Appendix F
Standard Operating Procedures

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STANDARD OPERATING PROCEDURE F1

SURFACE SEDIMENT COLLECTION

A Introduction

Surface sediment samples (0- to 10-cm) will be collected from a boat or from land following processing will follow standardized procedures as described in Ecology's Sediment Cleanup User's Manual II (SCUM II) (Ecology 2017) and Puget Sound Estuary Program (PSEP). The SOPs for these procedures are described below.

B Sample Collection by Boat

The primary method for surface sediment sample collection will be to use a pneumatic grab sampler deployed from a sampling vessel. Surface sediment samples will be collected as described in the following steps:

1. Using a differential global positioning system (DGPS)[1] with sub-meter accuracy, maneuver the sampling vessel to the sampling location.
2. Open the decontaminated grab sampler jaws to the deployment position.
3. Guide the sampler overboard until it is clear of the vessel.
4. Using DGPS, position the sampling vessel such that the DGPS receiver (located on top of the sampling frame) is within 3 m (10 feet) of the target sampling location.
5. Lower the sampler through the water column to the bottom at a speed of approximately 0.3 m/s.
6. Record the DGPS location of the boat when the sampler reaches the bottom.
7. Record the water depth and time.
8. Retrieve the sampler, raising it at a speed of approximately 0.3 m/s.
9. Guide the sampler aboard the vessel and place it on the work stand on the deck, taking care to avoid jostling that might disturb the integrity of the sample.
10. Examine the sample using the following sediment acceptance criteria:

- Sample contains sediment; samples that are predominately gravel, rock, or debris will be rejected.
- Sediment is not extruding from the upper face of the sampler (indicating sampler was advanced deeper than the target penetration depth).

1 A Trimble© SPS461 or similar DGPS receiver unit will be employed for the various sampling methods outlined in this QAPP. The DGPS receiver will be calibrated daily to ensure that it is accurately recording positions from known benchmarks and functioning within the individual unit's factory specifications.

- Overlying water is present (indicating minimal leakage).
- Sediment surface is relatively flat (indicating minimal disturbance or winnowing).
- A penetration depth of at least 11 cm has been achieved.

If these sample acceptance criteria are not met, the sample will be rejected. In addition, if there is any indication that the sediment has been recently disturbed then, the grab sample will be rejected. If the initial attempt to collect a sample is not successful due to difficult substrate (e.g., presence of riprap or other debris), up to three subsequent attempts will be made within 10 m (32 feet) of the proposed location. If the initial attempt and three subsequent attempts do not result in a sample that meets the appropriate acceptance criteria, a different sampling location may be selected in consultation with EPA and LDWG.

After sample acceptance, the following observations will be noted in the field logbook or surface sediment collection form:

- Elevation of bed at sampling location
- DGPS location
- Depth as read by the boat's depth sounder and sample collection time
- Maximum penetration depth (nearest 0.5 cm)

C Sample Collection from Shore

For intertidal locations that cannot be sampled from a boat and must be manually sampled from the shoreline during a lower tide, sediment will be collected by directly scooping sediment from the 0- to 10-cm depth with a clean, stainless steel spoon into a clean, stainless steel bowl.

The following observations will be noted in the field logbook or surface sediment collection form:

- Estimated elevation of bed at sampling location
- DGPS location
- Sample collection time

D Sample Processing

After sediment collection and homogenization has been completed, the following steps will be completed to process the sediment samples:

1. **Record information** – Record information regarding the depth of the sample (generally 10 cm), sediment characteristics (e.g., color, smell, grain size, presence of debris, redox layer [if visible], etc.), and any necessary revisions to the sampling location or comments relative

to sample quality, on the sediment collection forms. Take photographs of anything of note and document any deviations from the approved sampling plan on a Protocol Modification Form (Appendix D-1).

