element Correction Factors and Linear Limit Verification

11.2.1. Inter-element Correction Factors

11.2.1.1. Due to the spectral complexity of emission spectra, spectral overlap must be identified and corrected by the appropriate factors. All inter-element correction factors (IECs) are checked biannually for each element; Al, Ca, Fe and Mg may be checked more frequently, if indicated or major instrument repairs are made. The extent of spectral overlap is determined by analyzing an ICP grade single element standard at the linear limit and identifying apparent concentrations of other elements. ICP grade standards must be at least 99.9% purity, ideally 99.999% purity in order to avoid trace contaminants being identified as spectral interferents. The concentration of each of the standards for IEC determinations is at the linear limit as this maximizes the ability to detect interferences.

11.2.1.1.1. IEC Procedure. Click on the Workspace icon. Select IEC.wsp. Confirm that the method is the "background correction only" method. Type in a Results Data Set name; if the biannual IEC checks are going to be analyzed, choose a consistent name to be used for the multiple analytical runs. Calibrate as usual. Prepare each IEC standard (dilute fresh from the Inorganic Ventures stocks) at the concentration used in the last IEC check; most are at the linear limit though some will be higher based on instrument capability. There are several IEC autosampler tables which can be used or modified, if necessary. Baseline checks (CCBs) are required immediately after calibration and every sample to check for carryover and baseline shifts. A CCV should be run at the beginning and end of the run and periodically throughout the run. The IEC data can be compared to previous determinations to spot any discrepancies; any new apparent concentration is considered a possible standard contaminant. If contamination is suspected, first check the Inorganic Ventures standard certificate to find out if this is a known contaminant. If not, re-prepare the standard and reanalyze it. If the possible contaminant is confirmed again, then depending on the magnitude of the IEC, a new lot of stock standard may be required. After the IEC standards have

been analyzed, from the pulldown menu, select File | New | IEC Model. Then, from the pulldown menu, select Tools | IEC Model Builder. On the Setup tab, under Data Sets, click on [Open], then highlight the filename. On the Set Limits tab, in the "Minimum Concentration for Interference Correction" field, type in the RL except for As 0.01, Pb 0.01, Sb 0.025, Tl 0.025, Cr 0.0025, Zn 0.006 and Se 0.025 mg/L (also Na33 may need to be set higher due to baseline drift); for ScA and ScR, type 200%. On the Calculate Factors tab, click on [Select Samples], hold down the Ctrl key and click on each of the IEC standards to be calculated (they should be highlighted). Click on [OK]. For each IEC standard, in the Interfering Analyte column, select the wavelength required. The software will calculate the IEC: the apparent elements' concentrations are divided by the read value of the standard, then multiplied by 1000. Save the IEC file using the Save As function; if this is the biannual IEC update, name the file using the format IECX, X being the next number in the series. If this is a partial IEC update, create a temporary file for the IEC calculations, these IECs will then be edited into the latest biannual IEC table. On the Summarize Factors tab, print a copy of the IECs by clicking on [Print Factors]. Review the IECs for baseline shifts, contaminants, new IECs, etc. by comparing them to the IEC reference table; revise the IEC file as needed. Then if this is a partial IEC update, edit the IECs into the latest biannual IEC table. Note: when performing the edits, some IECs may now be zero that were previously values, so be sure to zero these. Click on the Workspace icon. Select Daily.wsp. Then, in the Method window, on the Process tab, Spectral Corrections subtab, under IEC Model, select the updated IEC file. Save the method. The IEC entries are then verified by the supervisor. The raw data is filed in the IECs and Linear Limits file, and the IECs printout is filed in the Optima IECs file.

11.2.2. Linear Range Verification. Linear range limits are determined during the methods development period, many of them are set below instrument capability, limited by other concerns, such as IEC accuracy and carry over. All linear limits (see table 8) are verified at least biannually, simultaneously with IEC checks, by analyzing each element at the linear limit and verifying that the concentration at the linear limit is linear, within 10% of the true value. If the concentration of each standard is not within 10% of the true value; remake and reanalyze the standard once. If the standard is still outside the 10% limit, recalibrating or lowering the standard concentration may be required. File the raw data in the IECs and Linear Limits file.

11.2.3. The instrument detection limit (IDL) is determined and verified at least quarterly for each element.

11.2.4. Detection and quantitation limits (DL and QL, respectively) are determined at least annually for each element as described in ARI SOP 1018, Determination of LOD, LOQ and RL.

11.3. Daily ICP Set-up

11.3.1. Preparing the uptake system and the torch

11.3.1.1. First check that the autosampler rinse bottle, containing a 5% nitric acid and 5% hydrochloric acid solution, is at least half full, and the waste level in the waste carboy is less than ¾ full.

11.3.1.2. Scandium is used as an internal standard to compensate for physical interferences including viscosity and surface tension effects in the uptake system and plasma-loading effects due to high dissolved solids. The internal standard is added to all standards, blanks, and samples using an on-line mixing block or “T” between the peristaltic pump and nebulizer. Verify that the internal standard reservoir if full of the Scandium solution prepared in section 7.2.7.

11.3.1.3. Replace the Sample and Internal Standard peristaltic tubing every 2 analytical runs; and the Drain tubing weekly or more frequently as required. Place each pump tubing line in the guides of the pump beds; ensure that the tubing is not twisted. For the 7300 with ESIFast the internal standard line (orange-green) is placed on the inside position, the sample tubing (black-black) is in the center position, and the waste tubing (red-red) is in the outside channel. On the 4300 AS91 the right side tubing is the waste line (red-red tubing), the center tubing is the internal standard line (red-orange tubing) and the left side tubing is the sample line (black-black tubing). Clamp the tubing in place with the tensioned pump bed clamps. Daily adjustment of the pump bed tension or pump speed is not usually required. The usual sample uptake rate for the 4300 is 1.8 to 1.9 mL/min and can be measured with a graduated cylinder and stop watch. If it is necessary to adjust the pump bed tension after new pump tubing is attached, use the adjustment screw on the pump bed clamp. With the pump ON, loosen the adjustment screw until an air segment does not proceed through the tubing, then tighten the adjustment screw until flow begins. Typically, a half turn tighter of the adjustment screw beyond this point is sufficient for a stable setting (look for a smooth flow rate of an air segment). The 7300 ESIFast has been experimentally optimized for loop size and pump speed and should not be changed. On the morning following an auto shutdown, the pump tubings should be unclamped for at least 1 hour. Alternatively, the tubings can be removed and saved in a bag labelled with as “used” (good for one more run), and new tubings can be installed.

11.3.1.4. On the PE4300 dry the injector adapter every day prior to starting the instrument. Remove the spray chamber from the injector adapter and insert a rolled up Kimwipe into the neck of the adapter to absorb any moisture that has accumulated. (Accumulated moisture can be blown onto the axial and radial windows during pre-ignition gas purging.)

11.3.1.5. The PE4300 torch injector should be changed after 3 analysis days.

11.3.1.6. If the computer is on, shutdown the computer (exit Windows, and turn off the computer); this is required daily to avoid software problems. Push the computer ON button. For the 7300 the ESIFast software should be opened and initialized before the Winlab software is opened. To open the ESIFast software, on the desktop click on the ESI icon and then “initialize”. To open the instrument software, from the desktop click on the WinLab32 icon. Wait for the software to connect the instrument to the autosampler and chiller. Then click on the Wrkspc (workspace) icon, select Daily.wsp on the 4300 or Fast.wsp on the 7300; this will open most of the windows required for operation.

11.3.1.7. The PE4300 autosampler (A.S 91) probe will move into the rinse station. Clamp the autosampler’s rinse station peristaltic pump tubing tension lever down (horizontally) and verify that rinse solution is filling the rinse station. Press <F11> to raise the probe and stop the rinse station pump. The pharmed tubings (2 types) of the autosampler rinse station peristaltic pump are replaced as needed (typically every 2 months); each tubing has 2 sections, so use each section 1 month before discarding them. There is a light oil for use with these tubings which should be applied to the tubing between the stops.

11.3.1.8. The ESI Fast autosampler for the PE7300 needs to be initialized and the carrier and IS solution probes (marked with blue and green tape) put into DI water before starting the plasma.

11.3.1.9. In the Plasma Control window, click on [ON], on the ON/OFF switch. Watch the plasma “light,” and note any lighting difficulties. Inspect the plasma and torch during the first minute for any abnormalities. Put the probes in the rinse solution bottle (5%HNO3 /5%HCL). Ensure that all of the peristaltic pump tubings are pumping solution correctly before leaving the room—if the waste line doesn’t pump out the accumulating solution, the spray chamber will overflow and the plasma will go out! Major maintenance could be required. Warm-up the instrument for 45 minutes.

11.3.1.10. AS91: Put the sample probe in the sampler holder and the IS tubing in the 20ppm Sc solution.

11.3.1.11. ESI Fast: Put the Carrier probe (blue tape) in the carrier soln. bottle and the IS probe (green tape) in the 10ppm Sc solution.

11.3.1.12. After the warm-up period, in the Spectrometer Control Window, click on **Hg**

Realign to perform a mercury profile. In the Spectrum and Results windows from the pull-down menu review the results. Print out the Spectrum and note the Offset, Drift, and Slit Adjustment values.

11.3.1.13. PE7300 with ESI Fast: Open the Blanks autosampler table (Blks.sif). Put Calibration Blank solution in position 1 on the autosampler tray and run several (5) blanks to rinse the sample loop. Note the IS level in the Blanks for stability and RSD levels below 3%.

11.4. Create a new results data set. In the Automated Analysis window, click the Setup tab. Click on Results Data Set then open. Enter the new data set name in the format: I(x)yymmdd, where x = instrument #, yy=year, mm=month and dd=day.

11.5. Proceed with calibration as outlined in Section 10.3. Make a copy of the calibration report, staple it to the Hg profile results and file.

11.6. Analyze the ICV and ICB standards. Confirm the standard recovery is within 10% (unless analyzing drinking water samples which requires the ICV to be within 5%) of the known value, and the ICB value is less than the RL. If these conditions are not satisfied analysis must stop, the problem corrected, the instrument recalibrated, and the Initial Standards rerun.

11.7. Analyze CRI Standard. Confirm the standard is within 50% of the known value (20% for DOD), or else problem must be corrected and CRI run within limits before samples may be analyzed.

11.8. Analyze ICSA/B Standards. Confirm the standards return values of less than the RL for all non-spiked elements (unless contamination can be documented), and within 20% of the known value for spiked analytes.

11.9. Samples Analysis

11.9.1. Samples Selection and Preparation

11.9.1.1. To select samples for a daily analytical run, refer to Element for prepared samples. Prioritize samples by due date and other considerations such as elements requested, whether a data package is required, digestion matrix, anticipated high levels, etc. A typical analytical run is started with water samples and leachates, then soil samples, queued from low levels to high levels (based on color or client history). Typically, a group of 20 samples is set-up at a time. On the first day of the work week (when calibration standards are prepared), analyze the weekly check of deionized water and the independent QC solutions, early in the analytical run.

11.9.2. Analytical Run Order

11.9.2.1. Routine. The analytical run order of 20 samples would be as follows: ICV, ICB, CRI, ICSA, ICSAB, CCV, CCB, 10 samples, CCV, CCB. Note that the CRI, ICSA, and

ICSAB are counted as samples so that if they are included in a sample group only 7 actual samples can be included. Arrange each group of 10 samples beginning with suspected low level samples, such as method blanks, and ending with higher level samples, such as matrix spikes and reference samples. An exception to this would be immediately after an ICSA and ICSAB, which may cause unacceptable carryover if low level samples requiring aluminum, calcium, iron, or magnesium follow it. A digestion QC group will typically be analyzed in the following order to facilitate acceptance limit checking: matrix duplicate, background sample, matrix spike, and reference sample.

11.9.2.2. CLP-Q. The analytical run order of 20 samples would be as follows: ICV, ICB, CRI, ICSA, ICSAB, 7 samples, CCV, CCB, 10 samples, CCV, CCB. Arrange each group of 10 samples using the Routine guidelines as described above.

11.9.2.3. DOD. The analytical run order should be as CLP-Q plus: a serial-dilution (a fivefold dilution must agree within 10% of the original determination) and a post-digestion spike is performed with recovery 80-120% of the expected result.

11.9.3. Label 13 X100 mm polystyrene test tubes with the sample ID and dilution in the order in which they will be analyzed. Pre-rinse the test tubes with 10% nitric acid, then with deionized water.

11.9.3.1. Pour each sample into its pre-rinsed test tube, taking care to avoid transferring particulates. Hotblock soil digestates are diluted at least 1/2. Filtration of digestates is required when suspended particulates are present; often these particulates are a light color that is difficult to see. Since the uptake system is susceptible to clogging in the tubing connectors or in the nebulizer, care should be taken to notice which samples require filtration. An alternative to filtration is centrifugation. To centrifuge, pour about 30 mL of each sample into a centrifuge tube, balance the tubes in the centrifuge, and centrifuge at 2000 to 2500 rpm for 5 minutes.

11.9.3.2. Samples requiring dilution, i.e. samples with element(s) above 90% of the linear limit or with high levels that are likely to have carryover effects, can often be anticipated by the appearance of the sample. Soil digestates with a dark yellow, green or orange color can be high in iron, copper, chromium, etc., and paint digestates are often high in lead; these samples are typically first analyzed at a 1/10 or greater dilution. TCLP leachates prepared with extraction fluid #2 are often high in calcium and typically require a 1/5 or greater dilution. Water digestates are often less predictable: color is often an indicator of high analyte levels, although some industrial dyes or paints are highly colored yet have relatively low analyte levels. Viscosity during the pipette transfer from the sample bottle to the sample tube can be an indicator of high salts; also dried salt crystals

on the sample tube cap threads indicate high salts. Also, a review of the client job list can indicate a client project with a history of high level samples.

11.9.3.3. Prepare all required serial dilution and post spike samples as described in sections 9.6 and 9.7.

11.9.4. Instrument or Analytical Spiking. Undigested water samples and digestates requiring post-digestion spiking are spiked at the instrument before the sample is analyzed. An 8 ml sample is pipetted into a centrifuge tube and 0.08 mL of the ICP routine spiking solution is added. Check the requested elements list for the specific elements to be spiked; some elements (antimony, boron, molybdenum, silicon, tin and titanium) are not included in the ICP spiking solution and require separate spiking. For most of these single element spiking solutions, 0.008 mL of 500 mg/L spiking solution is added to a 8 mL aliquot of sample. For Sb, use 0.016 mL of 1,000 mg/L; for Si, use 0.008 mL of 10,000 mg/L.

11.9.5. Analysis of Samples and Autosampler Table Preparation

11.9.5.1. After an acceptable calibration has been performed, the ICV, ICB, CRI, ICSA, and ICSAB are analyzed. The autosampler table for this has already been created as CRISET. After the post-calibration rinse (15 minute for the 4300 and ~5 minutes for the 7300), click on [Analyze Samples] to start the analysis of these samples.

11.9.5.2. To create an autosampler table, click on the Sample Info icon. From the pulldown menu, select File | New | Sample Info File. Select CRISET.sid from the “Available Designs” for the 1st group of 17 samples. Samples may be added to the sample table during analysis.

11.9.5.2.1. Enter the Element sample IDs. The dilution should be entered in the “Diluted to Vol” field. The Column Fill function (right click with the mouse) can be used for sequencing autosampler locations and to copy sample IDs. If Cut and Paste edits are performed, check that all the required fields are filled, especially “Diluted to Vol”, and “Volume Units” (mL). Also, carefully check the autosampler locations after cutting and pasting. An increased wash time can be entered if necessary.

11.9.5.2.2. After all the sample information has been entered into the table, from the pulldown menu, select File | Save As | Sample Info File. Type the filename using the format: mmdd.sif (mm=month, dd=day); a letter can be added after the day to indicate different files on the same date.

11.9.5.3. To analyze these samples, open the Automated Analysis Control window. Check that the Sample Information Filename is correct. Click on the Analysis tab. Click on [Analyze Samples] if the entire table is to be run. If only a partial group of samples from the autosampler table is required, the samples to be skipped can be deleted in the

Sample Info window, then save the autosampler table and analyze them in the Automated Analysis Control window. Alternatively, on the Set Up tab, “All Defined” can be changed to “Sample Nos”. Then the required samples can be typed into the “Sample Nos.” field as a range of samples or as specific samples: eg. 8-20 or 8,10,12. Remember to reset this to “All Defined”, after the samples have been run, for later tables.

11.9.6. Monitoring the Analysis

11.9.6.1. Periodically during the operation of the ICP, check the sample uptake flow, the appearance of the plasma, the level of solution in the autosampler QC vials, the autosampler probe position and the rinse bottle level. To pause the analytical run, click on [Analyze Samples], then choose from either [Stop Immediately] or [Complete All Replicates for Current Sample].

11.9.6.1.1. Method QC samples such as the CV and the CB should be monitored closely during the analytical run to check for calibration stability and baseline drift. If the CV and/or CB are outside or approaching the QC limits, then corrective action should be taken as soon as possible to minimize sample reruns. Corrective action could include recalibrating the blank or the appropriate standards, or extra rinsing time followed by another CV and CB.

11.9.6.1.2. Monitoring High Levels and Carryover. If any sample level is above the linear limit, the high level sample should be diluted and rerun (see table 8 for the linear limits). If high level samples are analyzed, carryover into the following samples may occur. Carryover usually exhibits high SD or RSD in the following samples. Sodium, lead and boron are prone to carryover. Pausing the autosampler after the high level sample and rinsing as needed can often minimize carryover. A blank may be analyzed as a sample to verify that adequate rinsing time has passed. Note: Some projects (DOD) require any sample analyte that exceeds the concentration of the calibration standard be diluted (see table 2 for standard concentrations). If required, appropriate instructions will be noted in Element and it is the analysts’ responsibility to follow the instructions and document the necessary dilutions on the raw data.

11.9.7. Partial Recalibration. During an analytical run, partial recalibration may be necessary. To reanalyze a standard or the blank, close the Automated Analysis Control window, then open the Manual Analysis Control window. Move the probe to the correct standard or blank tube, then with the correct standard number selected, click on [Analyze Standard], or click on [Analyze Blank]. After each solution has been analyzed, return to the rinse station. After the recommended rinse time, restart the analytical run with a CCV and CCB. Note: to reset the internal standard percentage of the calibration blank, a complete recalibration is

necessary.

11.10. Troubleshooting Instrument Problems during the run.

11.10.1. Clogs. The uptake lines and connectors should be monitored for clogs, which may form from sample particulates and from airborne particulates that can be in the autosampler vials, due to the nature of open vial autosampler operation.

11.10.2. Autosampler. The autosampler should be monitored for probe misses and tubing disconnections. The time that the plasma is running without any aerosol should be minimized.

11.11. ICP Shutdown. After completion of the autosampler run the instrument can be shutdown either manually or for overnight unattended runs automatically.

11.11.1. Manual (attended) Shutdown: Place the internal standard line in deionized water. Rinse the uptake system with the mixed 10% hydrochloric acid and 10% nitric acid solution for 10 minutes. Rinse with deionized water for 10 minutes. Remove the probe and the internal standard line from the deionized water bottle and let the lines pump dry. On the Plasma Control window, click on [OFF] on the ON/OFF switch.

11.11.2. Automated (unattended) Shutdown: On the Automated Analysis Control Window, click on [SET] next to Auto Shutdown. Click next to “Shutdown” and next to “At the End of Automated Analysis”. PE4300 only: Check that both “Wash Before Shutdown” and “Turn Off Plasma and Pump” are checked. Click on [OK] to complete the auto shutdown set-up. PE7300: add the “rinse set” to the end of the run (4 X’s Acid rinse and 4 X’s DI rinse). Click on OK to complete the auto-shutdown set-up.

11.11.3. Data storage: When the analytical run is done, the sample file should be exported for upload to Element. From the pulldown menu, select File | Utilites | Data Manager. Highlight the file name to be exported, then click on the Export icon. At #1, “Select Export Design”, click on [Use Existing Design], then click on [Browse] and select prnexpt . Advance to #4, “Select Export Options”, and enter the filename as I1yymmdd or I2yymmdd (yy=year, mm=month, dd=day). Advance to #8, “Export Data Set”, click on [Export Data], then click on [Finish].