2. **Collect and homogenize sample sediment** – The sediment at each location will be transferred directly from the grab sampler (or hole, if collected manually from shore) into a pre-cleaned stainless steel bowl or cauldron and stirred with a clean, dedicated, stainless steel spoon or spatula until texture and color homogeneity have been achieved (Ecology 2017). Any large non-sediment items, such as gravel, shells, wood chips, or organisms (e.g., clams), will be removed prior to homogenization.
3. **Dispense into jars** – Sediment will be dispensed into clean and labelled jars. For any location where toxicity testing is planned, samples will be dispensed from the bowl of homogenized sample material for both toxicity testing and (in separate jars) sulfides and ammonia analysis. These analyses will be expedited in order to have data available prior to the initiation of toxicity testing. Subsamples for sulfides and ammonia will be collected from the homogenized composite sample. The sulfide subsamples will be placed in a 4-oz jar with a Teflon® septa filled with zero headspace. The sample jar will contain 5 mL of 2 Normal zinc acetate per 30 g of sediment as a preservative. The sulfide sample will be placed in the jar, covered, and shaken vigorously to completely expose the sediment to the zinc acetate. The jar will be labeled to indicate that zinc acetate has been added and stored in the dark at 0 to 6°C.
4. **Label jars** – Sample labels will contain the project number, sampling personnel, date, time, and sample ID. A complete sample label will be affixed to each individual sample jar. Labels will be filled out as completely as possible prior to each sampling event.
5. **QC jars and forms** – Thoroughly check all sample containers for proper identification, analysis type, and lid tightness. The FC will be responsible for reviewing sediment sample information recorded on field forms (Appendix D) and will correct any improperly recorded information.
6. **Prepare for delivery to the analytical laboratory** – Pack each container carefully to prevent breakage and place inside a cooler with ice for storage at the proper temperature (≤ 4 ± 2°C) for delivery to the analytical laboratory.

STANDARD OPERATING PROCEDURE F2

SUBSURFACE SEDIMENT COLLECTION

A Introduction

Subsurface sediment core samples will be collected primarily collected from a sampling vessel (using a vibracorer), or will be manually from shore in intertidal areas where collect from a vessel is not possible. Procedures for these two collection options are described below.

B Sample Collection by Boat

B1 Collect Sediment

When sampling from a boat, the vibracorer will be deployed from the sampling vessel using an A-frame with a hydraulic winch system. The vibracorer consists of a vibrating power head attached to a 4-in.-diameter core barrel (length to be dependent on the target core depth). Sediment core samples will be collected and processed according to the following procedures:

1. The sampling vessel will be maneuvered to the proposed sampling location.
2. The vibracorer and a decontaminated core tube will be deployed.
3. Continuous core samples will be collected to the project depth requirement or until refusal.
4. The depth of core penetration will be measured and recorded.
5. The sample core tube will be extracted, and the assembly will be retrieved aboard the vessel.
6. The core sample will be evaluated at the visible ends of the core tube to verify retention of the sediment in the core tube.
7. If the sediment core is acceptable (see criteria below), the core will be capped, labelled, and held vertically pending transfer to a processing crew.

Acceptance criteria for a sediment core sample are as follows:

- The material is collected to the target depth within the first three attempts.
- Recovery is at least 75% of the penetration depth.
- The core appears to be intact without obstructions or blocking.

If sample acceptance criteria are not achieved, the sample will be rejected. If repeated deployment (i.e., maximum three attempts) does not result in a sample that meets the acceptance criteria, a different sampling location may be selected based on consultation with EPA and LDWG.

Field forms and notes for all core samples will be maintained as samples are collected. The following information will be included in the sediment core collection forms and field notes:

- Water depth and tidal elevation (i.e., raw data), as well as the calculated mudline elevation of each sediment core location relative to MLLW
- Location of each sediment core as determined using a DGPS with sub-meter accuracy
- Date and time of collection for each sediment core
- Names of field supervisor and person(s) collecting and logging the sample
- Core penetration and recovery measurements
- Designation of each coring attempt as "accepted" or "rejected"
- Observations made during sample collection, including weather conditions, complications, ship traffic, and other details associated with the sampling effort
- Core location ID
- Take photographs of anything of note.
- Any deviations from the approved sampling plan on a Protocol Modification Form (Appendix D-1).

B2 Process Core

Sediment cores collected from a boat will be processed as soon as possible after a core has been collected that meets the acceptance criteria. The steps for processing the samples are as follows:

1. Prior to processing, evaluate the amount of compaction that may have occurred, and calculate the compaction correction factor (CCF) to be applied during core processing.

    - Measure the core depth (i.e., the compacted depth).
    - To calculate the CCF, divide the compacted depth by the penetration depth (i.e., the depth recorded during core collection and acceptance).
    - Example: If the core depth (i.e., compacted depth) at the time of processing is 2.83 feet (i.e., 2 feet 10 in.), and the core penetration depth (i.e., the core depth recorded at the time of collection) was 3.33 feet (i.e., 3 feet 3 in.), the CCF would be 0.85.

2. Carefully cut along the core tube liner to expose the sediment core for processing and photograph each core.
3. Record the description of each core on the sediment core processing form, including the following parameters, as appropriate, and take photographs of anything of note.

- Core penetration depth (from the sediment core collection form)
- Compacted core depth and calculated CCF
- Corrected sample depth interval for each sample
- Odor (e.g., hydrogen sulfide, petroleum)
- Vegetation
- Debris
- Biological activity (e.g., detritus, shells, tubes, bioturbation, live or dead organisms)
- Presence of oil sheen
- Any other distinguishing characteristics or features.

4. For each core, separate the material from each target depth interval, applying (i.e., multiplying) the CCF to the target sample depth that will constitute the sample for laboratory analysis. For example, if the CCF for a subtidal sediment core is 0.85, the sample material to collect for a 0- to 60-cm analysis will come from the 0- to 51-cm interval (i.e., 60 cm × 0.85 = 51 cm).
5. Transfer sample into a separate stainless steel bowl for homogenization.

    - For intertidal sediment cores, the target sample depth interval is 0- to 45- cm.
    - For subtidal sediment cores, the target sample depth interval is 0- to 60- cm.
    - For shoaling areas, the target sample depth interval is dependent on the thickness of the shoaled material (see Appendix G for estimated shoal depths).
    - For samples in the FNC, 1-foot (30-cm) Z-samples will also be collected in shoaling areas and at locations with elevations shallower than -15 feet MLLW.

6. Homogenize the sediment until texture and color homogeneity have been achieved, removing large non-sediment items such as gravel, shells, wood chips, or organisms (e.g., clams) (Ecology 2017).
7. Dispense sediment into labeled sample containers. Sample labels will contain the project number, sampling personnel, date, time, and sample ID. A complete sample label will be affixed to each individual sample jar. Labels will be filled out as completely as possible prior to each sampling event.
8. Thoroughly check all sample containers for proper identification, analysis type, and lid tightness. The FC will be responsible for reviewing sediment sample information recorded on field forms (Appendix D) and will correct any improperly recorded information.
9. Pack each container carefully to prevent breakage and place inside a cooler with ice for storage at the proper temperature (≤ 4 ± 2°C) for delivery to the analytical laboratory.

C Sample Collection from Shore

If an intertidal sediment 0- to 45- cm core cannot be collected from the boat due to site access conditions (e.g., too shallow), then the core may be manually collected from shore during a lower tide. At the discretion of the field crew, one of the following two sampling options will be used, whichever is most suitable to the sampling location conditions. In addition, the field crew may use a combined or hybrid approach of the two methods, if necessary.

C1 Option 1: Use Shovel to Dig 45-cm-Deep Hole

The first sampling option is to dig a hole using a shovel and collect the sample directly from the sidewall of the hole. The process for this option is as follows.

1. **Dig hole** – Using a transplanting spade (i.e., a shovel with a narrow blade), dig a 45-cm-deep hole at the identified location. If it is not possible to reach a depth of 45 cm within three attempts, the deepest hole among the attempts will be sampled using the methodology described below, and the depth of refusal will be recorded on the sediment core collection form. At least one side of the hole should be approximately vertical to allow for the collection of the sample. Record any necessary revisions of the sampling location.

2. **Prepare for sampling** – Divide the vertical extent of the hole into three 15-cm sections (i.e., the bottom section 30 to 45 cm below the surface, the middle section 15 to 30 cm below the surface, and the top section from the surface down to 15 cm). If possible, use a spoon to draw a line in the sidewall of the hole at these breakpoints. The bottom section will be sampled first to ensure that the sample is collected prior to the hole filling with water.