11.11.4. Data Analysis and Calculations

11.12. The percent recovery for an aqueous LCS is calculated according to the following:

$$\%\ R = \frac{LCS}{s} * 100$$

Where:

%R: Percent Recovery

LCS: LCS, REF, or MBSPK Results

s: True concentration Data entry

11.13. Calculate the percent recovery for the matrix spike as follows:

$$\%\ R = \frac{C_s - C}{s} * 100$$

Where:

%R: Percent Recovery

Cs: Measured concentration in fortified sample matrix

C: Measured concentration in unfortified sample

s: Amount of analyte added to sample matrix

11.14. Calculate the RPD as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} * 100$$

Where:

RPD: Relative Percent Difference

D_1: Measured concentration of first sample

D_2: Measured concentration of replicate sample

12. Method Performance

12.1. Detection and quantitation limit studies are performed for all analytes as described in ARI SOP 1018, Determination of LOD, LOQ and RL.

12.1.1. The DLs must be lower than in-house QLs. If not, the QLs will need to be changed or the study replicated.

12.1.2. DLs and QLs shall be re-determined annually or following any change to the sample preparation procedure

12.2. Analytical accuracy is determined using LCS/MBSPK, SRM or MS analyzes. Acceptance limits for spike recovery are specified in the analytical methods and are normally 80 to 120% for LCS and 75 to 125% for matrix spikes. Acceptance limits for SRM analyzes are determined by the SRM supplier or manufacturer.

12.3. Laboratory precision is measured by performing replicate analyzes. Replicates (sample or matrix spike) acceptance limits are ± 20%.

12.4. Accuracy and precision acceptance limits are disseminated to the bench chemists and LIMS administrator for use in monitoring method performance in real time.

13. Pollution Prevention

13.1. All acidified sample waste must first be neutralized prior to sink disposal.

13.2. Dispose of expired standards into the designated barrel in the hazardous waste room.

13.3. Samples that are designated as hazardous waste by the LIMS “Hazardous Report” must be placed in the designated drum in the Hazardous Waste Storage Area when they are disposed. This process is described in SOP 1003S.

14. Data Assessment and Acceptance Criteria for Quality Control Measures

14.1. Data Review

14.1.1. The ICP raw data is reviewed by the analyst periodically during the analytical run and reviewed comprehensively before loading the data to Element. The data reviewer needs to be aware that there can be many project specific requirements and QC criteria that are not covered in this SOP. It is your responsibility to verify what QC limits are required for a specific project and make sure that the data is properly reviewed and that all necessary corrective actions are performed and documented.

14.1.2. Raw Data Review. Look through the raw data printout, highlighting the requested elements and concentrations of every client sample. Note on the instrument log and raw data any comments on instrument problems, delays, unusual occurrences, etc. Review the data for high levels, carryover, poor precision, method blank contamination, and any anomalies. All corrections should be initialed and dated. Also highlight any ICP-MS elements which are at concentrations higher than are feasible to be analyzed by ICP-MS. If any ICP-MS elements are switched or transferred to ICP analysis (with project manager approval), all associated QC samples must also be checked for that element (e.g. method blank, matrix duplicate, matrix spike, serial dilution, reference), and a “Transfer to ICP” form should be filled out.

14.2. QC Samples Review

14.2.1. Method QC solutions

14.2.1.1. Internal standards. The Sc internal standards intensity for each sample and standard must be within 70-130% of the calibration blank intensity with an RSD <3% to be acceptable. If the RSD is high review individual analytes and check SDs for acceptability. Reruns of samples can verify noise due to matrix effects. If the recovery is > 130% rerun effected samples. If the recovery is low <70%, the problem may be matrix related and samples should be rerun at dilution.

14.2.1.2. The calibration verification solutions ICV and CCV should be analyzed after initial calibration and again after every 10 samples are analyzed. The acceptance limits for the CVs are 90% to 110% of true values for each requested element; see table 5 for the concentrations of the CV solution elements. For drinking water samples analyzed with method 200.7 the ICV must be within 95% to 105% of the true value whereas all CCVs

have a control limit or 90% to 110%. If the concentrations are outside this range, the analyst should look for the possible cause. Corrective action should be taken immediately, typically recalibrating the appropriate standards, then after adequate rinsing the analytical run should be resumed with a CCV, CCB. All samples between the out-of-control standard and the last in-control standard must be reanalyzed. Samples must be bracketed by in-control calibration verification standards and blanks.

14.2.1.3. The initial calibration blank (ICB) is analyzed immediately after the ICV and the continuing calibration blank (CCB) is analyzed immediately after each CCV. The limits for the ICB/CCB are ± 1 RL for each requested element (see table 8 for RLs). DOD requires a control limit of 2 x MDL. It is the analysts' responsibility to verify which control limits are required for each batch of samples. All the appropriate information will be in the job folder and the raw data must be labeled as to which control limits are being used. If the concentrations are outside this range, the analyst should look for the possible cause (eg. calibration blank intensities too high, baseline drift, contamination, etc.). Corrective action should be taken immediately, typically recalibrating the blank solution, then the analytical run should be resumed with a CCV, CCB. All samples between the out-of-control blank and the last in-control blank must be reanalyzed. Samples must be bracketed by in-control calibration verification standards and blanks.

14.2.1.4. The interference check solutions, ICSA and ICSAB (see table 6), are analyzed to check the commonly applied IECs after calibration verification. For ICSAB solutions, QC limits are 80% to 120% of the true values for both interferents and analytes. For the ICSA, QC limits are 80% to 120% of the true values of the interferents and the apparent concentrations of non-spiked elements should be ± 2RL. DOD requires a control limit of <2 X MDL for non-spiked analytes (unless they are a verified trace impurity from one of the spiked analytes or a "common laboratory contaminant"). It is the analysts' responsibility to verify which control limits are required for each batch of samples. All the appropriate information will be in the job folder and the raw data must be labeled as to which control limits are being used. If any element(s) is outside these limits, it should be noted in the ICP logbook and the supervisor should be notified. If the out of limits reading is reproducible, the possible interference elements should be verified by analyzing single element linear limit standards and all IECs should be updated in the method.

14.2.1.5. CRI or reporting limit standard (see table 4) verifies the accuracy of the instrument at the RL for all analytes. This standard should be within 1/2 RL of the true value. DOD requires that the CRI to be within 20% of the true value. If required, appropriate

instructions will be in the job folder and it is the analysts' responsibility to follow the instructions and document the necessary control limits on the raw data. If the concentrations are outside the specified range, the analyst should look for the possible cause (eg. calibration blank intensities too high, baseline drift, contamination, etc.). Corrective action should be taken immediately, typically recalibrating the blank solution, then the analytical run should be resumed with a CCV, CCB, CRI, ICSA, and ICSAB. The CRI should be analyzed immediately before each ICSA / ICSAB.

14.2.1.6. Serial Dilution. A five-fold serial dilution is performed on a sample, typically the sample used for matrix QC, from each group of samples of a similar prepcode for each sample digestion batch. The serial dilution should not be performed on a field blank or equipment blank. If the analyte concentration is >10X the RL in the diluted sample, then the serial dilution sample should agree within 10% of the undiluted sample. If the analyte is outside the 10% limit, a matrix effect should be suspected. Fill out a green analyst notes form so the data can be qualified. DOD require a serial dilution be performed on at least one sample in their batch.

14.2.1.7. Post–digestion spike. A post spike is performed when matrix problems are suspected or on one sample in each batch for DOD samples. The sample is spiked at normal ICP levels or higher if necessary. The spike should be recovered at 80% to 120% or matrix effects should be suspected. Fill out a green analyst notes form so the data can be qualified.

14.2.2. Digestion / Batch QC Samples

14.2.2.1. Method Blanks. A method blank (MB) is prepared with every client batch of samples of 20 or fewer samples, and for each preparation type. The method blank must be < RL for every requested element. DOD requires a control limit of <1/2 the RL except for common laboratory contaminants. If required, appropriate instructions will be in the job folder and it is the analysts' responsibility to follow the instructions and document the necessary control limits on the raw data. Before corrective action is taken, rerun the method blank for confirmation. Also the baseline (CB) should be checked; if outside the limits, recalibrate the blank, analyze a CV and CB, and then reanalyze the method blank. If the detected element is greater than the limit, then all the associated samples must be re-digested and reanalyzed unless all samples are greater than 10 times the detected method blank concentration or in the case of DOD projects undetected. DOD soil projects also require the use of Teflon boiling chips as a matrix in the blanks. The analyst should fill out a corrective action form and the supervisor should be informed when results are out of control.

14.2.2.2. Matrix / Digestion Duplicate. A duplicate sample is prepared to test the reproducibility of the analysis and sample homogeneity. The acceptance limits are based on the analyte concentration. A matrix duplicate is prepared with every client batch of samples of 20 or fewer samples, and for each preparation type. If both background and duplicate sample concentrations are at least 5RL, then the relative percent difference (RPD) should be ≤20%. If either the background or duplicate sample concentration is < 5RL, then the absolute difference between the two concentrations should be 1 RL or less. For soil and tissue samples, the sample concentrations must be calculated in mg/Kg units. If a duplicate RPD is outside the acceptance limits, then a corrective action form should be filled out by the analyst and the supervisor should be informed.

14.2.2.3. Matrix / Digestion Spike. A matrix spike sample is spiked before digestion to detect losses during digestion and matrix effects on digestion efficiency. If the sample does not require digestion, it is spiked at the instrument. A matrix spike is prepared with every client batch of samples of 20 or fewer samples, and for each preparation type. The QC limits for spike recovery are 75% to 125%, or 80% to 120% for DOD projects. If the sample concentration is greater than 4X the spike added concentration, there are no QC limits; the matrix spike report will be flagged with an H flag indicating that the spiking level is not appropriate. For soil and tissue samples, the sample concentrations must be calculated in mg/Kg units, including the spike added; the “spike added” mg/Kg calculation, uses the spike sample weight. Antimony is difficult to recover from soil digestates; these are rarely re-digested and reanalyzed. If the matrix spike recovery is outside the QC limits, then the analyst should fill out a corrective action form, the data will be flagged and the supervisor should be informed. The background sample, the matrix duplicate and the matrix spike may be re-digested and reanalyzed. For CLP-Q type samples out-of-control spikes a post-digestion spike is performed (see Section 9.7).

14.2.2.4. References/MBSPK (LCS). A reference sample or an MBSPK/LCS (method blank spike/laboratory control sample) is a sample of known and/or certified analyte concentrations, is prepared with every client batch of samples of 20 or fewer samples, and for each preparation type. Water and soil references are used. For a water reference or for an MBSPK, the QC limits are 80% to 120%. Drinking water analysis by method 200.7 requires a control limit of 85% to 115%. For a soil reference, the certified ranges are used as QC limits (though a client may specify other limits). For soil and tissue samples, the reference concentrations should be calculated in mg/Kg units. If the recovery is outside the QC limits, then the entire sample batch must be re-digested and

reanalyzed. The analyst should fill out a corrective action form, and the supervisor should be informed.

14.3. Samples Review

14.3.1. Precision Criteria

14.3.1.1. For most elements that occur in samples at moderate (≥ 10RL) to high concentration levels, including both views of Sc (ScR and ScA), the RSD of the 3 replicates should be less than 3%. For elements that occur in samples at low concentration levels (<10 times the RL), the SD should be ± 1RL. Exceptions should be noted in the Log Book along with resolutions (i.e. reruns, comparison with previous results).

14.3.2. Carryover

14.3.2.1. Carryover is the effect of a higher level sample on a lower level sample which follows, causing the lower level sample to read higher than it would otherwise. The SD or RSD will sometimes be higher than normal in these cases. Sometimes high level carryover does not exhibit elevated SD or RSD, but is only evident in the blank as a consistently high level (all replicates higher than usual). Samples that are affected by possible carryover should be reanalyzed. The common carryover elements are boron, lead and sodium.

14.3.3. Linear Limit

14.3.3.1. All acceptable sample results must be less than 90% of the linear limit for each element in the sample. DOD projects require that no sample concentration exceeds the concentration of calibration standard. Samples that have any analyte concentrations (for both requested and non-requested elements) greater than 90% of the linear limit (or, on a project specific basis the calibration standard) should be diluted at the lowest possible dilution and reanalyzed.

14.3.4. Interelement Correction Factors. The interference check solutions may provide evidence of some IECs which need updating, if the QC limits for these solutions have not been met. Also samples may exhibit indications of IECs that may need slight adjusting: if a sample has a high level of an interferent element and other elements have concentrations that are negative lower than 2RLs. Also a wavelength scan of the sample could be performed to check for interference at the background correction point(s). Notify the supervisor of the problem so that it can be investigated.

14.3.5. Rounding

14.3.5.1. The rounding rule is to round to the even number if the digit following those to be retained is 5 (i.e. 40.55 would round up to 40.6 where 40.65 would round down to 40.6).

For rounding CBs or low level samples to the RL, round to the RL with 1 significant figure (i.e. Sn 0.014 would round to 0.01, the Sn RL).

14.3.5.2. When evaluating whether a QC sample is in control round all results before calculating recoveries. In the case of method blanks, detection and/or non-detects are determined before the result is rounded.

14.4. ICP Sample Logbook Review

14.4.1. The logbook pages should be dated with the analytical run start date, numbered sequentially, and initialed/dated for corrections, if applicable. The calibration standard numbers should be listed in the comments column. If the samples are CLP-Q or PKG, the CCVs and CCBs should be numbered sequentially. If a sample is checked for deletion, there should be a comment explaining the reason for the rerun or the reason for the deletion. After checking the analytical run's logbook pages for completeness, photocopy the appropriate ICP sample logbook pages that correspond to the raw data. Check every sample label (job number, sample letter, prepcode) and dilution factor. Highlight the client sample edits, sample analysis deletions, and dilution factor edits on the logbook photocopies so that they are not missed during the data loading process.

14.5. The logbook photocopies, along with the highlighted raw data are scanned to the calibration in Element. Fill out the Reviewer Checklist in Element, noting any out of control QC, sample re-preps, etc.

14.6. Contingencies for Handling Out-of-Control or Unacceptable Data

14.7. Calibration: If the calibration does not meet the criteria in section 15, then corrective action shall be taken before proceeding with recalibration. This could involve uptake rate optimization, clog removal, re-preparation of calibration standards, etc.

14.8. Instrumental QC checks: If an instrumental QC sample (CV, CB, QCS, etc.) is out of control, then corrective action shall be taken before proceeding with analysis. This could involve recalibration of the blank (resetting the baseline), repreparation of calibration standards and recalibration, etc.

14.9. Instrument malfunctions: When instrument malfunctions occur, consult with other experienced ICP operators or the supervisor for guidance. The maintenance logbook, the ICP hardware manual, or the ICP software manual could be helpful for troubleshooting. If the problem cannot be resolved contact Perkin Elmer service for immediate service. The instrument is covered under a service contract.

14.10. In the event of significant QC failure, analysis will stop and the analyst will perform corrective action as discussed above. In general, out-of-control sample results will not be reported. Reruns will be conducted based on sample availability. If insufficient sample remains, the client will be

notified to determine an appropriate course of action.

14.11. All corrective actions will be clearly and completely documented on a corrective action form. All required maintenance and instrument repairs will be clearly documented in the ICP maintenance log.

14.12. In the event of a major instrument failure immediately inform the project managers so all critical samples can be subcontracted if necessary.

15. Waste Management

15.1. ARI's Laboratory Chemical Hygiene Plan (CHP) describes internal hazardous waste handling procedures. All analysts must be familiar with these requirements.

15.2. ARI properly profiles and disposes all hazardous waste using an EPA registered TSD (Treatment, Storage and Disposal) facility.

16. Method References

16.1. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 6010C, Revision 3, February 2007

16.2. USEPA, Environmental Monitoring Systems Laboratory Office of Research and Development, Method 200.7, Revision 5 1998

16.3. DOD Quality Systems Manual for Environmental Laboratories, Version 5.0, July, 2013

17. Appendix and Tables

17.1. Instrument Maintenance

17.1.1. All maintenance should be noted in the ICP maintenance logbook.

17.1.2. Uptake System Peristaltic Pump Tubings. See section 11.3.1.3.

17.1.3. Autosampler Peristaltic Pump Tubings. See section 11.3.1.7.

17.1.4. Injector maintenance. The torch injector on the 4300 is changed every 3 analysis days; the injector on the 7300 is changed less frequently but should be checked and inspected daily. Salt and carbon deposits accumulate on the tip resulting in increased carryover effects. The injector replacement procedure is described in the Optima Hardware Guide, page 5-14 (chapter 5, page 14). After removing the old injector, clean the injector adapter with cotton swabs dipped in deionized water. Replace the used injector with a cleaned and thoroughly dry injector. The used injector should be rinsed with deionized water, then soaked in a mixed solution of 10% nitric acid and 10% hydrochloric acid for approximately 1 hour and rinsed with deionized water; thoroughly dry in a warm place for 24 hours. After an injector change, the axial and radial plasma viewing positions should be optimized. When the instrument has completed the warm-up period, perform a Hg profile. To optimize

the axial viewing position, in the Spectrometer Control window under Plasma, click on [Axial]. Aspirate the 1 mg/L Mn solution, then click on [Align View] and Mn will appear as the default element. Watch the readings as they are displayed in the Results window; observe the peak intensity and check for adequate intensity. To optimize the radial viewing position, in the Spectrometer Control window under Plasma, click on Radial]. For the 4300 aspirate the 10 mg/L Mn solution, for the 7300 continue to aspirate the 1 mg/L Mn solution, then click on [Align View] and Mn will appear as the default element. Again, observe the peak intensity and check for adequate intensity. After both optimizations are complete, record the data in the maintenance log: x and y positions, and Mn intensities.

17.1.5. Bimonthly maintenance. Approximately every 2 weeks, the spray chamber, the nebulizer, the mixing block, the axial and radial windows, and the air filters are cleaned.

17.1.5.1. Spray Chamber. The spray chamber replacement procedure is described in the Optima Hardware Guide, pages 5-14 to 5-27. To clean the spray chamber, rinse it with deionized water, then soak it in a mixed solution of 10% nitric acid and 10% hydrochloric acid for 30 minutes. Rinse it thoroughly with deionized water; drying is not necessary before use.

17.1.5.2. Nebulizer. The nebulizer replacement procedure for the 4300 is described in the Optima Hardware Guide, pages 5-67 to 5-68. An indicator of nebulizer clogging is an elevated nebulizer back pressure reading (normal range 180-200). Remove the plastic threaded inlet nut and remove the brass nut with the attached argon line. Backflush the Gemcone nebulizer with DI water or Blank solution then rinse thoroughly with deionized water. Dry the argon and sample inlets with a Kimwipe® rolled into a pointed blotter. Using a fine tip deionized water bottle, squirt deionized water through the plastic inlet nut. Replace the plastic inlet nut and the sample line. Then dry the gas passages of the nebulizer by connecting the brass argon gas fitting and turning on the nebulizer argon flow to 1 L/min; allow 5 minutes to completely dry the gas passages. Reset the nebulizer argon flow to 0.5 L/min. **The PFA ST nebulizer for the 7300 must not be backflushed or sonicated.** It should be soaked in the ICP acid rinse solution and then in MeOH to remove deposits. If it is clogged the Obstruction Removal Kit can be used. Note: PFA ST nebulizers can be sent to ESI for repair.

17.1.5.3. Mixing Block. Using a fine tip deionized water bottle, squirt deionized water through the orifices of the mixing block after the 3 fittings have been removed. Squirt deionized water through each of the fittings and their attached connector tubings. Replace the fittings carefully—do not cross-thread them.

17.1.5.4. I.S. “T”. Flush with DI using a syringe with a luer-lock fitting. If clogged, replace

and send the clogged fitting to ESI for repair.

17.1.5.5. Air filters. There are three air filters, one on the back (left side) of the instrument, one on the right side of the instrument and one on the chiller. Replace these with the clean spare filters. Clean the dirty filters with warm water, then air dry them before storing them.

17.1.5.6. Optical Windows. The axial and radial windows should be cleaned along with the nebulizer and spray chamber. The axial window requires removal from the instrument for cleaning, see the Optima Hardware Guide, pages 5-38 to 5-40. Loosen the 2 set screws on the shear gas nozzle bracket; move the bracket to the left. Remove the axial window assembly, as described in the manual. To clean it, remove the axial window from its housing, use cotton swabs dipped in 10% nitric acid to clean the isolated axial quartz window, followed with deionized water rinsing. Dry the window with lens paper and thoroughly dry in a warm place for 30 minutes. Reassemble the axial window assembly and fit it into place. Move the shear gas nozzle bracket back into place with the slit 5 mm from the axial window and straight up and down then secure the 2 set screws. The radial window can be cleaned in place using lens paper and methanol (if necessary, it can be removed as described in the Optima Hardware Guide on pages 5-35 to 5-38).

17.1.6. Torch maintenance. The torch is changed infrequently; with normal use, it will get clouded with both white and black residues, which rarely affect performance unless they cause warping or cracking of the torch. The torch replacement procedure is described in the Optima Hardware Guide, pages 5-14 to 5-27. Replace the torch with a cleaned and thoroughly dry torch with a new copper foil sticker positioned over the hole; the spare torch may have some white clouding which is acceptable. Check for excessive deformation of the quartz around the cutout; there is a normal offset between the sides of the cutout. To clean the torch, sonicate it in 1% Citranox® solution for 15 minutes, then rinse with deionized water. Then soak it in a mixed solution of 10% nitric acid and 10% hydrochloric acid for 30 minutes. Follow this soak with deionized water rinsing, then thoroughly dry it in a warm place for 24 hours.

TABLE 1
Optima Calibration Stocks

ICP STD2 Stock

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Ba	5% HNO_3	10,000	5	100	500
Cd	"	10,000	5	"	500
Co	"	10,000	5	"	500
Cr	"	10,000	5	"	500
Cu	"	10,000	5	"	500
Mn	"	10,000	5	"	500
V	"	10,000	5	"	500

ICP STD3 Stock

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Ag	5% HNO_3	1,000	5	100	50
As	"	10,000	5	"	500
B	"	10,000	5	"	500
Be	"	10,000	2.5	"	250
Na	"	10,000	25	"	2500
Ni	"	10,000	5	"	500
Pb	"	10,000	5	"	500
Se	"	10,000	5	"	500
Sr	"	10,000	2.5	"	250
Tl	"	10,000	5	"	500
Zn	"	10,000	5	"	500

TABLE 1 (cont.)

ICP STD4 Stock

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Mo	Deionized H_2O w/ plasticware	10,000	5	100	500
Sb	"	10,000	5	"	500
Si	"	10,000	5	"	500
Sn	"	10,000	5	"	500
Ti	"	10,000	5	"	500

ICP STD5 Stock

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Fe	5% HNO_3	10,000	50	200	2,500
K	"	10,000	50	"	2,500
Na	"	10,000	50	"	2,500
Al	"	10,000	15	"	750
Ca	"	10,000	15	"	750
Mg	"	10,000	15	"	750

TABLE 2

Optima Calibration Standards
All concentrations in mg/L (ppm)

STD 2	Stock Conc	Final Conc		STD 4	Stock Conc	Final Conc
Ba	500	10		Mo	500	10
Cd	500	10		Sb	500	10
Co	500	10		Si	500	10
Cr	500	10		Sn	500	10
Cu	500	10		Ti	500	10
Mn	500	10				
V	500	10				
STD 3	Stock Conc	Final Conc		STD 5	Stock Conc	Final Conc
Ag	50	1.0		Al	750	30
As	500	10		Ca	750	30
B	500	10		Fe	2500	100
Be	250	5.0		K	2500	100
Na	2500	50		Mg	750	30
Ni	500	10		Na	2500	100
Pb	500	10				
Se	500	10				
Sr	250	5				
Tl	500	10				
Zn	500	10				

TABLE 3

CRI/MDL Stock

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Ag	5% HNO_3	10,000	0.06	100	6
Al	"	10,000	1.0	"	100
As	"	10,000	1.0	"	100
B	"	10,000	0.4	"	40
Ba	"	10,000	0.06	"	6
Be	"	10,000	0.02	"	2
Ca	"	10,000	1.0	"	100
Cd	"	10,000	0.04	"	4
Co	"	10,000	0.06	"	6
Cr	"	10,000	0.1	"	10
Cu	"	10,000	0.04	"	4
Fe	"	10,000	1.0	"	100
K	"	10,000	10.0	"	1000
Mg	"	10,000	1.0	"	100
Mn	"	10,000	0.02	"	2
Mo	"	10,000	0.1	"	10
Na	"	10,000	10.0	"	1000
Ni	"	10,000	0.2	"	20
Pb	"	10,000	0.4	"	40
Sb	"	10,000	1.0	"	100
Se	"	10,000	1.0	"	100
Si	"	10,000	1.2	"	120
Sn	"	10,000	0.2	"	20
Sr	"	10,000	0.02	"	2
Ti	"	10,000	0.1	"	10
Tl	"	10,000	1.0	"	100
V	"	10,000	0.06	"	6
Zn	"	10,000	0.2	"	20

TABLE 4

CRI and MDL Solution Levels

Element	CRI Soln mg/L	MDL Soln mg/L		Element	CRI Soln mg/L	MDL Soln mg/L
Ag	0.003	0.012		Mn	0.001	0.004
Al	0.05	0.200		Mo	0.005	0.020
As	0.05	0.200		Na	0.50	2.0
B	0.02	0.080		Ni	0.01	0.040
Ba	0.003	0.012		Pb	0.02	0.080
Be	0.001	0.004		Sb	0.05	0.200
Ca	0.05	0.200		Se	0.05	0.200
Cd	0.002	0.008		Si	0.06	0.240
Co	0.003	0.012		Sn	0.01	0.040
Cr	0.005	0.020		Sr	0.001	0.004
Cu	0.002	0.008		Ti	0.005	0.020
Fe	0.05	0.200		Tl	0.05	0.200
K	0.50	2.0		V	0.003	0.012
Mg	0.05	0.200		Zn	0.01	0.040

TABLE 5

Calibration Verification (CV) Solution
1/100 Dilution of Inorganic Ventures AR-ICPCV-2 and AR-ICPCV-5
Matrix 5% HNO_3 and 5% HCl

Element	Conc mg/L		Element	Conc mg/L
Ag	1.0		Mn	1.0
Al	2.0		Mo	1.0
As	2.0		Na	50.0
B	1.0		Ni	1.0
Ba	1.0		Pb	2.0
Be	1.0		Sb	2.0
Ca	2.0		Se	2.0
Cd	1.0		Si	2.0
Co	1.0		Sn	1.0
Cr	1.0		Sr	1.0
Cu	1.0		Ti	1.0
Fe	2.0		Tl	2.0
K	20.0		V	1.0
Mg	2.0		Zn	1.0

TABLE 6
ICP Interference Check Solutions

ICSAB Stock

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Ag	5% HNO_3	10,000	1.0	100	100
As	"	10,000	1.0	"	100
Ba	"	10,000	1.0	"	100
Be	"	10,000	1.0	"	100
Cd	"	10,000	1.0	"	100
Co	"	10,000	1.0	"	100
Cr	"	10,000	1.0	"	100
Co	"	10,000	1.0	"	100
Cr	"	10,000	1.0	"	100
Cu	"	10,000	1.0	"	100
Mn	"	10,000	1.0	"	100
Ni	"	10,000	1.0	"	100
Pb	"	10,000	1.0	"	100
Sb	"	10.000	1.0	"	100
Se	"	10,000	1.0	"	100
Tl	"	10,000	1.0	"	100
V	"	10,000	1.0	"	100
Zn	"	10,000	1.0	"	100

ICSA Solution

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Al	5% HCl, 5% HNO_3	10,000	20	1000	200
Ca	"	10,000	10	"	100
Fe	"	10,000	20	"	200
Mg	"	10,000	10	"	100

TABLE 6 (cont.)

ICSAB Solution

Element	Matrix	Stock Conc. mg/L	Stock Vol. mL	Final Vol. mL	Final Conc. mg/L
Al	5% HCl, 5% HNO_3	10,000	20	1000	200
Ca	"	10,000	10	"	100
Fe	"	10,000	20	"	200
Mg	"	10,000	10	"	100
ICSAB stock	"	100	10	"	1.0

TABLE 7: ICSA and ICSAB Solution Levels

ICSA: Interferents

Element	Conc mg/L
Al	200
Ca	100
Fe	200
Mg	100

ICSAB: Interferents with Analytes

Element	Conc mg/L
Ag	1.0
Al	200
As	1.0
Ba	1.0
Be	1.0
Ca	100
Cd	1.0
Co	1.0
Cr	1.0
Cu	1.0
Fe	200
Mg	100
Mn	1.0
Ni	1.0
Pb	1.0
Sb	1.0
Se	1.0
Tl	1.0
V	1.0
Zn	1.0

TABLE 8: OPTIMA 4300DV Emission Lines, RLs and Linear Limits

Element	Emission Line (nm)	Axial (A) Radial (R)	RL (mg/L)	Linear Limit (mg/L)
ScA	357.253	A	n/a	n/a
ScR	361.383	R	n/a	n/a
Ag	328.068	A	0.003	5
Al	308.215	R	0.05	250
As	188.979	A	0.05	30
B	249.677	R	0.02	80
Ba	233.527	R	0.003	100
Be	313.042	R	0.001	5
Ca	317.933	R	0.05	500
Cd	228.802	A	0.002	20
Co	228.616	A	0.003	50
Cr	267.716	R	0.005	100
Cu	324.752	A	0.002	40
Fe	273.955	R	0.05	250
K	766.490	R	0.5	500
Mg	279.077	R	0.05	500
Mn	257.610	R	0.001	30
Mo	202.031	A	0.005	40
Na	589.592	R	0.5	50
Na	330.237	R	50	5000
Ni	231.604	R	0.01	100
Pb	220.353	A	0.02	300
Sb	206.836	A	0.05	30
Se	196.026	A	0.05	20
Si	288.158	R	0.06	100
Sn	189.927	A	0.01	10
Sr	421.552	R	0.001	5
Ti	334.903	R	0.005	100
Tl	190.801	A	0.05	30
V	292.402	A	0.003	50
Zn	206.200	R	0.010	100

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Metals Analysis – NexIon ICP-MS

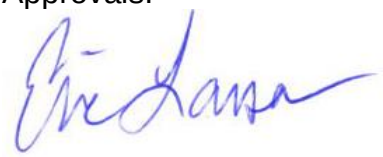
SOP 543S
Version 003.3

Revision Date: 2/23/17
Effective Date: 2/23/17

Prepared by:

Jay Kuhn / Eric Larson

Approvals:



Eric Larson, Inorganics Division Manager

David R. Mitchell, Quality Assurance Manager

Annual Review

SOP Number: 543S

Title: Metals Analysis – NexIon MS

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This Standard Operating Procedure describes the daily operation, tuning, optimization, and analysis procedures for the analysis of samples on an ICP-MS according to EPA Method 200.8 Ver 5.5 1998 and SW-846 Method 6020A 2007. See Appendix 10 for a list of isotopes.

1.2. Most samples will require some form of sample preparation, preservation, filtration and/or digestion, prior to analysis. This procedure is applicable to aqueous samples and acid digestates of solid samples.

1.3. Routine operation and maintenance procedures for the NexION® ICP-MS may be found in the NexION® Manual provided by the instrument manufacturer.

1.4. Detailed instructions on the use of the NexION® ICP-MS operating software may be found in the NexION Software Manual.

1.5. Instructions on the use of the ESI Fast system may be found in the ESI Software Manual.

2. Summary of the Procedure

2.1. This method describes the multi-element determination of trace elements by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Sample material in solution is introduced by nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio. The separated ions are detected and the ion information processed by a data handling system.

2.2. Interferences related to the technique must be recognized and corrected. Such corrections may include compensation for isobaric elemental interferences and interferences from poyatomic ions derived from plasma gas, reagents, or sample matrix.

2.3. Instrumental drift, as well as suppressions or enhancements of instrument response, must be corrected by the use of internal standards.

3. Definitions

3.1. ICP-MS (Inductively Coupled Plasma - Mass Spectrometer): Refers to an ICP MS spectrometer or to analytical method(s) that specify the use of an ICP-MS to identify and quantify trace elements in environmental samples.

3.2. IDL (Instrument Detection Limit): The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the selected analytical mass(es).

3.3. RL (Reporting Limit): The RL is the lowest value at which a given analyte is reported. The RL is based on the IDL, MDL, method efficiency, and analyst's judgment. The RL will, at minimum, equal the statistical MDL.

3.4. MDL (Method Detection Limit): As defined in 40 CFR Appendix E Part 136.

3.5. CRDL (Contract Required Detection Limit): Contract specified minimum level of detection.

3.6. ICV (Initial Calibration Verification): A mid-range second source standard, run immediately after calibration to verify the accuracy of the calibration.

3.7. CCV (Continuing Calibration Verification): A mid-range calibration standard, run after every group of 10 samples and at the end of an analytical sequence to verify calibration accuracy during the analytical run.

3.8. ICB (Initial Calibration Blank): A calibration blank run, immediately after the ICV to verify the baseline and to check for carry-over.

3.9. CCB (Continuing Calibration Blank): A calibration blank, run immediately after every CCV to verify the baseline and to check for carry-over.

3.10. QCS (Quality Control Sample): A QC solution supplied by a source independent from the source of the calibration standards. It is used to verify the accuracy of the newly prepared calibration standards.

3.11. IS (Internal Standard): Pure analyte(s) (which is not a sample component) added to a sample, extract, or standard solution in known amounts and used to measure the relative responses of other method analytes that are components of the same sample of solution.

3.12. LR (Linear Range): The linear range of an instrument is the upper limit of accurate quantitation with practical rinse-down times. It varies for each isotope and with instrumental conditions.

3.13. CRI (Low Check Standard): This low level standard is at 1RL.

3.14. SD: Standard Deviation

3.15. RSD (Relative Percent Standard Deviation): The SD divided by the mean, multiplied by 100.

3.16. RPD (Relative Percent Difference): The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.

3.17. %R (Spike Percent Recovery): The difference between the matrix spike concentration and the background sample concentration divided by the concentration of the spike added multiplied by 100.

3.18. Analytical Batch: An analytical batch shall consist of no more than 20 samples.

3.19. MB (Method Blank.): An aliquot of analyte-free matrix taken through the sample preparation procedure with each analytical batch.

3.20. LCS/MBSPK (Laboratory Control Sample, or Method Blank Spike): A reference solution of known concentration processed along with the analytical batch to test the digestion procedure for accuracy. Both soil references and aqueous references (reference solutions or method blank spikes) are LCSS.

3.21. SRM (Standard Reference Material): A reference sample of known concentration processed along with the samples to test the digestion procedure for accuracy. For a soil sample the reference used is typically an ERA Soil SRM.

3.22. MS (Matrix Spike): A sample prepared by adding a known amount of analyte to a specified amount of sample matrix. Matrix spikes are used to determine the effect of the sample matrix on the method's recovery efficiency.

3.23. MSD (Matrix Spike Duplicate): A second replicate matrix spike sample prepared and analyzed as above (Sec. 3.21) to measure precision with respect to a given matrix.

3.24. MD (Matrix Duplicate): A second replicate matrix sample prepared and analyzed with a sample batch to measure precision with respect to a given matrix.

3.25. ICSA, ICSAB (Interference Check Solutions): The ICSA solution contains interfering elements, at levels often found in samples, to test the efficacy of instrument correction equations. The ICSAB solution contains the same elements as the ICSA at the same concentrations, plus analytes at moderate levels to test the accuracy of analyte measurement in the presence of interferants.

3.26. Carry-over: The effect of a high level sample on a lower level sample which follows. Residual analyte from the high level sample may remain in the uptake lines, in the nebulizer, in the spray chamber or in the torch. The lower level sample which follows may or may not show successively decreasing exposures as evidence of carry-over. A true test for carry-over is the analysis of a blank, which has either elevated analyte or successively decreasing exposures. Carry-over may also be referred to as memory effect. If carry-over is suspected, the lower level sample should be rerun following a blank, another low level sample, or an extended rinse time.

3.27. Set-up (Tuning) Solution: A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.

3.28. Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using high purity solutions purchased from a reputable commercial source (Inorganic Ventures).

3.29. Analysis Protocols:

3.29.1. Routine or Package: Follows SW-846 6020 and EPA 200.8. If the analysis comment is Package (PKG), a data package will be generated from the Routine analytical run and Routine

QC samples. Other modifications that are necessary for certain quality assurance plans and/or agencies will be detailed in individual sections.

3.29.2. CLP-Q: Follows Routine protocol with CLP-type and DOD QC standards analyzed at CLP QC frequency, in order to generate a CLP-type data package.

4. Interferences

4.1. Isobaric interference occurs when an isotope of one element is at the same nominal mass as an isotope of another element (e.g., 98Mo and 98Ru). Corrections for isobaric interference may be made by measuring the intensity due to the interfering element at another isotope and using its natural abundance ratios to correct for its presence at the analytical mass of interest. Most commonly used corrections for isobaric interference are already present as default interference equations in the NexION® software. Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample.

4.2. Molecular interferences are caused by molecular species formed in the plasma with argon plasma or matrix ions (examples of common molecular interference include ArCl, ClO, nitrogen dimer, oxygen dimer, oxide species, double charged species, etc.). Predictions about the type of molecular interference may be made using knowledge about the sample matrix. Molecular interference can often be corrected for in the same manner as isobaric interference, i.e., measuring the intensity present at another isotope and using isotope ratios to calculate the amount of the interfering species. For example, corrections for interference of $^{40}Ar^{35}Cl$ on As at mass 75 may be made by measuring the intensity of ArCl present at mass 77 ($^{40}Ar^{37}Cl$) and converting to the apparent intensity of ArCl at mass 75 by using the isotopic ratio of ^{37}Cl to ^{35}Cl. A list of the correction equations used is given in Appendix 9.

4.3. Physical interferences are associated with solution viscosity and surface tension differences between standard solutions and samples. These interferences may occur in transfer of solution to nebulizer, at the point of aerosol formation and transport to the plasma, or during the excitation and ionization process within the plasma. Internal standardization is used to compensate for many physical interference effects. Five internal standards are chosen to closely match the analytical behavior of the elements being determined.

4.4. Memory Interferences: Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample (Carry-over as defined in Section. 3.26). If a memory interference is suspected, the sample should be reanalyzed after a long rinse period.

5. Safety

5.1. The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory technique and safety practices shall be followed at all times.

5.2. Safety glasses shall be worn at all times when handling samples, reagents, or when in the vicinity of others handling these items.

5.3. Liquid argon represents a potential cryogenic hazard and safe handling procedures shall be used at all times when handling liquid argon tanks.

5.4. The NexION ICP-MS is fully interlocked to protect the user from dangers such as high voltages, radio frequency generators, and intense ultra-violet light. At no time should the operator attempt to disable these interlocks or operate the NexION if any safety interlock is known to be disabled or malfunctioning.

5.5. Spilled samples, reagents, and water shall be cleaned up from instrument and autosampler surfaces immediately.

5.6. All additional company safety practices shall be followed at all times.

6. Equipment and Supplies

6.1. Perkin-Elmer NexION ICP-MS system: includes the NexION® instrument, a peristaltic pump, a computer system, NexION® software, a printer, and an ESI FAST autosampler with Version 2.4 software.

6.2. Supplies

6.2.1. Peristaltic pump tubing:

6.2.1.1. Black/Black PVC - 0.76 mm id used for sample introduction

6.2.1.2. 1.30 mm id Gray/Gray Santoprene used for rinse solution

6.2.1.3. Orange/Green PVC – 0.38 mm id for Internal Standard

6.2.2. Calibrated mechanical pipettes with metal-free plastic pipette tips

6.2.3. 15 mL and 50 mL polypropylene metal-free auto-sampler tubes with caps

6.2.4. 100, 200, 500 and 1000 mL polyethylene volumetric flasks

6.2.5. Fast supplies: 1.0mm id Sample Probe (gray marker), Internal Standard and Carrier Solution probes (0.5mm id). Sample loop (size varies according to method). Spare valve parts including: Stator, Rotor, Valve head.

7. Reagents and Standards

7.1. Reagents

7.1.1. All reagents may contain impurities that may affect the integrity of the analytical results. Due to the high sensitivity of ICP-MS, high purity reagents, water, and acids must be used whenever possible. All acids used for this method must be of high purity grade. Nitric acid is preferred for ICP-MS in order to minimize polyatomic interference.

7.1.2. Nitric acid (HNO3), concentrated. Trace Grade HNO3 that has Lot QC documentation to verify that it is acceptable for trace metals use.