3. **Collect and homogenize sample** – Collect the same amount of sediment from each of the three 15-cm subsections along the vertical extent of the hole, sufficient to fill a 16-oz stainless steel measuring cup. When filling the measuring cup (as described in steps 3a-3c), exclude any debris larger than approximately 5 mm in width. If differences pertaining to the diameter of the hole are apparent (e.g., the presence of differently colored material), the resulting sample should proportionally represent all material in the hole.

    a. Starting with the bottom section of the hole (i.e., 45 to 30 cm), use a small, clean, stainless steel spoon to carefully collect an even amount of sediment from the sidewall by scraping the sidewall from the bottom of the hole to the marked 30-cm line. Fill the 16-oz measuring cup using this method, and dispense the contents into a large, stainless steel bowl.

b. Repeat process in the middle section of the hole (i.e., scrape the sidewall from the 30-cm to the 15-cm line) to fill the measuring cup, and dispense the contents into the bowl containing the sediment from step 3a.

c. Repeat process in the top third of the hole (i.e., 15 cm to the surface) to again fill the measuring cup, making sure to capture the full extent of this layer, including the surface material. Dispense the contents into the bowl containing the sediment from steps 3a and 3b.

d. Homogenize the contents of the bowl with a stainless steel spoon until texture and color homogeneity have been achieved, and dispense the contents into clean and labelled jars.

The procedures for processing shore-collected cores are presented below.

C2 Option 2: Use Hand-core Tube to Collect 45-cm Core

The second sampling option is to use a hand-core tube to collect a 45-cm core, extrude the core, and then collect the sample from the interior of the core. This process for this option is as follows:

1. **Collect core** – Drive the pre-cleaned hand-core tube (internal diameter of 7 cm) into the sediment to a depth of 45 cm at the identified location, or as near as possible based on the substrate and debris. Cap the top of the tube and pull core out of the sediment. If it is not possible to reach a depth of 45 cm on the first attempt, up to three attempts should be made in that area (initial attempts will be retained in the core tube or extruded onto a piece of foil). After the third attempt, sample the deepest core using the methodology described below, and record the depth of refusal on the surface sediment collection form (Appendix D-1). Record any necessary movement of the sampling location.

2. **Collect and homogenize sample** – Extrude the contents of the core into a pre-cleaned stainless steel bowl and homogenize with a clean, stainless steel spoon until texture and color homogeneity have been achieved. Any debris wider than approximately 5 mm will be discarded.

The procedures for processing shore-collected cores are presented below.

C3 Processing Cores Collected from Shore

After sediment collection and homogenization has been completed, the following steps will be completed to process the sediment cores:

1. **Record information** – Record information regarding the depth of the core (generally 45 cm), sediment characteristics (e.g., color, smell, grain size, presence of debris, etc.), and necessary revisions to the sampling location on the sediment core collection and processing forms. Take photographs of anything of note and document any deviations from the approved sampling plan on a Protocol Modification Form (Appendix D-1).
2. **Dispense into jars** – Sediment will be dispensed into clean and labelled jars. Sample labels will contain the project number, sampling personnel, date, time, and sample ID. A complete sample label will be affixed to each individual sample jar. Labels will be filled out as completely as possible prior to each sampling event.
3. **QC jars and forms** – Thoroughly check all sample containers for proper identification, analysis type, and lid tightness. The FC will be responsible for reviewing sediment sample information recorded on field forms (Appendix D) and will correct any improperly recorded information.
4. **Prepare for delivery to the analytical laboratory** – Pack each container carefully to prevent breakage and place inside a cooler with ice for storage at the proper temperature (≤ 4 ± 2°C) for delivery to the analytical laboratory.

Title: Determining Wet-Sieve Grain Size of Sediment	SOP No.:	SAM002.02w
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1.0 SCOPE

This protocol provides a gross field or laboratory measurement of percent fines in a sediment sample.

2.0 SUMMARY OF PROCEDURE

Field collected material from a given sample location is sieved using a USA Standard Testing Sieve #230 (63µm) to determine volume of fines. The volume retained in the sieve, subtracted from the original aliquot, provides the volume of fines.

3.0 EQUIPMENT

- Modified ponar grab with line of an appropriate length and accessories. Includes any needed shackles or swivels.
- USA Standard Testing Sieve #230 (63µm)
- 50-mL measuring cup
- 100-mL graduated cylinder
- Small plastic funnel
- Plastic spoon
- Squirt bottle filled with water (site water or deionized water)
- A pump-action compression garden sprayer (1 to 2 gallon size)
- Safety glasses or goggles and chemical-resistant gloves (if contamination is suspected to be present)

4.0 PROCEDURE

1 Thoroughly rinse the sieve and all other equipment to ensure that no sediment or other detritus is present.

2 Collect a homogenized sediment aliquot in a 50-mL cup, removing excess sediment from the top and side of the cup.

3 Transfer the 50-mL sediment aliquot from the cup to the sieve using the spoon. Thoroughly rinse the cup and spoon into the sieve with water to ensure the entire aliquot has been transferred.

4 Gentle rinse the sieve with running water until the stream of water coming from the bottom of the sieve is clear. Rinse the remaining sediment to one side of the sieve.

5 Place a plastic funnel into the 100-mL graduated cylinder and position the lip of the sieve over the funnel. Using the squirt bottle, rinse the retained sediment into the graduated cylinder, directing the stream of water through the back of the sieve. Continue rinsing until all the sediment has been transferred to the graduated cylinder. If needed, rinse any sediment that may have adhered to the funnel. The rinse water should not overflow the graduated cylinder. If it appears the graduated cylinder will overflow before all sediment has been transferred, discard the sample and repeat the entire procedure.

6 Allow the sediment to settle completely in the graduated cylinder (~1-2 minutes) and record the amount of sediment present. This measurement represents the ***volume retained***. Also record any turbidity observed in the overlying water.

7 The ***volume retained*** (in mL), subtracted from the original 50-mL aliquot, provides the volume that passed through the sieve, or ***volume of fines***, in the 50-mL sample. Multiplying this remainder by two gives the volume of fines in 100-mL or ***percent fines***. The formula can be stated as:
***Percent fines* = (50-mL – Volume Retained in mL) × 2.**

6.0 SAFETY

The standard safety considerations for aquatic sampling - caution deploying and retrieving equipment, utilizing proper clothing and safety gear, and stepping in the bight of lines or cables - apply to the field crew during sampling. The designated safety officer on the vessel shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an accident or emergency. Particular care should be given to fingers and hands when working with any sampling device. The sediment, soil, and water samples may contain contaminants. Care should be taken to avoid contact with the samples. Protective gloves, glasses and proper clothing should be worn. Waste sample material should be properly disposed.

7.0 PERSONNEL

Persons who will perform this procedure should first read this SOP and then operate under the supervision of an experienced individual for at least one series of grain size determinations.

8.0 REFERENCES

PSEP. 1997. Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound. Puget Sound Estuary Program. Sampling Chapter. April 1997.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)	SOP No.: SED002.09w Effective Date: 11/11/19 Page No.: 1 of 15

1.0 SCOPE

This test determines the short term, adverse effects of potentially contaminated sediment on marine amphipods. Sediment toxicity testing will be conducted according to procedures outlined in **Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**, including modifications from the Sediment Management Annual Review Meeting (SMARM) clarification papers. Other references include **USACE/USEPA (1991) (OTM)** and **USACE/USEPA (1998) (ITM)** (for dredged sediments), **ASTM E 1367**, and **EPA/600/R-94/025**.

2.0 SUMMARY OF TEST

2.1 Approach

Table 1. Conditions for Performing 10-Day Solid Phase Toxicity Testing on Marine Amphipods

Test type	Static Non-renewal*
Test duration	10 Day
Lighting	Ambient and Constant
Test chamber size	1-L glass beaker
Test sediment depth	2 cm (~175 mL)
Test solution volume	775 mL (Chamber Vol. up to 950 mL)
Renewal of test solution	None*
No. of organisms per chamber	20
No. of replicates per treatment	5 test replicates 2 sacrificial chambers (one being the water quality surrogate) recommended minimum
Feeding	None
Test solution aeration	Trickle-flow (sufficient to maintain DO levels above 60% saturation)

* Static renewal, intermittent flow or continuous flow tests may be used where it is necessary to maintain water quality parameters, e.g., dissolved oxygen (DO) or ammonia.