7.1.3. Hydrochloric acid (HCL), concentrated, Trace Grade HCL that has Lot QC documentation to verify that it is acceptable for trace metals use.

7.1.4. Deionized water (DI). Type I reagent water (18.3 megaohm).

7.1.5. 1% (vol/vol) nitric acid. Add 10 mL of trace grade nitric acid to a 1-liter volumetric flask containing 900 mL of DI water. Mix well and bring to volume.

7.2. Standards: All standards must be labeled with the analyst's initials, preparation date, expiration date, and standard identification number (from Element). The preparation of all standards and analytic solutions must be documented in Element. Standards are stored in the metals lab either on the standard shelves or near the point of use. All standards are marked with an expiration date derived from the expiration date of the stock from which it is made, or from method requirements.

7.2.1. Single element stock standards of the elements at the highest purity available form Inorganic Ventures. All single element standards and Intermediate Standards are checked by ICP and/or ICP-MS prior to use.

7.2.2. Setup Solution:

7.2.2.1. Setup Solution Intermediate (10 mg/L Be, Mg, Fe, In, Li6, Ce, U and Pb in 1% HNO3): Prepare by pipetting 1.0 mL of each 1000 mg/L single element stock standard into a 100 mL volumetric flask containing 90 mL DI water and 1.0 mL concentrated HNO3. Dilute to 100 mL with DI water and mix well (see Appendix 1 Section 2).

7.2.2.2. Working standard (1 □g/L Be, Mg, Fe, In, Li6, Ce, U and Pb in 1% HNO_3): Prepare by pipetting 0.10 mL of Tuning Solution Intermediate into a 1000 mL volumetric flask containing 900 mL of DI water, and 10 mL of concentrated HNO_3. Dilute to 1000 mL with DI water and mix well.

7.3. Internal Standard Solution:

7.3.1. Solution Preparation (0.15 mg/L 6Li, 0.6 mg/L Ge, 0.12 mg/L Sc; and 0.05 mg/L Y, In, Tb and 0.2 Bi): Prepare by pipetting 0.15 mL 6Li, 0.6 mL Ge, 0.12 mL Sc, and 0.05 mL each Y, In, Tb, and 0.2 mL Bi of 1000 mg/L individual stock standards into a 1000 mL volumetric flask

containing 800 mL DI water and 10 mL concentrated HNO3. Dilute to 1000 mL with DI water and mix well (see Appendix 1 Section 1).

7.3.2. Internal Standard Solution is pumped to all Standards and Samples by a "T" prior to the Nebulizer.

7.4. Calibration Standard Stocks (see Appendix 2):

7.4.1. Calibration Stock 1 - containing 100 mg/L Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, Th, U, V, and Zn.

7.4.2. Calibration Stock 2 - containing 100 mg/L Mo and Sb.

7.4.3. Individual Stock Standards each containing 10,000 mg/L of Al, Ca, Fe, K, Mg, and Na

7.5. Calibration Intermediate Standard (See Appendix 3) is prepared, as needed, by adding 10.0 mL of each of the Stock Standards 1 and 2, and the individual elements of Al, Ca, Fe, K, Mg, and Na into a 100 mL volumetric flask containing 10 mL DI water and 1.0 mL of concentrated HNO3. Bring to volume with DI water and mix well.

7.6. Calibration working standards: Prepare fresh every two weeks or as needed at the specified concentrations in Appendix 4. (NOTE: The low standard is the CRI.)

7.7. QCS: The QCS, typically an ERA or NIST solution, is prepared as recommended by the supplier. It is diluted appropriately and analyzed as a sample when required (see section 15.4.1.1).

7.8. Initial Calibration Verification Standard: This is a second source calibration verification standard prepared from 2 second source stock solutions purchased from Inorganic Ventures Inc. (see Appendix 5). Prepare by pipetting 20.0 mL of AR-ICVMS-1 stock and 20.0 mL of AR-ICVMS-2 stock into a 1000 mL volumetric flask containing 900 mL of DI water, and 10 mL of concentrated HNO3. Dilute to 1000 mL with DI water and mix well.

7.9. Low Check Solution (CRI): A solution prepared at the RL for each element to check the accuracy at low levels. NOTE: CRI is also used as the first (and lowest) calibration solution.

7.9.1. Low Standard/Low Check Intermediate (see Appendix 7): Prepare by pipetting the specified amount of single element stock standard into a 100 mL volumetric flask containing 80 mL DI water and 1.0 mL concentrated HNO3. Dilute to 100 mL with DI water and mix well.

7.9.2. Low Standard/Low Check Solution (levels at 1RL): Prepare by pipetting 0.10 mL of Low Check Intermediate into a 200 mL volumetric flask containing 90 mL of DI water, and 2.0 mL of concentrated HNO3. Dilute to 200 mL with DI water and mix well.

7.10. Continuing Calibration Verification: Standard 4 (50 □g/L non-minerals and 5000 □g/L minerals), the mid-range calibration standard, is used.

7.11. Calibration Blank: A solution containing 1% (v/v) concentrated HNO3 in DI water. Fill a 1-L volumetric flask with approximately 900 mL of DI water. Pipette 10 mL of concentrated HNO3 into the flask, dilute to 1000 mL with DI water and mix well. NOTE: Cal. Blank is also used as the "carrier solution".

7.12. Dual Detector Calibration Solution: contains 50 □g/L each of Al, As, Be, K, Mg, Na, Ni, Pb, Th, Tl, U, Zn, 6Li, Sc, Ge, Y, In, Tb, Bi and 100ug/L of V, Cr, Co, Mn and 500 ug/L of Ca, Fe and 250ug/L of Mo, Ag, Cd, Cu, Sb, Ba. (see Appendix 6).

7.12.1. Dual Detector Calibration Elan Intermediate Solution 1: Prepare by adding 1.0 mL of each of the above 1000 mg/L elements into a 200 mL volumetric flask containing 150 mL DI water and 2 mL concentrated HNO_3. Dilute to 200 mL with DI water and mix well. Note: There is no need to add Se or additional internal standards to this solution.

7.12.2. Dual Detector Calibration Supplementary Elements for Nexion: Prepare by adding 0.01mL each of 1000 mg/l of V, Cr, Co, Mn and 0.09 mL of Ca, Fe, and 0.04 mL of Mo, Ag, Cd, Cu, Sb, Ba into a 200 mL volumetric flask containing 2.0 mL of Intermediate Standard 1 and 2 mL of concentrated HNO3. Dilute to 200 mL with DI water and mix well.

7.13. Interference Check Solutions (ICSA, ICSAB): These solutions are made from Inorganic Ventures multiple element stock standards (see Appendix 8). Prepare as needed.

7.13.1. ICSA: Prepare by pipetting 20.0 mL of Inorganic Ventures AR-6020ICS-OA10 stock into a 100mL volumetric flask containing 70 mL of DI water, and 1.0 mL of concentrated HNO3. Dilute to 100 mL with DI water.

7.13.2. ICSAB: Prepare by pipetting 20.0 mL of Inorganic Ventures AR-6020ICS-OA10 stock and 1.0 mL of ICP-MS ICSAB stock into a 100 mL volumetric flask containing 70 mL of DI water, and 1.0 mL of concentrated HNO_3. Dilute to 100 mL with DI water.

7.13.2.1. ICP-MS ICSAB STOCK: Prepare by pipetting 0.10 mL each of 1000mg/L stock standards Ag, As, Cd, Co, Cr, Cu, Mn, Ni, Zn into a 50 mL volumetric flask containing 20 mL of DI water and o.5 mL of concentrated HNO3. Mix well and transfer to a 60 mL clean Nalgene container.

8. Sample Collection, Preservation, Shipment and Storage

8.1. All samples should be received in appropriate collection containers and have been properly preserved by the clients.

8.2. Samples are checked for proper preservation and stored refrigerated for a maximum of 180 days prior to sample preparation.

8.3. Some samples are shared with the organic extractions and or conventionals laboratories. Sample receiving places these samples in a share bin in Refrigerator 5. SOP 1019S includes procedures for handling shared samples.

9. Quality Control

9.1. Documentation

9.1.1. Instrument logbooks

9.1.1.1. Daily analysis: The ICP-MS Sample logbook shall be used as a run sequence log, for sample specific notes, for QC limit notes, and for any notes pertaining to the run.

9.1.1.2. Maintenance logbook: Shall be used for notes of periodic checks of instrument performance and of all maintenance procedures including physical changes (tubing, cones etc.) and operational maintenance routines (i.e. Dual Detector Calibrations)

9.1.2. ICP-MS Files

9.1.2.1. Daily Tuning, Performance, and AutoLens® results are filed daily.

9.1.2.2. Dual detector summary results are filed with that days Tuning, Performance and Autolens.

9.1.2.3. Standard Certificates: Contains a Certificate of Analysis for all Inorganic Venture Standards as well as standards obtained from other sources.

9.2. Calibration Standards: All standards are prepared every two weeks (or as needed) by dilution from known intermediates and verified by the analysis of certified second-source QC standards (Section 7.4-7.6).

9.2.1. Calibration verification must be performed immediately after calibration with an Initial Calibration Verification Standard (ICV) and after every 10 samples and at the end of the analytical run with a Continuing Calibration Verification Standard (CCV). The ICV is made from a source other than that used for the preparation of the standard curve. The CCV is the mid-range Calibration Standard.

9.2.2. Calibration Verification Blanks (ICB/CCB) are analyzed to confirm the absence of blank contamination, baseline drift and/or carryover. Immediately after the ICV and every CCV a Calibration Verification Blank must be run.

9.2.3. Independent QC solutions: This standard is used to check the calibration stock standards stability, concentrations, and preparation. They are analyzed on the day new calibration standards are prepared.

9.3. Low Check (CRI) Standard is analyzed following calibration verification for each element. The standard is used to verify the analytical performance at the low end of the calibration or reporting limit.

9.4. Interference Check Solutions (ICSA/B) The interference check solutions (See Appendix 8) are analyzed to check the accuracy of correction equations. These standards are analyzed after the Low Check Standard.

9.5. Serial Dilution: A five-fold dilution should be performed on any new or unusual sample matrix. This dilution test will help identify a matrix interference if one is present. The dilution is performed on a sample, typically the sample used for matrix QC, from each group of samples of a similar prepcode for each sample digestion batch. Some projects (including DOD, CLP-Q) require a serial dilution be performed on at least one sample in their batch.

9.6. Post Digestion Spike: A post digestion spike should be performed on a new or unusual sample matrix, along with the serial dilution. This sample is intended to help identify matrix interference problems. Some projects, including DOD, require that a post digestion spike be performed on at least one sample in their batch. For CLP type samples this spike is required only for elements that are outside control limits in the Matrix Spike sample. For DOD samples all requested elements must be spiked.

9.7. Matrix QC samples: With each preparation batch various matrix QC samples must be analyzed. At a minimum a matrix spike, matrix duplicate, method blank, and a laboratory control sample should be prepared and analyzed. For some projects matrix spike duplicates, laboratory control sample duplicates, and/or certified reference materials may also be required. The analyst must check all paper work to make sure all necessary QC samples have been prepared and analyzed.

9.8. All logbooks are reviewed monthly for completeness and accuracy by laboratory personnel.

9.9. The QA section will periodically review the standard preparation process, including standard bottles, logbooks, standard certificates and traceability to standardized sources.

9.10. Initial Demonstration of Laboratory Performance - The following items must be completed before the analysis of any samples is performed by using this method

9.10.1. Instrument Detection Limits (IDLs) shall be determined for all analytes when first putting an instrument into service, and before using this method.

9.10.1.1. IDLs shall be verified following any significant change to the instrument (new detector or different sample introduction system used).

9.10.1.2. Calibrate the instrument, and then run the usual QC sample sequence.

9.10.1.3. Run the blank solution as a series of 10 sequential samples with rinsing in between each sample.

9.10.1.4. Calculate the standard deviation of the 10 blank samples for each isotope.

9.10.2. Method detection limits (MDLs) shall be established for all analytes by the method outlined in 40 CFR Part 136 at least annually. An MDL check sample must be run on a routine basis to verify detection limits. The check sample is run at ½ the RL.

9.10.2.1. Fortify a reagent blank with a concentration of each analyte that is two to five times the estimated detection limit (the IDL can be used to estimate this). This solution is called the MDL solution.

9.10.2.2. Take eight replicate aliquots of this solution and process through the entire method, including any sample preparation steps. Run these as samples with rinsing between each sample. Calculate the standard deviation of the samples for each isotope. Multiply the standard deviation by 2.998 (student's t value for 99% confidence level and n=8) to obtain the MDL.

9.10.2.3. The MDLs must be lower than in-house RLs. If not, the RLs will need to be changed or the MDL analysis redone.

9.10.2.4. MDLs shall be re-determined annually or following any change to the sample preparation procedure.

9.10.3. Run four LCS or SRM standards and verify the mean concentration is within 10% of the stated value (or within the acceptance limits listed in Table 8 Revision 5.4 EPA METHOD 200.8).

10. Calibration and Standardization

10.1. The instrument must be calibrated using a blank and 4-5 calibration standards before analysis. The high concentration standard will contain 100 □g/L of all analytes except for the minerals at a concentration of 5,000 or 10,000 μg/L.

10.1.1. The concentrations of the standards have been entered into the calibration page of the analytical method in the NexION® software according to the values of the standards prepared in Section 7.6.

10.1.2. Positions of the Standards are entered in the Sampling page of the Method along with any special rinse times needed.

10.1.2.1. A "Linear Through Zero" curve type should be selected for all analytes.

10.1.2.2. The calibration blank should be run as a blank, before the analysis of any calibration standards.

10.1.2.3. The first standard run should be the lowest level standard, followed by standards of increasing concentration in order to minimize cross-contamination and carry-over.

10.2. Load the calibration blank and the calibration standards into the autosampler positions specified on the Sampling page of the analytical method.

10.2.1. Start calibration in the Samples Table by highlighting the 1st row of the batch labeled "Rinse Sample" with calibration action "Run Blank, Standards, and Samples". Click on Analyze Batch. Click on Yes to clear the previous calibration.

10.2.2. After calibration has run review the data for acceptable RSDs and internal standard recoveries (see Section 15). View the curve-fit on the Calibration View page for poor curve fit (apparent standard levels >5% from true value), then print a calibration summary. To print a calibration summary, click on the Report page, and under Report View, Report Options Template select arical.rop. Then click on the Dataset Icon, highlight the latest calibration standard row and click on Reprocess. Save the calibration with the name of that run i.e. yymmdd and A, B… for the 1st, 2nd, etc. calibration if re-calibration is necessary.

10.2.3. Review the r-values for any that are <0.998

10.2.4. If poor curve fit and/or poor r-value are found, rerun a standard or recalibrate (also see Section 1.1). To reset the usual report options template, click on the Report page, and under Report View, Report Options Template select ariquant.rop.

10.3. Analyze Required QC Samples

10.3.1. Analyze the ICV and ICB standards. Confirm the standard recovery is within 10% of the known value, and the ICB value is less than the RL (unless analyzing DOD samples, when the CB value must be less than 2X MDL). If these conditions are not satisfied the analysis must stop, the problem corrected, the instrument recalibrated and the Initial Standards rerun.

10.3.2. Analyze Low Check Standard (CRI). Confirm the standard is within 50% of the known value (20% for DOD), else the problem must be corrected and the CRI run within limits before samples may be analyzed.

10.3.3. Analyze ICSA/B Standards. Confirm the standards return values of less than the RL for all non-spiked elements (unless contamination can be documented), and within 20% of the known value for spiked analytes. (For DOD the absolute value for all non-spiked analytes shall be <2XMDL, unless a verified trace impurity from one of the spiked analytes exists.)

10.3.4. Analyze the independent QC solution(s) if fresh calibration standards were prepared on this day. This standard serves as an additional check of the calibration solutions. The concentrations should be within the certified limit range provided by the supplier. If the results

are outside this range, the analyst should compare the percentages to the nearest CV and rerun the QC solution, recalibrate, or prepare new calibration standard(s).

11. Procedure

11.1. Initial Demonstration of Laboratory Performance: The following items must be completed before the analysis of any samples is performed using this method.

11.1.1. Instrument Detection Limits (IDLs) shall be determined for all analytes when first putting an instrument into service, and before using this method.

11.1.1.1. IDLs shall be verified following any significant change to the instrument (new detector or different sample introduction system used).

11.1.1.2. Calibrate the instrument, and then run the usual QC sample sequence.

11.1.1.3. Run the blank solution as a series of 10 sequential samples with rinsing in between each sample.

11.1.1.4. Calculate the standard deviation of the 10 blank samples for each isotope.

11.1.1.5. IDLs shall be determined whenever there is any significant change to the instrument (i.e. new detector or a different sample introduction system used)

11.1.2. Method detection limits (MDLs) shall be established for all analytes by the method outlined in 40 CFR Part 136, at least annually.

11.1.2.1. Fortify a reagent blank with a concentration of each analyte that is two to five times the estimated detection limit (the IDL can be used to estimate this). This solution is called the MDL solution.

11.1.2.2. Take eight replicate aliquots of this solution and process through the entire method including sample preparation steps. Run these as samples with rinsing between each sample. The resulting values are entered into the spread sheet for MDL calculations. Following the MDL determination an MDL verification check sample may be run (spiked at approximately 2XMDL). The MDL check must produce a response at least 3X instrument noise level.

11.1.2.3. The MDLs must be lower than the in-house RLs. If not, the RLs will need to be changed or the MDL analysis redone.

11.1.2.4. MDLs shall be re-determined whenever there is any change to the sample preparation procedure.

11.1.3. Linear Range Verification: Linear range limits are determined during the methods development period. Many of them are set below instrument capability, limited by other concerns such as carry-over and rinse-out times. Linear Limits used are verified on an on-

going basis and at least every six months. Linear Range standards (LR200, LR300) are analyzed to verify each element is within 10% of expected value and results may be reported to that level.

11.2. Daily Procedure

11.2.1. Preparing the uptake system and interface

11.2.1.1. Open the instrument cover and slide the torch mount door away from the Interface using the button on the outside of the instrument. Check the condition of the cones for deposits and wipe the sampler cone with a Kimwipe® wetted with a small amount of DI water. When deposits are severe, change or clean the cones.

11.2.1.2. Attach the three pump tubings to the peristaltic pump: Black-black tubing for the sample line, gray-gray for the spray chamber drain line and Green/Orange tubing for the Internal Standard. Make sure the tubing is not flattened, or else change to new tubing for optimum performance. Place the I.S. probe (green tape) and the Carrier probe (blue tape) in a DI container.

11.2.1.3. Initiate the plasma and place the I.S. and Carrier probes into a 1% HNO3 rinse solution and allow a warm-up of at least 45 minutes. Ensure that the spray chamber is pumping out smoothly. Turn on the Peltier Cooling for the Spray chamber.

11.2.2. Open the **ariDaily.wrk** workspace to perform the tuning. Check the active folders and dataset in use for accuracy. (Month and Year can be used for the Dataset Name.)

11.2.2.1. Manually aspirate (without the autosampler) the 1 μg/L Tuning solution by placing the Internal Standard and Carrier Solution probes in the solution. This solution will be continuously aspirated for the torch alignment, tuning, the AutoLens® calibration and the daily performance checks. **Prior to Tuning and Autolens routines it is helpful to run a Daily performance to check for adequate element intensities.**

11.2.3. Right Click the Daily Performance button to perform the daily performance check.

11.2.3.1. Continue to aspirate the 1 μg/L tuning solution.

11.2.3.2. Click on the Analyze Sample button in Sample window to start analysis.

11.2.3.3. Check that the RSDs for five replicates for Be, In, Mg, Pb and U are all ≤5% as required by EPA Methods 6020 and 200.8 (typically all are <3%).

11.2.3.4. Monitor the daily performance measures (as recommended by Perkin Elmer) of Be, Mg, In, and U, sensitivity, background, % double charged and % oxide levels: Be at >3000cps, Mg at >20,000cps, In at >50,000 cps, Pb >20,000cps, and U at >30,000cps . If the element intensities are low the Nebulizer Flow rate can be increased. (see 11.2.7.3).