2.2 Physical Requirements

Table 2. Species Specific Test Condition Summaries

Species	*Ampelisca abdita*	*Rhepoxynius abronius*	*Eohaustorius estuaries*	*Leptocheirus plumulosus*[5]
Life Stage Tested	Immature amphipods	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 2-4 mm, mixed sexes
Feeding	Will not be fed	Will not be fed	Will not be fed	Will not be fed
Temperature (°C)	20 ± 1	15 ± 1	15 ± 1	25 ± 2
Salinity (ppt)	28 ± 1	28 ± 1	28 ± 1 or ambient[4]	20 ± 2
pH	7-9	7-9	7-9	7-9
DO (≥ 60% Saturation)	4.6 mg/L	5.1 mg/L	5.1 mg/L	4.4 mg/L
Grain Size [1]	> 60% fines (> 20% clay fraction)[2]	< 60% fines	0 – 99.4% silt-clay; Provided clay fraction < 20%[2]	< 70% fines, <70% sand
Total Ammonia (mg/L, pH 7.7)	< 30	< 30	< 60	< 60
Un-ionized Ammonia (mg/L, pH 7.7)	< 0.4	< 0.4	< 0.8	< 0.8
Sulfides	N/A[3]	N/A[3]	N/A[3]	N/A[3]

[1] Grain size distributions are recommended guidelines and should not be considered absolute criteria. Species selection generally includes discussion with regulatory agencies and share holders and can be chosen exclusive from grain size characteristics (i.e. comparison to historical data with same species, species availability, etc.)
[2] SMARM clarification paper: 10/20/99
[3] Specific guidance for sulfide sensitivities have not been well established.
[4] Test salinity for *E. estuarius* may be conducted at the interstitial salinity (ambient) of the test sediments. The target test salinity should be approved by the client or regulatory agency, and will vary agency depending upon the objectives of the testing program.
[5] Direct guidance for *L. plumulosus* is not given under PSEP guidelines; however, test conditions are similar to that of *E. estuarius* and described in other guidance documents (EPA 1991, 1994).

3.0 TEST ORGANISM

The test organism should be selected based on availability, sensitivity to test materials, tolerance to ecological conditions, ecological importance, and ease of handling in the laboratory. Ideally, organisms with wide geographical distribution should be selected so test results can be compared among laboratories with similar organisms. Test conditions for each amphipod species are summarized in Tables 1 and 2.

Table 3. Test Organism Suppliers

Species	*Ampelisca abdita*	*Rhepoxynius abronius*	*Eohaustorius estuaries*	*Leptocheirus plumulosus*
Life Stage Tested	Immature amphipods, or mature females only	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 3-5 mm, mixed sexes
Sources	John Brezina and Associates, Dillon Beach, CA; Aquatic Research Organisms, Hampton, NH;	Doug Henderson, Puget Sound Organisms; John Brezina and Associates, Dillon Beach, CA	Northwest Aquatic Sciences, Newport, OR	Aquatic BioSystems, Fort Collins, CO; Aquatic Research Organisms, Hampton, NH;

3.1 Test Organism Care

Records will be kept, including the date and location collected, feeding regime, and sediment characteristics.

Holding time for amphipods is standardized to between 2 and 10 days.

4.0 TEST SUBSTANCE

The test sediments will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the facility. The sediments will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 – 6 °C in the dark, in a secure and distinct storage area. Containers should also have as little air as possible over the sediment or be stored with nitrogen gas in the overlying head space.

Test sediments should not be sieved prior to testing unless there is potential concern of similar species, competitors, or predators. Native sediments should always be sieved to remove amphipods from the material to be used as the Control treatment. A 0.5 mm sieve is sufficient to remove the amphipods and sediments should only be dry sieved (manually pushed through the sieve) using only the water present in the sample. These procedures can be performed prior to test set-up and stored under the conditions described above.

5.0 EQUIPMENT

5.1 Instrumentation/Equipment

Microprocessor-controlled recorder, and a digital thermometer
Light meter
DO meter and probe
Salinity meter and probe
pH meter and probe
Ammonia probe meter and ancillary supplies
Microbalance capable of measuring weights to the nearest 0.0001 mg
Environmental test chamber or water bath capable of maintaining test temperature within 1ºC
1 L and 250 mL test chambers
Clean filtered seawater
Deionized water
Pipets
Camel hair brushes
Miscellaneous labware (wash bottles, tally counters, culture bowls, etc.)
500 µm stainless steel sieves
Holding cups (food grade plastic is acceptable)
Stir plate and teflon stir bars
Centrifuge for collecting pore water

5.2 Apparatus

5.2.1 Test Area

The test area consists of a water bath or temperature controlled room with constant monitoring of test temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Overhead lighting will be ambient and continuous (24-hour).