11.2.3.4.1. Background at mass 220 < 30 cps

11.2.3.4.2. Ce +2 <0.025 (% double charged < 2.5%)

11.2.3.4.3. CeO <0.03 (% oxides < 3%)

11.2.4. Right click on Torch Alignment. Record the x and y results.

11.2.5. Right Click on the Calibration and Resolution button in the Smartune window.

11.2.5.1. After the tuning solution has run, a tuning report for each of the tunings performed will be automatically sent to the printer. Check that the mass calibration for each of the measured masses is ± 0.05 AMU of the true mass. Methods 6020 and 200.8 require ± 0.1 AMU.

11.2.5.2. Check that the resolution for all elements is 0.7 ± 0.03 AMU (measured at 10 % peak height). EPA Method 6020 requires <0.9 amu at 10% peak height; Method 200.8 requires 0.75 amu at 5% peak height.

11.2.5.3. . If both the resolution and mass calibration are acceptable a report of acceptability will be automatically printed.

11.2.5.4. If any of the tuning parameters are not meeting method specifications and the instrument requires adjustment, the instrument will automatically rerun the tuning routine (# of Retries can be set in the method) see the NexION Software Manual. It is typical to run several tunings to get all 5 elements within specifications.

11.2.6. Right Click on the **Autolens** button to perform the AutoLens® calibration.

11.2.6.1. Continue to aspirate the 1 µg/L Set-up solution.

11.2.6.2. Print an Interactive Graph (add all elements) and save the AutoLens® Calibration.

11.2.6.3. Review the AutoLens® calibration graphs.

11.2.7. Right Click the Daily Performance button to perform the daily performance check.

11.2.7.1. Continue to aspirate the 1 µg/L Set-up solution.

11.2.7.2. Check that the RSDs for five replicates for Be, In, Mg, Pb and U are all ≤5% as required by EPA Methods 6020 and 200.8 (typically all are <3%).

11.2.7.3. Monitor the daily performance measures (as recommended by Perkin Elmer) of Be, Mg, In, Pb and U sensitivity, background, % double charged and % oxide levels:

11.2.7.3.1. Be at >3000 cps, Mg at > 20,000 cps, In at > 50,000 cps, Pb at >20,000cps, and U at > 40,000 cps.

11.2.7.3.2. Background at mass 220 < 30 cps

11.2.7.3.3. Ce +2 <0.025 (% double charged < 2.5%)

11.2.7.3.4. CeO <0.03 (% oxides < 3%)

11.2.7.3.5. Oxides and double charged levels can be reduced by slightly decreasing the nebulizer flow rate or increased by slightly increasing the nebulizer flow rate. To adjust the flow, click on the Conditions Icon, Manual Adjust, and then adjust the nebulizer gas flow arrows: try using 0.01-0.02 increments to adjust Ce +2 and CeO levels. Alternately the Nebulizer adjust routine can be added to the optimization window and will automatically set the Gas flow.

11.2.7.3.6. Other Optimization Routines are available in the SmartTune window by clicking on the Edit button.

11.2.7.3.7. After the Optimizations have been run place the probes in the Rinse container for 5-10 minutes. And then Place the Carrier Probe (Blue tape) and the I.S. probe (Green tape) in the appropriate solutions.

11.3. Sample Analysis

11.3.1. Open the ARIQuant workspace and load the applicable method for the analytes required (see the method list at the instrument). In the Method window, click on the Report page. Change the report filename to reflect the run date m2yymmdd.rep, where m2 is the analysis method and instrument, yy are the last 2 digits of the year, mm is the month and dd is the day of the month). Save the method file.

11.3.2. New sample types can be screened by ICP or the semi-quantitative ICP-MS procedure, Total Quant. Use the report TotalQuantSummary.rop. To screen a sample using Total Quant, first open the TotalQuantAnalysis.wrk workspace. Calibrate using the 1% HNO3 diluent as the calibration blank and standard 50 µg/L non-minerals and 5000 µg/L minerals) as the single calibration standard. Run an ICV and an ICB before running samples at an appropriate dilution; new sample types are diluted at least 1/10, more dilute (1/50 or 1/100) if warranted.

11.3.3. Samples Analysis Setup

11.3.3.1. Edit the Samples window to enter new samples in the autosampler sequence.

11.3.3.2. The starting sample sequence is ICV, ICB, CCV1, CCB1, Low Check, ICSA, ICSAB, CCV2, CCB2 and then 10 client samples. 10 samples can be run between CCV/CCB pairs (Low Check, ICSA and ICSAB count as samples). Run the QCS (if necessary) early in the run. Linear range checks, LR200 and LR300, can be run any time after the Low Check, ICSA, ICSAB group. Enter the autosampler sample position in the A/S Loc column. Enter the dilution factor in the Batch ID column. REN and RHN preps are run undiluted. SWN preps are diluted 1/20. Enter the sample identification in the Sample ID column (e.g. 16A0001-01). The calibration action for all samples is “Analyze Sample”.

11.3.3.3. In the Method under the samples tab enter peristaltic pump control speeds for all samples: -3 for normal speed. Enter the number of seconds required for sample flush, read delay and wash.

11.3.3.4. Check the autosampler positions.

11.3.3.5. Rinse 15ml metals free tubes in groups of six. Rinse with 10% Nitric Acid followed by Di. Prepare the sample dilutions according to sample prep method and knowledge of sample analyte levels. Mix the samples using the small vortex mixer.

11.3.3.6. Load the samples into the autosampler positions specified in the sample table. Save the sample file.

11.3.3.7. Select the samples to be analyzed by highlighting the rows.

11.3.3.8. Click on Analyze Batch. A Pop-up window will ask if you wish to clear the current calibration – Click on NO unless you wish to recalibrate. Click on Yes will clear the current calibration).

11.3.4. During the run, the instrument condition and sample results are monitored so appropriate actions can be performed as needed. The CVs, CBs, QC solutions, Linear Range standards, MBs, LCSs, duplicates, matrix spikes, and internal standard recoveries should be checked during the run or soon thereafter. See Section 15 for acceptance criteria.

11.3.5. Analytical Run Order

11.3.5.1. Routine: After acceptable initial QC has been run, every group of 10 samples must be preceded and followed by a CCV, CCB pair. Typically, each group of ten may be started with suspected low level samples, such as matrix blanks and ending with higher level samples such as reference materials, or matrix spikes. In order to facilitate acceptance limit checking samples may be run: matrix duplicate, background sample, matrix spike, reference sample.

11.3.5.2. CLP-Q/DOD The analytical run order is as above plus: a serial-dilution (a fivefold dilution must agree within 10% of the undiluted sample if the analyte levels are >10RL. A post-digestion spike is performed on DOD/CLP-Q samples with recovery outside 75-125% of the expected result.

11.3.6. Monitoring the Analysis

11.3.6.1. Periodically during the run check the sample uptake flow, the level of solution in the autosampler QC vials, the autosampler probe position and the rinse bottle level. To stop the run, click on “Stop” (to stop immediately) or ‘Stop after current sample. To pause the run after the current sample click the “Pause” button in the Run window.

11.3.6.2. Method QC samples such as CV/CB should be monitored closely during the analytical run to check for calibration stability and baseline drift. If the CV and/or the CB are outside or approaching the QC limits, then corrective action should be taken as soon as possible to minimize sample reruns. Corrective action could include recalibrating the Blank or extra rinsing time followed by another CV and CB.

11.3.6.3. Monitoring High Levels and Carryover: If any sample level is above 10% of the linear limit, the sample should be diluted and rerun for the affected element. If high level samples are analyzed, carryover into the following samples may occur. Carryover usually exhibits high SD or RSD in the following samples. If carryover is suspected the affected sample should be reanalyzed. Note: Some projects (including DOD) require any sample analyte that exceeds the concentration of the high calibration standard be diluted. If required, appropriate instructions will be noted in Element and it is the analyst's responsibility to follow the instructions and document the necessary dilutions on the raw data.

11.3.7. Recalibrating the Calibration Blank: (It is possible to recalibrate the Blank and re-set the internal standards during a run):

11.3.7.1. Stop the run and insert a CV/CB pair in the AS table

11.3.7.2. Right click on the Analyze sample option in the sample table. Choose Run Blank and Sample option. This will insert a Calibration Blank in the Run table. After the blank and CV/CB pair has run return to the Batch Sample Mode. Any recalibration of the Blank must be followed by a CV/CB within QC limits before samples may be run.

11.3.8. Shut Down

11.3.8.1. Run 5% HNO3 for 3 or 4 times, and then run DI water for 3 or 4 times. Move the probes to air to drain the uptake lines and the spray chamber. When the spray chamber drain line is empty, extinguish the plasma. Loosen the peristaltic pump tubing and turn off the spray chamber cooling

11.3.8.2. Auto-shutdown (unattended shutdown) requires adding two or more 5% HNO3 samples (use autosampler position 9) and two or more DI water samples (use autosampler position 10) to the last autosampler sequence. In the Run List window, click on Auto Stop to set shutdown after run is complete. Start the autosampler batch. On the following workday, run the peristaltic pump to completely drain the uptake lines and the spray chamber, then loosen the pump tubing. Allow the pump tubing to relax for at least 1 hour. Alternatively, the tubing can be removed and saved in a bag labeled as "used" and new tubing installed.

12. Data Analysis and Calculations

12.1. Data Entry

12.1.1. To transfer the data file: On the desktop, double click on the Report Output folder. Highlight the filename and drag it to the desired folder (i.e. Element).

12.1.2. To archive raw data files: Every few runs, move the raw sample files (except those from the most recent run) from the C drive the sub-directory Dataset\Default to the "annual" Archive. On the desktop, double click on the Default folder. Highlight the files and drag them to the "annual" folder.

13. Method Performance

13.1. MDL studies are performed for all analytes as described in Section 9.11.

13.2. The MDLs must be lower than in-house RLs. If not, the RLs will need to be changed or the MDL study replicated.

13.3. MDLs shall be re-determined following any change to the sample preparation procedure.

13.4. Analytical accuracy is determined using LCS/MBSPK, SRM or MS analyzes. Acceptance limits for spike recovery are specified in the analytical methods and are normally 80 to 120% for LCS and 75 to 125% for matrix spikes. Acceptance limits for SRM analyzes are determined by the SRM supplier or manufacturer.

13.5. Laboratory precision is measured by performing replicate analyzes. Replicates (sample or matrix spike) acceptance limits are ± 20%.

13.6. Accuracy and precision acceptance limits are disseminated to the bench chemists and LIMS administrator for use in monitoring method performance in real time.

14. Pollution Prevention

14.1. All acidified sample waste must first be neutralized prior to sink disposal.

14.2. Dispose of expired standards into the designated barrel in the hazardous waste room.

14.3. Samples that are designated as hazardous waste by the LIMS "Hazardous Report" must be placed in the designated drum in the Hazardous Waste Storage Area when they are disposed. This process is described in SOP 1003S.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Precision Criteria: Intensity RSDs should be ≤5% for concentrations ≥10RLs, Conc. SD ≤1RL for concentrations <10RLs. If a sample has poor precision (RSD or a SD outside these limits), rerun the sample. If the RSDs or SDs are still outside the limits, then the sample may need to be rerun at dilution (if no instrumental precision problems are suspected).

15.2. Internal Standard Responses

15.2.1. The internal standard intensities for all internal standards used will be monitored and compared to the intensity in the most recently run calibration blank.

15.2.2. The intensities of the internal standards in all samples, QC, and continuing calibration checks should be 60-125% of the original response in the calibration blank. If the responses are not within the limits, rinse for 10-15 minutes, then run a CCB to check the intensities of the internal standards in the blank. If the intensities are now close to the intensities of the internal standards in the original calibration blank, dilute the sample by a factor of 2 to 5, and reanalyze.

15.3. Isotope Selection:

15.3.1. Look for significant differences (>2% for concentrations ≥50RLs, or >1RL for concentrations <50RLs) between isotopes on those elements which have multiple isotopes. If the difference is significant, choose the isotope with the lowest concentration.

15.3.2. If As or Se is required, evaluate the difference between ^{78}Se and ^{82}Se. If ^{82}Se is significantly higher (≥ 2RL) than ^{78}Se, bromide interference is indicated, and ^{78}Se must be used. ^{78}Se is noisier and more susceptible to baseline drift than ^{82}Se; watch the precision and the baseline checks. When ^{82}Se is used, report the As#1 result (1st As value listed) which has an ^{82}Se correction equation. When ^{78}Se is used, report the As#2 result (2nd As value listed) which has an ^{78}Se correction equation.

15.3.3. V#1 (1st V value listed) has a ^{52}Cr and ^{53}Cr correction equation. V#2 (2nd V value listed) has no corrections; this is for informational purposes only.

15.3.4. Highlight the raw data for the acceptable values of the requested elements. If an isotope other than the first one listed is chosen, make a dash with highlighter pen into the margin to the left of isotope.

15.3.5. For indications of possible interference, refer to the interference information in the Equations window of the method.

15.4. QC Samples Review

15.4.1. Method QC Solutions:

15.4.1.1.1. QCS analysis should be performed when new standards are prepared to verify the accuracy of the calibration standards.

15.4.1.1.1.1. Whenever the QCS is analyzed the results should be within the certified QC range. If the limits are not met, rerun the QCS. If the limits are still not met, re-preparation of standards and/or recalibration may be indicated. Notify the supervisor of QCS problems.

15.4.1.2. Calibration Verifications (ICV, CCV): Calibration verification QC samples are run to verify calibration stability. The ICV is run immediately after calibration and the CCV is run before and after groups of up to 10 samples. Both ICV and CCV readings should be ±10% of the true value for all requested elements for each isotope used. If this limit is not met, recalibrate and rerun the samples; or rinsing (10-15 minutes) may correct a matrix carry-over effect, followed by rerunning the CCV, CCB, and the affected samples.

15.4.1.3. Calibration Blanks (ICB, CCB): Calibration blanks are run after every ICV or CCV to verify baseline stability and to check for carry-over. Both ICB and CCB readings should be <1RL (DOD projects require that no analyte is detected >2 x MDL). If this limit is not met, recalibrate the blank, rerun the CCV, CCB, and then rerun the samples that were not bracketed by in-control blanks. Rinsing (5-10 minutes) before recalibrating the blank may correct a carry-over effect.

15.4.1.4. Interference Check Solutions: The interference check solutions, ICSA and ICSAB, are run near the start of the run. See Appendix 8 for the concentrations of these solutions.

15.4.1.4.1. ICSA: The ICSA contains the following interferants: Al, C, Ca, Cl, Fe, K, Mg, Mo, Na, P, S, and Ti. The interferants which are analyzed should be ±20% of true values. The analyte (analytes which are spiked in the ICSAB) concentrations should typically run ±2RL, although no QC limits are used. DOD requires the absolute value of all non-spiked analytes to be <2 X MDL (unless they are a verified trace impurity from one of the spiked analytes.

15.4.1.4.2. ICSAB: The ICSAB solution contains the same interferants as the ICSA at the same levels, plus some commonly requested analytes. These analytes are Ag, As, Cd, Co, Cr, Cu, Mn, Ni, and Zn; they are all at 20 µg/L in the ICSAB solution. Both the interferants which are analyzed and the analytes should be ±20% of true values.

15.4.1.5. Low Check Standard: This low level standard verifies the accuracy of the instrument at the RL for all analytes. The limits are ±1/2 RL. DOD requires limits within 20% of the expected value. If the concentrations are outside this range, the analyst should look for the possible cause (e.g. calibration blank intensities too high, baseline drift, contamination, etc.). Re-preparation of the blank, recalibration of the blank, or rinsing the instrument may be required.

15.4.1.6. Linear Range Solutions: The linear range of an instrument for an isotope is the upper limit of accurate quantitation with practical rinse-down times. It varies for each isotope and with instrumental conditions. Two LR solutions can be analyzed on a daily basis if the

samples are expected or found to be above the calibration range. LR200 (200 □g/L non-minerals, 20,000 □g/L minerals) and LR300 (300 □g/L non-minerals, 30,000 □g/L minerals) are the linear range solutions. The LR solution concentration must be within 10% of the true value to extend the calibration range of that isotope. DOD requires samples to be diluted and reanalyzed (if possible) to bring them within the calibration curve.

15.4.2. Digestion / Batch QC Samples

15.4.2.1. Method Blank (MB/BLK): A method blank (MB) should be run with every client batch of samples or every CLP sample delivery group (SDG). A minimum of one MB must be run for every batch of 20 samples of the same matrix. For solid matrix DOD projects, add Teflon boiling chips.

15.4.2.2. MB values greater than the RL indicate laboratory or reagent contamination.

15.4.2.3. The method blank concentration should be <1RL for all requested elements. If a requested element is detected in the method blank ≥RL, then all the associated samples need to be re-digested and reanalyzed unless all samples are > 10 times the detected method blank concentration. The analyst should fill out a corrective action form and the supervisor should be informed.

15.4.2.4. Reference Sample or Method Blank Spike / Blank Spike (REF / MBSPK / BS)

15.4.2.4.1. One REF or MBSPK/BS (of the same matrix type as the samples), should be analyzed with each batch of samples of the same preparation procedure.

15.4.2.4.2. For an aqueous MBSPK/BS or REF, the quality control sample must be carried through all the procedures with which the samples are subjected. The MBSPK is prepared by spiking an aliquot of the method blank at the appropriate levels. The REF sample is prepared by diluting a QC standard to the appropriate levels.

15.4.2.4.3. The percent recovery for an aqueous LCS is calculated according to the following:

$$\%R = \frac{LCS}{s} * 100$$

Where:

%R: Percent Recovery

LCS: LCS, REF, or MBSPK Results

s: True concentration

15.4.2.4.4. The Percent Recovery for the aqueous REF sample or MBSPK should be within the required control limits of 80-120% (85-115% for Method 200.8). If the recovery is

outside the QC limits, then the source of the problem shall be identified and resolved before re-preparation of the sample batch. The analyst should fill out a corrective action form, and the supervisor should be informed.

15.4.2.4.5. For a soil reference, typically an ERA SRM, the certified ranges are used as recovery limits, though a client may specify other statistical limits. The reference sample concentration must be calculated in mg/kg units. If the recovery is outside the certified range, then the source of the problem shall be identified and resolved before re-preparation of the sample batch. The analyst should fill out a corrective action form, and the supervisor should be informed.

15.4.2.5. Matrix Spike/Matrix Spike Duplicate.

15.4.2.5.1. . A matrix spike should be run with every client batch of samples or every CLP sample delivery group (SDG). The laboratory must spike a known amount of analyte into a minimum of one sample per batch not to exceed 20 samples. DOD requires an MS/MSD for each batch of 20 samples.

15.4.2.5.2. Calculate the percent recovery for the matrix spike as follows:

$$\%R = \frac{C_s - C}{s} * 100$$

Where:

%R: Percent Recovery

Cs: Measured concentration in fortified sample matrix

C: Measured concentration in unfortified sample

s: Amount of analyte added to sample matrix

15.4.2.5.3. The recovery of the matrix spike should be within the designated QC limits of 75-125%. If it is not within this range, and the LCS recovery is acceptable, the data user will be informed that the result in the unfortified sample is suspect due to heterogeneity or an uncorrected interference effect. Recovery calculations are not required if the concentration of the analyte added is <25% of the analyte present in the sample. If the matrix spike %R is outside the QC limits, the analyst should fill out a corrective action form and the supervisor should be informed. For DOD spike recovery acceptance criteria is 85-115%. Also, DOD requires a post digestion spike for out of control analytes.

15.4.2.6. Laboratory Duplicate

15.4.2.6.1. A laboratory duplicate should be run with every client batch of samples or every CLP sample delivery group (SDG). There must be at least one laboratory duplicate prepared with each batch of samples not to exceed 20 samples.

15.4.2.6.2. Calculate the RPD as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} * 100$$

Where:

RPD: Relative Percent Difference

D1: Measured concentration of first sample

D2: Measured concentration of replicate sample

15.4.2.6.3. A control limit of ≤20% shall be used for the RPD if the sample concentration is ≥5RL. A control limit of ±1RL shall be used if either the sample or the duplicate sample concentration is <5RL. If it is not within this range, the analyst should fill out a corrective action form and the supervisor should be informed. The project manager will be informed of the poor duplication, and project specific corrective action will be taken.

16. Contingencies for Handling Out-of-Control or Unacceptable Data

16.1. Calibration: If the calibration does not meet the criteria in Section 11.3.3.2, then corrective action shall be taken before proceeding with recalibration. This could involve uptake rate optimization, clog removal, re-preparation of calibration standards, etc.

16.2. Instrumental QC checks: If an instrumental QC sample (CV, CB, QCS, etc.) is out of control, then corrective action shall be taken before proceeding with analysis. This could involve recalibration of the blank (resetting the baseline), re-preparation of calibration standards and recalibration, analysis of an alternate QCS, etc.

16.3. Instrument malfunctions: When instrument malfunctions occur, consult with other experienced ICP-MS operators or the supervisor for guidance. The maintenance logbook, the ICP-MS hardware manual, or the ICP-MS software manual could be helpful for troubleshooting.

16.4. In the event of significant QC failure, analysis will stop and the analyst will perform corrective action as discussed above. In general, out-of-control sample results will not be reported. Reruns will be conducted based on sample availability. If insufficient sample remains, the client will be notified to determine an appropriate course of action.

17. Waste Management

17.1. Metals analysis results in the generation of two waste streams which must be given special treatment.

17.1.1. Acidic solutions having pH <2 and little or no trace metal concentrations: These should be neutralized to pH 7 and then sink discharged. A log book for Elementary Neutralization Activities is available in the Neutralization Area of the Lab. The Date, Source, Volume, Initial and Final pH, and Analyst initials should be recorded each time waste is neutralized.

17.1.2. Samples and sample preparation solutions having pH <2 and Hazardous levels of trace metals. A list of such samples is computer generated from sample analysis data. This list is used to mark all samples and sample solutions requiring segregation and disposal as Hazardous Waste. All such wastes are collected in a polyethylene satellite container in the Metals Instrument Lab or in the Metals Waste Drum in the Hazardous Waste Accumulation site. When the containers are full the Hazardous Materials Coordinator is notified for offsite disposal.

18. Method References

18.1. “Methods for the Determination of Metals in Environmental Samples - Supplement 1”, “Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry”, Revision 5.5, EPA-600/R-94-111, May 1998.

18.2. NexION Hardware Manual, 2011, Perkin-Elmer Corporation

18.3. NexION ICP-MS Software Manual, 2011, Perkin-Elmer Corporation

18.4. EPA SW-846 “Method 6020A Inductively Coupled Plasma – Mass Spectrometry”, Revision 1, Feb. 2007

19. Appendices

19.1. Appendix 1: Internal Standards and Tuning Solutions

19.2. Appendix 2: Calibration Stocks

19.3. Appendix 3: Calibration Intermediate

19.4. Appendix 4: Calibration Standards and Linear Range Solutions

19.5. Appendix 5: Inorganic Ventures ICV

19.6. Appendix 6: Dual Detector Solution

19.7. Appendix 7: Low Check Solution

19.8. Appendix 8: Interference Check Solutions (ICSA, ICSAB)

19.9. Appendix 9: Interference Correction Equations

19.10. Appendix 10: Analytical Isotopes and Additional Monitored Isotopes

19.11. Appendix 11: ICP-MS Reporting Limits

19.12. Appendix 12: Troubleshooting

19.13. Appendix 13: Instrument Maintenance

Appendix 1

ICP-MS INTERNAL STANDARDS AND TUNING SOLUTIONS

All concentrations in mg/L

1. INTERNAL STANDARD SOLUTION

Use at 1/100 for final levels, all concentrations in mg/L

ELEMENT	STOCK CONC	VOL OF STK IN 1000 ml	FINAL CONC in 1% HNO_3
^{6}Li	1000	0.15	0.15
Sc	1000	0.12	0.120
Ge	1000	0.6	0.600
Y	1000	0.05	0.050
In	1000	0.05	0.050
Tb	1000	0.05	0.050
Bi	1000	0.2	0.200

2. SETUP SOLUTION

Use at 1/100 for final levels, all concentrations in mg/L

ELEMENT	STOCK CONC	VOL OF STK IN 100 ml	INT CONC	FINAL CONC in 1% HNO_3
Be	1000	0.10	1.0	0.001
Mg	1000	0.10	1.0	0.001
Fe	1000	0.10	1.0	0.001
In	1000	0.10	1.0	0.001
Li	1000	0.10	1.0	0.001
Ce	1000	0.10	1.0	0.001
U	1000	0.10	1.0	0.001
Pb	1000	0.10	1.0	0.001

Appendix 2

ICP-MS CALIBRATION STOCKS

STOCK #1

Prepare in 1% trace grade HNO_3. All concentrations in mg/L

ELEMENT	STOCK CONC	VOL OF STD IN 100 mL	STOCK CONC
Ag	10000	1.0	100
As	10000	1.0	100
Ba	10000	1.0	100
Be	10000	1.0	100
Cd	10000	1.0	100
Co	10000	1.0	100
Cr	10000	1.0	100
Cu	10000	1.0	100
Mn	10000	1.0	100
Ni	10000	1.0	100
Pb	10000	1.0	100
Se	10000	1.0	100
Tl	10000	1.0	100
Th	10000	1.0	100
U	1000	10.0	100
V	10000	1.0	100
Zn	10000	1.0	100

STOCK #2

Prepare in DI H_2O

Sb	10000	1.0	100
Mo	10000	1.0	100

Appendix 3

ICP-MS CALIBRATION INTERMEDIATE

All concentrations in mg/L
Prepare in 1% trace grade HNO_3

ELEMENT	STOCK CONC	VOL OF STK **IN 100 mL**	INT CONC
Al	10000	10.0	1000
Ca	10000	10.0	1000
Fe	10000	10.0	1000
K	10000	10.0	1000
Mg	10000	10.0	1000
Na	10000	10.0	1000
STOCK #1	see table 2	10.0	10
STOCK #2	see table 2	10.0	10

Appendix 4

ICP-MS CALIBRATION STANDARDS and LINEAR RANGE SOLUTIONS

Add the intermediate to a 100 mL volumetric flask containing 1.0 mL trace metal grade HNO_3 and bring to volume. Standard 3 is made up to 200 mL with addition of 2.0 mL HNO_3.
NOTE: *Standard 1 is a standard at the RL (Low Check Standard) level see Section 7.9 and Appendix 7 for solution preparation.*

Standard	mL	Concentration μg/L in 1% HNO_3	
	Intermediate	Non-minerals	Minerals
1 see Note	0.10	RL	RL
2	0.1	10	1000
3	0.2	20	2000
4	1.0	50	5000
5	1.0	100	10000
LR200	2.0	200	20000
LR300	3.0	300	30000

Appendix 5

ICP-MS INORGANIC VENTURES ICV

All concentrations in mg/L

ELEMENT	STOCK CONC	FINAL CONC
Ag	2.5	0.050
Al	250	5.000
As	2.5	0.050
Ba	2.5	0.050
Be	2.5	0.050
Ca	250	5.000
Cd	2.5	0.050
Co	2.5	0.050
Cr	2.5	0.050
Cu	2.5	0.050
Fe	250	5.000
K	250	5.000
Mg	250	5.000
Mn	2.5	0.050
Mo	2.5	0.050
Na	250	5.000
Ni	2.5	0.050
Pb	2.5	0.050
Sb	2.5	0.050
Se	4.0	0.080
Th	2.5	0.050
Tl	2.5	0.050
U	2.5	0.050
V	2.5	0.050
Zn	2.5	0.050

Appendix 6

ICP-MS DUAL DETECTOR CALIBRATION SOLUTION

All concentrations in mg/L
Use Intermediate 1 at 1/200

ELEMENT	STOCK CONC	VOL OF STOCK (Elan) Intermediate 1 IN 200 ml	VOL OF SUPPLEMENT 1000mg/L individual elements	FINAL CALIB SOL'N CONC µg/L (in 1% HNO_3)
Ag	1000	1.0	0.04	0.250
Al	1000	1.0		0.050
As	1000	1.0		0.050
Ba	1000	1.0	0.04	0.250
Be	1000	1.0		0.050
Bi	1000	1.0		0.050
Ca	1000	1.0	0.09	0.500
Cd	1000	1.0	0.04	0.250
Co	1000	1.0	0.01	0.100
Cr	1000	1.0	0.01	0.100
Cu	1000	1.0	0.04	0.250
Fe	1000	1.0	0.09	0.500
Ge	1000	1.0		0.050
In	1000	1.0		0.050
K	1000	1.0		0.050
^{6}Li	1000	1.0		0.050
Mg	1000	1.0		0.050
Mn	1000	1.0	0.01	0.100
Mo	1000	1.0	0.04	0.250
Na	1000	1.0		0.050
Ni	1000	1.0		0.050
Pb	1000	1.0		0.050
Sb	1000	1.0	0.04	0.250
Sc	1000	1.0		0.050
Tb	1000	1.0		0.050
Th	1000	1.0		0.050
Tl	1000	1.0		0.050
U	1000	1.0		0.050
V	1000	1.0	0.01	0.100
Y	1000	1.0		0.050
Zn	1000	1.0		0.050

Appendix 7

ICP-MS LOW CHECK SOLUTION

Use Intermediate at 0.05/100 for final levels

ELEMENT	STOCK CONC mg/L	VOL OF STOCK IN 100 mL	INT CONC mg/L	FINAL CONC µg/L (in 1% HNO_3)
Ag	1000	0.04	0.4	0.2
Al	10000	0.4	40	20
As	1000	0.04	0.4	0.2
Ba	1000	0.1	1	0.5
Be	1000	0.04	0.4	0.2
Ca	10000	1	100	50
Cd	1000	0.02	0.2	0.1
Co	1000	0.04	0.4	0.2
Cr	1000	0.1	1	0.5
Cu	1000	0.1	1	0.5
Fe	10000	0.4	40	20
K	10000	0.4	40	20
Mg	10000	0.4	40	20
Mn	1000	0.1	1	0.5
Mo	1000	0.04	0.4	0.2
Na	10000	2	200	100
Ni	1000	0.1	1	0.5
Pb	1000	0.02	0.2	0.1
Sb	1000	0.04	0.4	0.2
Se	1000	0.1	1	0.5
Th	1000	0.04	0.4	0.2
Tl	1000	0.04	0.4	0.2
U	1000	0.04	0.4	0.2
V	1000	0.04	0.4	0.2
Zn	1000	0.8	8	4

Appendix 8

ICP-MS Interference Check Solutions: ICSA and ICSAB
All concentrations in mg/L
* AR-6020ICS-A10 Custom Stock Solution from Inorganic Ventures.

ELEMENT	ICSA STOCK CONC*	ICSA FINAL CONC	ICSAB STOCK CONC	ICSAB FINAL CONC (in 1% HNO_3)
Ag			2.0	0.02
Al	100	20		20
As			2.0	0.02
C	200	40		40
Ca	100	20		20
Cd			2.0	0.02
Cl	1000	200		200
Co			2.0	0.02
Cr			2.0	0.02
Cu			2.0	0.02
Fe	100	20		20
K	100	20		20
Mg	100	20		20
Mn			2.0	0.02
Mo	2	0.4		0.4
Na	100	20		20
Ni			2.0	0.02
P	100	20		20
S	100	20		20
Ti	2	0.4		0.4
Zn			2.0	0.02

Appendix 9

ICP-MS INTERFERENCE CORRECTION EQUATIONS

ANALYTE	MASS	EQUATION
V	50.944	-3.127*(Cr53-(0.133*Cr52))
Fe	53.94	-0.028226*Cr52
As	74.922	-3.127*(ArCl 77-(0.815*Se82))
As #1	74.922	-3.127*(ArCl 77-(0.3209*Se78))
Se	77.917	-0.030435*Kr83
Se	81.917	-1.008696*Kr83
Mo	97.906	-0.109613*Ru101
Cd	110.904	-1.073*(MoO 108-(0.712*Pd106))
Cd	113.904	-0.027250*Sn118
In	114.904	-0.014038*Sn118
Sb	122.904	-0.125884*Te125
Pb	207.977	+1*Pb206+1*Pb207

Appendix 10

ANALYTICAL ISOTOPES AND ADDITIONAL MONITORED ISOTOPES

1. ANALYTICAL ISOTOPES	
ELEMENT	ISOTOPE (S)
Li	6
Be	9
Sc	45
Na	23
Mg	24
Al	27
K	39
Ca	44
V	51
Cr	52, 53
Fe	54, 57
Mn	55
Co	59
Ge	72
Ni	60, 62
Cu	63, 65
Zn	66, 67, 68
As	75
Se	78, 82
Mo	98
Y	89
Kr	83
Ag	107
Cd	111, 114
In	115
Sb	121, 123
Ba	135, 137
Tb	159
Tl	205
Pb	206, 207, 208
Bi	209
Th	232
U	238

2. ADDITIONAL ISOTOPES	
ELEMENT	ISOTOPE (S)
Ru	101
Pd	106
Sn	118
Te	125

Appendix 11

ICP-MS REPORTING LIMITS

ELEMENT	RL µg/L
Ag	0.2
Al	20
As	0.2
Ba	0.5
Be	0.2
Ca	50
Cd	0.1
Co	0.2
Cr	0.5
Cu	0.5
Fe	20
K	20
Mg	20
Mn	0.5
Mo	0.2
Na	100
Ni	0.5
Pb	0.1
Sb	0.2
Se	0.5
Th	0.2
Tl	0.2
U	0.2
V	0.2
Zn	4

Appendix 12

Troubleshooting

1. The following sections describe some commonly occurring problems and proposed solutions:

1.1. Poor Curve Fit

1.1.1. Poor curve fit may require individual standards to be rerun or re-prepared; a complete recalibration may be required.

1.1.2. If the curve fit appears to be off between pulse readings (less than approx. 1.5 million-cps) and analog readings (approx. 2 million to 1 billion cps), then a new dual detector optimization/calibration may be required. Poor Pb or Tl curve fit is a good indicator of when this is necessary (other indicator elements are Mn, Th, U).

1.2. Dual Detector Calibration/Optimization: Edit the Smart Tune file in use by adding Detector Voltage optimization and Dual Detector optimization routines. Or go to **DUALDET.SWZ**

1.2.1. Check the files to be used. For the Detector optimization both a Pulse and Analog method will be listed in the Setup section of the SmartTune window. Perform the Detector optimization by aspirating Blank solution. The results will be automatically printed at the end of the procedure.

1.2.2. Check the files to be used. Make sure the DualDetectorNew.mth is listed. Perform a dual detector calibration. Aspirate the dual detector calibration solution. Click on Calibrate. This calibration will take approximately 10 minutes to run. Save the file. An optimization summary will be automatically printed. Note the range of gain values from the optimization print out; record the range of gain values in the maintenance log and compare with those from several previous dual detector calibrations. On the optimization summary, make a note of any r-values <0.9995 and number of points <10. On the Interactive page, check the individual calibration graphs for good curve fits.

1.2.3. Run a daily performance check to check sensitivity. Compare the sensitivity before and after the dual detector calibration.

1.3. Poor relative standard deviation (precision) on standards and samples: Poor RSDs have many potential causes. Recalibrate if any adjustments are made.

1.3.1. First, check that the peristaltic pump tubing is in good condition and not worn. When a probe is removed and reinserted in the rinse solution an air bubble will be visible in the tubing.

Watch the progress of this bubble and check that the flow is smooth without any pulsation. Only adjust the tension on the pump tubing beds if necessary.

1.3.2. Check that the nebulizer is operating properly by first by checking the back pressure in the instrument window (Diagnostics Tab). The aerosol may be checked with the plasma off and the nebulizer removed from the spray chamber. Turn on the nebulizer gas and the peristaltic pump; there should be a visible aerosol leaving the spray chamber. If there is not, clean or replace the nebulizer. NOTE: If a clogged nebulizer is suspected use the "Nebulizer Obstruction Removal Kit" to unclog. Do not sonicate the nebulizer as this will render it non-operational.

1.3.3. Check that the interface cones are in good condition and the orifices all of the cones are round and of the proper size.

1.4. Low Sensitivity

1.4.1. First check the x-y adjustment of the torch to sampler cone: this is normally done during the daily optimization routine.

1.4.2. Check the sample uptake as recommended in section 1.3.2. If it is too low, then check the tubing for clogs and check the air bubble progress in the uptake tubing.

1.4.3. With the plasma off, check the sampler cone to torch spacing using the Perkin Elmer spacer tool. Also check the condition of the cones.

1.4.4. Check the 6-port Valve. Aspirate DI water, then air until all water is removed from the sample introduction system. Turn off the Plasma.

1.4.5. See the maintenance section (pp117-120) of the ESI Manual before disassembling the valve. Inspect valve parts and surfaces for cleanliness and clogs. Clean parts as recommended in the ESI manual. Replace the rotor or stator is necessary (check for scratches on the rotor surface).

1.4.6. Note: the sample probe and sample Loop can be removed from the valve for cleaning and flushing while the instrument is running provided the valve is in the LOAD position. These should be flushed with ~2% Nitric acid solution, Methanol, followed by DI water and air.

Appendix 13

Instrument Maintenance

1. Daily Maintenance

1.1. Cones: The sample cone is inspected daily for build-up of salts and soot. No cleaning is required for light build-up. Swab lightly with a slightly DI water moistened cotton swab to remove moderate build-up. Allow to air dry for 5 minutes. If the salt build-up is heavy, remove both the sample and the skimmer cone assembly (Skimmer and attached hyper skimmer), and sonicate after the removal of their O-rings (see page 111-121 of the NexION® Maintenance Manual).

1.1.1. Peristaltic Pump Tubing: Inspect the peristaltic pump tubing daily for flat areas and wear. Typically, they require replacement after 2 to 3 sample runs.

1.1.2. Water Chiller: Check the water chiller daily for the following settings. The temperature meter should be 14-16° C. The temperature can be adjusted using the knob below the meter (wait 5 minutes between adjustments). Check the coolant level under the small square panel on the top right corner of the chiller. It should be almost full (to the line below the cap threads). Otherwise, fill with DI water to the line. Check the pressure gauge on the front panel; it should be 54-56 psi. The pressure can be adjusted at the regulator located on the back (see page 5-31 of the hardware guide).

1.1.3. Vacuum Pump: Use the maintenance Section of the Instrument window to check Oil change parameters.

1.2. Maintenance as Needed:

1.2.1. Nebulizer: The PFA-ST nebulizer may require maintenance if a lowered uptake rate is suspected. Check all tubing connectors and sample probe for clogs first. To change the nebulizer, extinguish the plasma, and replace the nebulizer with a spare one.

1.2.2. Torch: The torch, which is made up of a quartz torch body, a quartz injector and a Lexan adapter/base, requires replacement periodically. Torch body discoloration is acceptable unless performance is affected. If the torch has an arc spot, be aware that it may develop into a crack or hole. Sensitivity losses may necessitate torch maintenance to eliminate it as a possible cause.

1.2.3. Load Coil: The load coil requires replacement periodically. Inconsistent torch lighting may necessitate cleaning of the coil. Replace the coil if the surface becomes pitted from excessive arcing.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

USEPA CLP 245.5M and SW-846 Method 7471A
ARI Prep Code: SMM

SOP 511S
Version 011.1

Revision Date: 2/22/17
Effective Date: 2/22/17

Prepared By:

Jay Kuhn

Approvals:

Laboratory Manager

David R Mitchell

Quality Assurance

Annual Review

SOP Number: 511S

Title: Metals Sample Prep: SMM

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

Standard Operating Procedure - Metals
USEPA CLP 245.5M and SW-846 Method 7471A
ARI Prep Code SMM

1. Scope and Application

1.1. This is the routine “In-house” digestion procedure used by Analytical Resources for mercury analysis of soil samples. The method is a combination, with modifications, of the USEPA CLP 245.5M and SW-846 7471A. This digestion is applicable to soil, sediments, and sludge type materials for mercury analysis by the cold vapor atomic absorption method (CVAA). Samples prepared by this method will be labeled with the "SMM" preparation code.

1.2. This standard operating procedure describes a procedure using a “HotBlock” with 100 mL polypropylene digestion vessels.

2. Summary of the Procedure

2.1. The sample is homogenized and a portion is weighed out into a polypropylene digest tube. Deionized water, concentrated nitric acid and concentrated sulfuric acid is added to the tube before loosely capping it. The sample is then heated in a hot block for 2 minutes. After this more deionized water as well as potassium permanganate and potassium persulfate are added to the digestion tube. The tubes are then heated in a hot block for 30 minutes. Samples are then allowed to cool and finally one last amount of deionized water is added to bring the digestion up to the appropriate volume.

3. Definitions

3.1. N/A

4. Interferences

4.1. The work area, including bench top and fume hoods should be cleaned periodically to prevent sample contamination.

5. Safety

5.1. Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

5.2. All acid and sample waste must be disposed of following ARI Waste Management Plan.

6. 6. Equipment and Supplies

6.1. HotBlock

6.2. 100 mL graduated polypropylene digestion tubes

6.3. Volumetric flasks

6.4. Automatic pipettes and/or dispensers for standard and reagent additions

6.5. Balance

7. Reagents and Standards

7.1. Concentrated sulfuric acid (H_2SO_4 96.8%): Use trace metal grade sulfuric acid.

7.2. Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.

7.3. Potassium permanganate solution ($KMnO_4$): 5% solution, w/v. Dissolve 50 grams of $KMnO_4$ in 1000 mL of deionized water.

7.4. Potassium persulfate solution ($K_2S_2O_8$): 5% solution, w/v. Dissolve 50 grams of $K_2S_2O_8$ in 1000 mL of deionized water.

7.5. Deionized water, ASTM type I.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Samples will be collected in certified clean containers.

8.2. Samples will be stored in a refrigerator after arrival.

8.3. The holding time for samples awaiting Hg analysis is 28 days from time of collection.

8.4. Unless otherwise specified by the client, samples will be stored for 3 months after digestion is complete.

8.5. Occasionally ARI will receive multiphase heterogeneous samples. Do not process multiphase samples without specific, documented instructions from ARI's Project Manager or Client. Note: When conducting an environmental investigation, the investigator generally has some specific purpose in mind. He/she then designs and executes a sampling program oriented toward providing information relative to that specific purpose. One goal of environmental sampling is that the sample be representative of either the environment from which it was taken or some specific characteristic of interest. Any unbiased environmental sample has the potential to contain materials (rocks, biological material, multiple phases etc.) that are non-representative of either the matrix or the characteristic. Such materials will often be excluded or separated from the sample when they are judged to be irrelevant to the specific purpose of the investigation or the characteristic of interest. A fundamental principle of environmental sampling is that only the designer of the sampling program makes decisions concerning the representativeness of materials contained within a sample. That person makes the decision to exclude materials from the sample. When a sample arrives at the laboratory, ARI can only assume that it represents the specific purpose and desires of the investigator. Decisions as to the exclusion of materials or separation of phases have already been made by the investigator and sampling personnel. It is not the role of ARI personnel to exclude

materials or phases from a sample for analysis unless it is done with the knowledge and under the specific direction of ARI's client.

9. Quality Control

9.1. All glassware and bottles should be washed and prepared followings the procedure outlined in SOP 500S, Metals Glassware Prep.

9.2. All quality control samples are assigned when samples are batched in Element.

9.3. Verify the following:

9.3.1. Method blanks are processed with each analytical batch, or every twenty samples. For solid matrix DOD projects, add Teflon boiling chips to the blank.

9.3.2. Other QC samples, spikes, duplicates, reference materials, and/or laboratory control samples are processed as requested in Element and/or at a minimum of one set per batch of up to twenty samples.

9.4. For spiked samples the spiking solutions must be added, when possible, directly onto the sample. Weigh the appropriate amount of sample into the digestion tube, add no reagents, and inform the person who will do the spiking so they can make the proper additions. For spiking instructions see SOP 527S.

10. Calibration and Standardization

10.1. All spiking pipettes will be calibrated by the Metals Instrument Lab as detailed in ARI SOP 1015S.

10.2. All balances will be checked for proper calibration daily as detailed in ARI SOP 1003S.

11. Procedure

11.1. Section 7.1 of 7471A requires triplicate 0.2 gram samples be weighed, ARI uses 0.2 to 2.0 grams of sample depending on client requested reporting limits. Also, ARI substitutes 5 mL H_2SO_4 and 2 mL HNO_3 for the 5 mL DI water and 5 mL aqua regia specified in the method, which is consistent with CLP 245.5M. ARI adds 8mL $K_2S_2O_8$ along with the $KMnO_4$ before heating, also consistent with CLP.

11.2. Section 5.8 of 7471A states "Acidity of the working standard should be maintained at 0.15%". ARI has found that 0.5% adds additional standard stability and better matrix matches the preserved client sample. There is no evidence that this modification effects the performance and/or results of the analysis.

11.3. This procedure has been modified to take advantage of the HotBlock using 100 mL graduated polypropylene digestion tubes. The modification has been implemented to help comply with Washington State Department of Ecology pollution minimization requirements.

11.4. Standard Preparation

11.4.1. Calibration Stock Solution (1000 mg/L Hg): Certified stock standard solutions are purchased. All appropriate lot information should be entered in the Standard section of Element.

11.4.2. Intermediate Calibration Standard Solution (0.5 mg/L Hg): Pipette 0.050 mL of 1000 mg/L Hg stock standard, 11.4.1., into a 100 mL glass volumetric flask containing approximately 25 mL of deionized water and 0.5 mL of HNO_3. Dilute to 100 mL with deionized water and mix. Make this standard fresh daily and enter all information in the standard section of Element.

11.4.3. Calibration Standards: Create new standard ID's in Element, entering the stock standard ID# and the quantity of each standard to be made. Add the following amounts of the 0.5 mg/L intermediate mercury solution, 11.4.2., to 100 mL HotBlock tubes containing 10 mL of deionized water in order to make the indicated calibration standards and mix thoroughly:

11.4.4.

mL Intermediate Std.	Final Volume mL	µg/L Hg
0.00	50	0.0
0.01	50	0.1
0.05	50	0.5
0.10	50	1.0
0.20	50	2.0
0.50	50	5.0
1.00	50	10.0

11.4.4.1. Add 2.5 mL of concentrated H_2SO_4 and mix.

11.4.4.2. Add 1.25 mL of concentrated HNO_3 cap and mix.

11.4.4.3. Heat in a 95°C HotBlock for 5 minutes.

11.4.4.4. Cool the samples.

11.4.4.5. Add 25 mL of deionized water and mix.

11.4.4.6. Add 7.5 mL of $KMnO_4$ solution and mix.

11.4.4.7. Add 4 mL of $K_2S_2O_8$ solution and mix.

11.4.4.8. Cap tube and heat at 95° C in a HotBlock for 30 minutes. After adding the samples to the HotBlock, it may take as much as 15 minutes for the samples to reach 95° C. Start measuring the 30 minutes' time only after the samples have reached appropriate temperature. Record the digest start and end times on the log form.

11.4.4.9. Cool the samples.

11.4.4.10. Add 25 mL deionized water.

11.4.4.11. Record the final volume, 50 mL

11.4.4.12. Cool to room temperature. The standards are now ready for analysis.

11.5. Calibration Verification Standards

11.5.1. Calibration Verification Stock, CV, (5.00 mg/L Hg): This is a certified solution from a different source than that used to prepare the calibration standards. The bottle is labeled “Second Source” for CV. All the appropriate lot information should be entered in Element.

11.5.2. Initial Calibration Verification Standards, ICV, (8.00 μg/L Hg): To make each ICV standard, add 0.08 mL of the 5.00 mg/L stock CV mercury solution, 11.5.1., to a 100 mL HotBlock tube containing 10 mL of deionized water. Follow steps 11.4.4.1. to 11.4.4.12. for each ICV bottle. Enter all information in Element.

11.5.3. Continuing Calibration Verification Standards, CCV, (4.00 μg/L Hg): To make each CCV standard, add 0.04 mL of the 5.00 mg/L stock CV mercury solution, 11.5.1., to a 100 mL HotBlock tube containing 5 mL of deionized water. Follow steps 11.4.3.1. to 11.4.3.12. for each CCV bottle. Enter all information in Element. At a minimum prepare at least two CCV standards. It is better to have prepared one or two extra than to find that you do not have enough to finish the analytic sequence.

11.6. Sample Preparation

11.6.1. Fill out digestion log, entering header information, analyst, date, matrix, start time and prep code(s). With each sample bottle enter the ARI sample ID. At the bottom of the log record the Chemical/Reagent ID for each reagent and the digestion tube lot number that will be used for this batch of samples.

11.6.2. Mix the sample thoroughly to achieve homogeneity. If there are any artifacts, large rocks, sticks, or other articles that are not representative of the sample, do not include them in the digest and describe them in the comments section of the form. If the entire sample consists of material such as this, the sample may need to be ground or crushed to reduce the particle size, contact the supervisor/project manager for additional instructions from the client.

11.6.3. Weigh triplicate 0.2 gram portions of wet sample into a digestion tube. Up to 2.0 grams may be used to meet required client specified detection limits. Record the exact weight, to the nearest 0.001 gram, on the log form.

11.7. At the same time prepare the appropriate QC samples.

11.7.1. For samples that are to be spiked, weigh the appropriate amount of sample into a HotBlock tube, add no reagents, and inform the person who will do the spiking. Once the sample is spiked process it like the rest of the sample batch. The spiked sample is identified with the extension “MS”. For spiking instructions see SOP 527S.

11.7.2. Duplicate samples are treated exactly the same way as the original sample. Try to keep the weights of the two samples, original and duplicate, similar. The duplicate sample is identified with the extension “DUP”.

11.7.3. Method blanks are prepared by adding only the reagents in the same order and at the same times as the samples, to a clean HotBlock tube. When samples are designated for DoD-QSM analysis, use Teflon® boiling chips as a “QC matrix” when preparing method blanks. Method blanks will be identified as “BLK”.

11.7.4. Method blank spike samples are prepared by adding 5 mL of deionized water to a clean HotBlock tube. As with the matrix spike sample inform the person who will be doing the spiking so they can add the appropriate standards. Again, once spiked, process the QC sample with the rest of the sample batch starting at Section 11.10.

11.7.4.1. NOTE: Do Not add the additional 5 mL of deionized water in section 11.9. The sample will be identified “BS”. For spiking instructions see SOP 527S.

11.8. At the same time, weigh another portion of sample for determining the percent solids. If more than one soil prep is being performed per sample only one solids determination is required. See Percent Solids SOP #529S.

11.9. Add 10 mL of deionized water.

11.10. Add 2.5 mL of concentrated H_2SO_4 and mix.

11.11. Add 1.25 mL of concentrated HNO_3 and mix.

11.12. Heat in a 95°C HotBlock for 5 minutes

11.13. Cool the samples.

11.14. Add 25 mL of deionized water and mix.

11.15. Add 7.5 mL of $KMnO_4$ solution and mix.

11.16. Add 4 mL of $K_2S_2O_8$ solution and mix.

11.17. Cap tube and heat in a 95° C HotBlock for 30 minutes. After adding the samples to the HotBlock, it may take as much as 15 minutes for the samples to reach 95° C. Start measuring the 30 minutes time only after the samples have reached the appropriate temperature. Record the digest start and end times on the log form.

11.18. Cool the samples.

11.19. Add 25 mL deionized water.

11.20. Record the final volume, 50 mL.

11.21. Cool to room temperature. The samples and standards are now ready for analysis. See SOP 513S for analysis.

11.22. Scan the completed digestion log to the sample batch in Element.

12. Data Analysis and Calculations

12.1. Verify that all information has been properly entered in the digestion log and scan log to the batch in Element.

12.2. All unused space in the log must be crossed out and initialed by the analyst.

13. Method Performance

13.1. N/A

14. Pollution Prevention

14.1. To help comply with Washington State Department of Ecology pollution minimization requirements, this procedure has been modified to use 100 mL graduated polypropylene digestion tubes. This modification allows the use of less reagents and therefore produces less waste to be returned to the environment.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. N/A

16. Corrective Actions for Out-of-Control Events

16.1. Any unusual sample or problem that arises must be noted on the digestion log, or an analyst notes form (a “green sheet”) and brought to the attention of the supervisor/manager.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. A corrective action form will be filled out for any out-of-control or unacceptable data.

17.2. If necessary, the sample/job will be logged in as a redo and prepped again.

18. Waste Management

18.1. See the ARI Waste Management Plan.

19. Method References

19.1. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7471A, September 1994.

19.2. USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, Document Number ILMO4.0.

20. Appendices N/A

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Metals Sample Preparation Mercury
EPA Method 7471A
ARI Prep Code: SWM

SOP 532S
Version 008.1

Revision Date: 2/23/17
Effective Date: 2/23/17

Prepared By:

Jay Kuhn

Approvals:

Laboratory Manager

David R Mitchell

Quality Assurance

Annual Review

SOP Number: 532S

Title: SWM

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

Metals Sample Preparation Procedure

SW-846 Method 7471A

ARI Prep Code SWM

1. Scope and Application

1.1. This is the aqua regia digestion procedure identified in the SW-846 EPA Solid Waste Manual as Method 7471A for the preparation of samples prior to mercury analysis. This digestion is applicable to soil and sediment samples for analysis by the cold vapor atomic absorption method (CVAA). Samples prepared by this method will be labeled with the preparation code "SWM".

1.2. This standard operating procedure describes a procedure using a “HotBlock” with 100 mL polypropylene digestion vessels.

2. Summary of the Procedure

2.1. The sample is homogenized and a portion is weighed out into a labeled polypropylene digest tube. Deionized water and aqua regia are added to the tube before loosely capping it. The sample is then heated in a hot block for 2 minutes. After this more deionized water as well as potassium permanganate are added to the digestion tube. The tubes are then heated in a hot block for 30 minutes. Samples are then allowed to cool and finally one last amount of deionized water is added to bring the digestion up to the appropriate volume.

3. Definitions

3.1. N/A

4. Interferences

4.1. The work area, including bench top and fume hoods should be cleaned periodically to prevent sample contamination.

5. Safety

5.1. Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

5.2. All acid and sample waste must be disposed of following ARI Waste Management Plan.

6. Equipment and Supplies

6.1. HotBlock.

6.2. 100 mL graduated polypropylene digestion tubes.

6.3. Volumetric flasks.

6.4. Automatic pipettes and/or dispensers for standard and reagent additions.

6.5. Balance.

7. Reagents and Standards

7.1. Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.

7.2. Concentrated hydrochloric acid (HCl 37%): Use trace metal grade hydrochloric acid that has been lot QC checked.

7.3. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.4. Potassium permanganate solution ($KMnO_4$): 5% solution, w/v. Dissolve 50 grams of $KMnO_4$ in 1000 mL of deionized water.

7.5. Deionized water, ASTM type I.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Samples will be collected in certified clean containers.

8.2. Samples will be stored in a refrigerator after arrival.

8.3. The holding time for samples awaiting Hg analysis is 28 days from time of collection.

8.4. Unless otherwise specified by the client, samples will be stored for 3 months after digestion is complete.

8.5. Occasionally ARI will receive multiphase heterogeneous samples. Do not process multiphase samples without specific, documented instructions from ARI's Project Manager or Client. Note: When conducting an environmental investigation, the investigator generally has some specific purpose in mind. He/she then designs and executes a sampling program oriented toward providing information relative to that specific purpose. One goal of environmental sampling is that the sample be representative of either the environment from which it was taken or some specific characteristic of interest. Any unbiased environmental sample has the potential to contain materials (rocks, biological material, multiple phases etc.) that are non-representative of either the matrix or the characteristic. Such materials will often be excluded or separated from the sample when they are judged to be irrelevant to the specific purpose of the investigation or the characteristic of interest. A fundamental principle of environmental sampling is that only the designer of the sampling program makes decisions concerning the representativeness of materials contained within a sample. That person makes the decision to exclude materials from the sample. When a sample arrives at the laboratory, ARI can only assume that it represents the specific purpose and desires of the investigator. Decisions as to the exclusion of materials or separation of phases have already been made by the investigator and sampling personnel. It is not the role of ARI personnel to exclude

materials or phases from a sample for analysis unless it is done with the knowledge and under the specific direction of ARI's client.

9. Quality Control

9.1. All glassware and bottles should be washed and prepared followings the procedure outlined in SOP 500S, Metals Glassware Prep.

9.2. All quality control samples are assigned when the samples are batched in Element..

9.3. Verify the following:

9.3.1. Method blanks are processed with each analytical batch, or every twenty samples.

9.3.2. Other QC samples, spikes, duplicates, reference materials, and/or laboratory control samples are processed as requested in Element and/or at a minimum of one set per batch of up to twenty samples.

9.4. For spiked samples the spiking solutions must be added, when possible, directly onto the sample. Weigh the appropriate amount of sample into the digestion tube, add no reagents, and inform the person who will do the spiking so they can make the proper additions. For spiking instructions see SOP 527S.

10. Calibration and Standardization

10.1. All spiking pipettes will be calibrated by the Metals Instrument Lab as detailed in ARI SOP 1015S.

10.2. All balances will be checked for proper calibration daily as detailed in ARI SOP 1003S.

11. Procedure

11.1. Section 7.1 of SW-846 7471A specifies weighing triplicate 0.2 gram portions of sample for analysis. ARI uses a single 0.5 - 2.0 gram portion as required to meet client specified detection limits.

11.2. Section 7.1 of SW-846 7471A adds the Hydroxylamine solution before the final addition of water. ARI has found that this helps improve the stability of the Hg in the digest when the permanganate is reduced just prior to analysis. This is also an accepted procedure in EPA Method 245.5 section 11.5 through 11.6.

11.3. Section 5.8 of 7471A states "Acidity of the working standard should be maintained at 0.15%". ARI has found that 0.5% adds additional standard stability and better matrix matches the preserved client sample. There is no evidence that this modification affects the performance and/or results of the analysis

11.4. This procedure has been modified to take advantage of the HotBlock using 100 mL graduated polypropylene digestion tubes. The modification has been implemented to help comply with Washington State Department of Ecology pollution minimization requirements.

11.5. Standard Preparation

11.5.1. Calibration Stock Solution (1000 mg/L Hg): Certified stock standard solutions are purchased. All appropriate lot information should be entered in the Standard section of Element.

11.5.2. Intermediate Calibration Standard Solution (0.5 mg/L Hg): Pipette 0.050 mL of 1000 mg/L Hg stock standard, 11.5.1., into a 100 mL glass volumetric flask containing approximately 25 mL of deionized water and 0.5 mL of HNO_3. Dilute to 100 mL with deionized water and mix. Make this standard fresh daily and record all information in the Standard section of Element.

11.5.3. Calibration Standards: Fill out Mercury Standard Prep Log, entering all header information, the stock standard ID# and the quantity of each standard to be made. Add the following amounts of the 0.50 mg/L intermediate mercury solution, 11.5.2., to 100 mL HotBlock tubes containing 5 mL of deionized water in order to make the indicated calibration standards and mix thoroughly.

mL Intermediate Std.	Final Volume mL	µg/L Hg
0.00	100	0.0
0.01	100	0.1
0.05	100	0.5
0.10	100	1.0
0.20	100	2.0
0.50	100	5.0
1.00	100	10.0

11.5.3.1. Add 2.5 mL of aqua regia mix.

11.5.3.2. Cap bottles and heat in a 95°C water bath for 2 minutes.

11.5.3.3. Allow the samples to cool.

11.5.3.4. Add 25 mL of DI water.

11.5.3.5. Add 7.5 mL of $KMnO_4$ solution and mix.

11.5.3.6. Cap and return to the water bath and heat at 95°C for 30 minutes. After adding the samples to the HotBlock, it may take as much as 15 minutes for the samples to reach 95° C. Start measuring the 30 minutes time only after the samples have reached appropriate temperature. Record the digest start and end times on the log form.

11.5.3.7. Allow the samples to cool.

11.5.3.8. Add 25 mL of DI water.

11.5.3.9. The standards are now ready to be analyzed.

11.6. Calibration Verification Standards

11.6.1. Calibration Verification Stock, CV, (5.00 mg/L Hg): This is a certified solution from a different source than that used to prepare the calibration standards. The bottle is labeled "Second Source" for CV. All the appropriate lot information should be entered in the Standard section of Element.

11.6.2. Initial Calibration Verification Standards, ICV, (8.00 μg/L Hg): To make each ICV standard, add 0.08 mL of the 5.00 mg/L stock CV mercury solution, 11.6.1., to a 100 mL HotBlock tube containing 5.0 mL of deionized water. Follow steps 11.5.3.1. to 11.5.3.8. for each ICV bottle. Record all information on the Standard section of Element.

11.6.3. Continuing Calibration Verification Standards, CCV, (4.00 μg/L Hg): To make each CCV standard, add 0.04 mL of the 5.00 mg/L stock CV mercury solution, 11.6.1., to a 100 mL HotBlock tube containing 5.0 mL of deionized water. Follow steps 11.5.3.1. to 11.5.3.8. for each CCV bottle. Record all information in Element. At a minimum prepare at least two CCV standards. It is better to have prepared one or two extra than to find that you do not have enough to finish the analytic sequence.

11.7. Sample Preparation

11.7.1. Fill out digestion log, entering header information, analyst, date, matrix, start time and prep code(s). With each sample bottle enter the ARI sample ID and the bottle number. At the bottom of the log record the Chemical/Reagent ID for each reagent and the digestion tube lot number that will be used for this batch of samples.

11.7.2. Mix the sample thoroughly to achieve homogeneity. If there are any artifacts, large rocks, sticks, or other articles that are not representative of the sample, do not include them in the digest and describe them in the comments section of the form. If the entire sample consists of material such as this, the sample may need to be ground or crushed to reduce the particle size, contact the supervisor/manager for additional instructions from the client.

11.7.3. Weigh 0.5 grams of wet sample, up to 2.0 grams can be used to meet required client specified detection limits, into a 100 mL HotBlock tube and record the exact weight, to the nearest 0.001 gram, on the log form.

11.8. At the same time prepare the appropriate QC samples.

11.8.1. For samples that are to be spiked, weigh the appropriate amount of sample into a HotBlock tube, add no reagents, and inform the person who will do the spiking (see 9.4.) Once the sample is spiked, process it like the rest of the sample batch. The spiked sample is identified with the extension "MS". For spiking instructions see SOP 527S.

11.8.2. Duplicate samples are treated exactly the same way as the original sample. Try to keep the weights of the two samples, original and duplicate, similar. The duplicate sample is identified with the extension "DUP".

11.8.3. Method blanks are prepared by adding only the reagents, in the same order and at the same times as the samples, to a clean 100 mL HotBlock tube. When samples are designated for DoD-QSM analysis, use Teflon® boiling chips as a "QC matrix" when preparing method blanks. Method blanks will be identified as "BLK".

11.8.4. Method blank spike samples are prepared by adding 5 mL of DI water, to a HotBlock digestion tube. As with the matrix spike sample inform the person who will be doing the spiking so they can add the appropriate standards. Again, once spiked, process the QC sample with the rest of the sample batch starting at Section 11.11. For spiking instructions see SOP 527S.

11.8.4.1. NOTE: Do Not add the additional 5 mL of deionized water in section 11.10. The sample will be identified "BS".

11.9. At the same time, weigh another portion of sample for determining the percent solids. If more than one soil prep is being performed per sample only one solids determination is required. See Percent Solids SOP #529S.

11.10. Add 5 mL of deionized water.

11.11. Add 2.5 mL of aqua regia and mix.

11.12. Cap bottles and heat in a 95°C water bath for 2 minutes.

11.13. Cool the samples.

11.14. Add 25 mL of deionized water and mix.

11.15. Add 7.5 mL of $KMnO_4$ solution and mix.

11.16. Cap and return to the water bath and heat at 95°C for 30 minutes. After adding the samples to the HotBlock, it may take as much as 15 minutes for the samples to reach 95° C. Start measuring the 30 minutes time only after the samples have reached appropriate temperature. Record the digest start and end times on the log form.

11.17. Cool the samples.

11.18. Add 25 mL deionized water.

11.19. Record the finial volume as 50 mL. This volume is based on the calibration standards concentrations, which are calculated using a finial volume of 50 mL, and prepared in the same manner as the samples.

11.20. Cool to room temperature. The samples and standards are now ready for analysis. See SOP 539S for analysis.

11.21. Scan the completed digestion log to the batch in Element.

11.22. Data Analysis and Calculations

11.23. Verify that all information has been properly entered in the digestion log, and the log has been scanned to Element.

11.24. All unused space in the log must be crossed out and initialed by the analyst.

12. Method Performance

12.1. N/A

13. Pollution Prevention

13.1. To help comply with Washington State Department of Ecology pollution minimization requirements, this procedure has been modified to use 100 mL graduated polypropylene digestion tubes. This modification allows the use of fewer reagents and therefore produces less waste to be returned to the environment.

14. Data Assessment and Acceptance Criteria for Quality Control Measures

14.1. N/A

15. Corrective Actions for Out-of-Control Events

15.1. Any unusual sample or problem that arises must be noted on the digestion log, an analyst notes form (a “green sheet”) and brought to the attention of the supervisor/manager.

16. Contingencies for Handling Out-of-Control or Unacceptable Data

16.1. A corrective action form will be filled out for any out-of-control or unacceptable data.

16.2. If necessary, the sample/job will be logged in as a redo and prepped again.

17. Waste Management

17.1. See the ARI Waste Management Plan.

18. Method References

18.1. USEPA Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7471A, September 1994

19. Appendices

19.1. N/A

ATTACHMENT B-2

Example Field Forms

LANDAU ASSOCIATES

☐ Seattle/Edmonds (425) 778-0907
☐ Tacoma (253) 926-2493
☐ Spokane (509) 327-9737
☐ Portland (503) 542-1080
☐ _____

Chain-of-Custody Record

Date _____

Page _____ of _____

Project Name _____ Project No. _____

Project Location/Event _____

Sampler's Name _____

Project Contact _____

Send Results To _____

Testing Parameters

Turnaround Time
☐ Standard
☐ Accelerated
☐ _____

Sample I.D.	Date	Time	Matrix	No. of Containers	Observations/Comments
					X Allow water samples to settle, collect aliquot from clear portion
					___ NWTPH-Dx - run acid wash silica gel cleanup
					___ Analyze for EPH if no specific product identified
					VOC/BTEX/VPH (soil):
					___ non-preserved
					___ preserved w/methanol
					___ preserved w/sodium bisulfate
					___ Freeze upon receipt
					___ Dissolved metal water samples field filtered
					Other _____

Special Shipment/Handling or Storage Requirements

Method of Shipment

Relinquished by	Received by	Relinquished by	Received by
Signature	Signature	Signature	Signature
Printed Name	Printed Name	Printed Name	Printed Name
Company	Company	Company	Company
Date Time	Date Time	Date Time	Date Time

WHITE COPY - Project File YELLOW COPY - Laboratory PINK COPY - Client Representative

12/2014

LANDAU ASSOCIATES

Boeing Developmental Center
Tukwila, Washington

Sample Chain-of-Custody Form

Figure
B-2-1

LANDAU ASSOCIATES

Field Report

Project No.: _____ Report No.: _____

Client: _____ Date: _____

Project Name: _____ DPD Permit No.: _____

Location: _____

Weather Conditions: _____

Prepared By: _____

Visitors: _____

Unsatisfactory Conditions & Recommended Correction: _____

Attachments: _____

Signed: _____

LANDAU ASSOCIATES

Groundwater Low-Flow Sample Collection Form

Project Name: _____ Project Number: _____

Event: _____ Date/Time: _____

Sample Number: _____ Weather: _____

Landau Representative: _____

WATER LEVEL/WELL/PURGE DATA

Well Condition: Secure (YES or NO) Damaged (YES or NO) Describe: _____

DTW Before Purging (ft) _____ Time: _____ Flow through cell vol. _____ GW Meter No.(s) _____

Begin Purge: Date/Time: _____ End Purge: Date/Time: _____ Gallons Purged: _____

Purge water disposed to: ☐ 55-gal Drum ☐ Storage Tank ☐ Ground ☐ Other _____

Time	Temp (°F/°C)	Cond. (uS/cm)	D.O. (mg/L)	pH	ORP (mV)	Turbidity (NTU)	DTW (ft)	Internal Purge Volume (gal)	Comments/ Observations
	Purge Goals: Stablization of Parameters for three consecutive readings within the following limits							**>/= 1 flow through cell**	
	+/- 3%	**+/- 3%**	**+/- 10%**	**+/- 0.1 units**	**+/- 10 mV**	**+/- 10%**	**< 0.3 ft**		

SAMPLE COLLECTION DATA

Sample Collected With: ☐ Bailer ☐ Pump/Pump Type _____

Made of: ☐ Stainless Steel ☐ PVC ☐ Teflon ☐ Polyethylene ☐ Other ☐ Dedicated

Decon Procedure: ☐ Alconox Wash ☐ Tap Rinse ☐ DI Water ☐ Dedicated

(By Numerical Order) ☐ Other _____

Sample Description (color, turbidity, odor, sheen, etc.): _____

Replicate	Temp (°F/°C)	Cond. (uS/cm)	D.O. (mg/L)	pH	ORP (mV)	Turbidity (NTU)	DTW (ft)	Ferrous iron (Fe II)	Comments/ Observations
1									
2									
3									
4									
Average:									

QUANTITY	TYPICAL ANALYSIS ALLOWED PER BOTTLE TYPE (Circle applicable or write non-standard analysis below)		
	(8260) (8010) (8020) (NWTPH-G) (NWTPH-Gx) (BTEX)	WA ☐	OR ☐
	(8270) (PAH) (NWTPH-D) (NWTPH-Dx) (TPH-HCID) (8081) (8141) (Oil & Grease)	WA ☐	OR ☐
	(pH) (Conductivity) (TDS) (TSS) (BOD) (Turbidity) (Alkalinity) (HCO3/CO3) (Cl) (SO4) (NO3) (NO2) (F)		
	(COD) (TOC) (Total PO4) (Total Kiedahl Nitrogen) (NH3) (NO3/NO2)		
	(Total Cyanide) (WAD Cyanide) (Free Cyanide)		
	(Total Metals) (As) (Sb) (Ba) (Be) (Ca) (Cd) (Co) (Cr) (Cu) (Fe) (Pb) (Mg) (Mn) (Ni) (Ag) (Se) (Tl) (V) (Zn) (Hg) (K) (Na)		
	(Dissolved Metals) (As) (Sb) (Ba) (Be) (Ca) (Cd) (Co) (Cr) (Cu) (Fe) (Pb) (Mg) (Mn) (Ni) (Ag) (Se) (Tl) (V) (Zn) (Hg) (K) (Na) (Hardness) (Silic		
	VOC (Boeing short list)		
	Methane Ethane Ethene Acetylene		
	others		

Duplicate Sample No(s): _____

Comments: _____

Signature: _____ Date: _____

LANDAU ASSOCIATES

Exploration No. _____
Date _____ Hour _____

Log of Exploration

Project Name _____ Project No. _____

Client/owner _____ Exploration Operator _____

Exploration Method _____

_____

Logged by _____ Exploration Completed _____

Ground Surface Conditions _____

Weather Conditions _____

Location Sketch (show dimensions to mapped features)

North Arrow

(East) (North)

Coordinates: "x" _____ "y" _____ Method _____

Elevations _____ Datum _____

Sample Depth (top) (ft.) / Sample Length (ft.)	Recovery Length (ft.)	Retained Depth (top) (ft.) / Retained Length (ft.)	Sample Number	Sampler/Hammer Codes	Blow Counts	Other Test Data) _____	USCS Symbol / Unit Contact	Depth Scale (ft)	Sample Description Color, secondary soil type, PRIMARY SOIL TYPE with modifiers and minor components (density/consistency, moisture)(geologic unit)	Comments on Heave, Water Conditions, & Drilling Action
								0		
								1		
								2		
								3		
								4		
								5		
								6		
								7		
								8		
								9		
								0		
								1		
								2		
								3		
								4		
								5		
								6		
								7		
								8		
								9		
								0		

Sampler and Hammer Information

a = 3.25-in. O.D. – D&M	1 = 300-lb./30-in. Drop
b = 2.0-in. O.D. – SPT	2 = 140-lb./30-in. Drop
c = Shelby Tube	3 = Pushed
d = Grab Sample	4 = Vibrocore
g = 2.5-in. O.D.– WSDOT	5 = _____
h = 3.0-in. O.D. – M.Calif.	
i = _____	

Water Level Information

Date		
Time		
Depth to Water		
Hole Depth		
Casing Depth		

Total Depth _____ Finish Date _____ Hour _____ Continued

LANDAU ASSOCIATES

PROJECT _____ PROJECT NO. _____

EVENT _____

SAMPLE NO. _____

DATE COLLECTED _____ TIME _____

Soil/Sediment Sample Collection Form

Weather _____ Collector(s) _____

SAMPLE LOCATION/COMPOSITE DATA

Sample Type: o Soil o Sediment o Other _____

Sample Location: _____

Sample Composited: o Horizontally Locations: _____
o Vertically Depth Ranges: _____
o Not Composited o Other: _____

Elevation and Reference: _____

SAMPLE COLLECTION DATA

Sample Collected From: o Hand-Dug Hole o Test Pit o Boring o Catch Basin/Manhole o Other _____

Sample Collected With: o Bowl o Spoon o Split Barrel o Shovel o Auger o Other _____

Made of: o Stainless Steel o Steel o Other _____

Decon Procedure: *(By Numerical Order)* o Alconox Wash o Tap Rinse o DI Water Rinse o Other _____ o Other _____
o Other _____

SAMPLE DESCRIPTION (color, grain size, density, moisture, etc.): _____

SIZE	QUANTITY	TYPE	LABORATORY ANALYSIS
_____	_____	o Glass o Plastic o Other _____	_____
_____	_____	o Glass o Plastic o Other _____	_____
_____	_____	o Glass o Plastic o Other _____	_____

Co-Located/Duplicate Sample No(s). _____

Photo No. _____ Roll No. _____

Comments: _____

o *Continued on Back*

Signature _____ Date _____

LANDAU ASSOCIATES

Survey Field Notes Form

Project Name: _____ Project Number: _____

Location: _____ Date: _____

Client: _____ Landau Rep: _____

Station	$B^{(+)}$ s	H I	$F^{(-)}$ s	Elevation	Description/Comments

LANDAU ASSOCIATES

As-Built Well Completion Form

Exploration No.: _____

Well No. (If different than Expl. No.): _____

Client/Owner: _____ Project No.: _____

Project Name: _____

Drilling Co.: _____

LAI Rep(s): _____

Installation Start Date: _____ Hour: _____

Installation Finish Date: _____ Hour: _____

Well Type: ☐ Single ☐ Nested ☐ Clustered

BORING AND WELL DIMENSIONS AND INSTALLATION DETAILS

DOE Unique Well No.: _____

Number of Pipes in Boring: _____

Boring Diameter at Top of Hole: _____

Does Diameter of Hole Change? _____

Boring Diameter at First Step Down: _____

Depth of First Step Down: _____

Boring Diameter at Second Step Down: _____

Depth of Second Step Down: _____

Well Completion Date: _____

Elevation of Well Cover: _____

Elevation of Top of Well Pipe: _____

Depth to Water: _____

Date: _____ Time: _____

_____

_____

MATERIALS USED

_____ Sacks of _____ Sand

_____ Sacks of _____ Concrete/Cement

_____ Sacks of _____ Grout Mix Used

_____ Sacks of Bentonite Chips

_____ Feet of _____-inch PVC Blank Casing

_____ Feet of _____-inch PVC Slotted Screen

_____ Threaded End Cap

_____ Waterproof Well Seal/Slip Cap

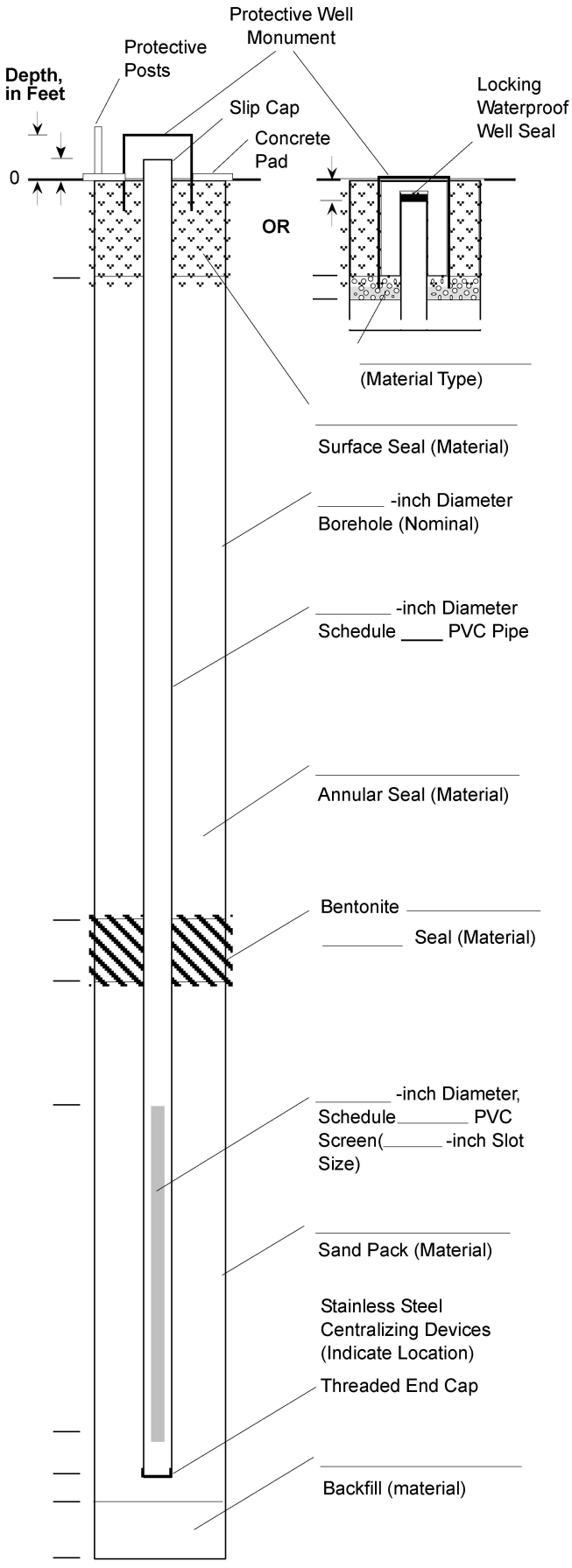
_____ Flush Mount/Aboveground Protective Monument

_____ Protective Posts

_____

_____

_____



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LANDAU ASSOCIATES

Well Development Record

Project Name: _____ Project No. _____
Location: _____ Date: _____
Client: _____ Landau Representative: _____

Well Number: _____ Time: _____

Depth to Water: _____
Well Depth: _____
Casing Diameter: _____
Casing Volume: _____

Volume of Schedule 40 PVC Pipe

Diameter (inch)	O.D. (inch)	I.D. (inch)	Volume (gal/ln ft)	Wt. Water (lbs/ln ft)
1.25	1.660	1.380	0.08	0.64
2	2.375	2.067	0.17	1.45
4	4.500	4.026	0.66	5.51
6			1.47	12.24

Est. Purge Volume: _____

Method of Development: _____ Surge Block: Yes ____ No ____

Begin Development: Time: Final Volume Purged: _____
Finish Development: Time: Water Disposal: ☐ 55-gal drum ☐ Storage Tank ☐ Ground ☐ Other _____

Initial Water Quality: (Turbidity, Color, Odor, Other) _____ Initial Yield: _____
pH: _____ Temp: _____ Conductivity: _____ Turbidity: ___
Notes: _____

Water Quality Notes: _____

Gallons	pH	Temperature	Conductivity	Turbidity	Comments

Final Water Quality: (Turbidity, Color, Odor, Other) _____
Final Yield: _____
pH: _____ Temperature: _____ Conductivity: _____ Turbidity: _____

Depth to Water After Development: _____ Well Depth After Development: _____

LANDAU ASSOCIATES

Seep Reconnaissance Survey Form

Project Name: _____ Project Number: _____

Event: _____ Date/Time: _____

Seep ID number: _____ Weather: _____

Landau Representative: _____

FLOW AND FIELD MEASUREMENT DATA

Seep Condition: Accessible (YES or NO) Flowing (YES or NO) Describe: _____

Estimated Flow Rate: Volume: _____ mL Time: _____ seconds

Calculation: _____ Flow rate: _____ mL/s

Flow description (steady, intermittent, none, etc.): _____

Seep water description (color, turbidity, odor, sheen, etc.): _____

Replicate	Temp (°F/°C)	Cond. (uS/cm)	D.O. (mg/L)	pH	ORP (mV)	Turbidity (NTU)	Comments/Observations
1							
2							
3							
4							
Average:							

GENERAL OBSERVATIONS

GPS coordinates: Latitude: _____ Longitude: _____

Photo numbers: _____

Comments: _____

Sketch:

Other comments: _____

Signature: _____ Date: _____