5.2.3 Test Chambers

l-L glass jars with a l0-cm internal diameter, covered with a petri dish.

6.0 PROCEDURE

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in tap or deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware with also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

Natural seawater will be obtained from North Hood Canal, sand filtered, and filtered to 0.45µm. Seawater will be adjusted as necessary to maintain a target test salinity. Salinity should be lowered with the addition of high purity deionized water or increased with the addition of bioassay grade sea salts or brine.

6.1.3 Test Organism Acclimation

For acclimation, amphipods will be held in control sediment with salinity adjusted dilution water. Gentle aeration will be provided for the duration of the acclimation period. Two to three days are sufficient for acclimation to the test conditions. Organisms may be fed a slurry of ground alfalfa or Tetramin™ if held for an extended period.

Amphipods in holding containers will be checked daily before the initiation of a test. Individuals that emerge from the sediment and appear dead or unhealthy will be discarded. If greater than 10% of the amphipods die or appear unhealthy during 48 hours preceding the test, the health of the batch of organisms should be evaluated for use in the proposed testing. This may include an additional day of holding to determine if mortalities or abnormal behavior are due to shipping or acclimation stress, and not indicative of an overly sensitive population.

6.2 Primary Task

6.2.1 Pre-Test Analyses

Prior to test initiation, and preferably as soon as sediments are received at the testing facility, pore water should be collected from a homogenized sample from each sediment treatment (including reference and controls). This sample should be analyzed for interstitial salinity, ammonia, and sulfides. The parameters listed in Table 3 are recommendations based upon the tolerance of each species. If conditions within the sediment are outside the tolerance ranges, the project manager and/or client should be notified and possible corrective actions discussed. The most common corrective action involves test chamber overlying water renewal or purging to bring test conditions with tolerance ranges. These procedures are described further in Section 6.2.3.

Table 4. Species Specific Test Condition Summaries

Species	*Ampelisca abdita*	*Rhepoxynius abronius*	*Eohaustorius estuarius*	*Leptocheirus plumulosus*[2]
Total Ammonia (mg/L, pH 7.7)	< 30	< 30	< 60	< 60
Un-ionized Ammonia (mg/L, pH 7.7)	< 0.4	< 0.4	< 0.8	< 0.8
Sulfides	N/A[1]	N/A[1]	N/A[1]	N/A[1]

[1] Specific guidance for sulfide sensitivities have not been well established.
[2] Direct guidance for *L. plumulosus* is not given under PSEP guidelines; however, test conditions are similar to that of *E. estuarius* and described in other guidance documents (EPA 1991, 1994).

6.2.2 Test Sediment Addition

Test sediment will be prepared using glassware cleaned according to Section 6.1.1, pre-cleaned glassware of a disposable nature, or non-toxic food grade plastic. All test chambers should be labeled accordingly with corresponding random number positions. After setup, the test chambers are distributed throughout the testing area based upon their position numbers. All 5 treatment replicates, including the corresponding Water Quality Surrogate (see Section 6.2.3), should be included in the randomized test matrix.

If necessary, sieving of the control sediment and/or test treatments will be performed (see Section 4.0). On the day before the test begins, each test sediment sample will be thoroughly homogenized within its storage container, and an aliquot added to a test chamber depth of 2 cm.

The sediment within the test chamber will be settled by tapping the test chamber against the side of the hand. Prepared seawater is gently added up to the 950-mL level (about 775 mL). A solid disk attached to a rod is placed inside the chamber to limit the suspension of the sediment into the water column by diffusing the water down the inside of the test chamber. The disc should be maintained just above the water surface as the

test chamber is filled. The sample is left overnight with gentle aeration to allow suspended particles to settle and equilibrium to be established between sediment and overlying water before the amphipods are added.

6.2.3 Sample Adjustments

If the water quality conditions in the test chamber are not suitable to support the selected amphipod species, it may be necessary to adjust those conditions to within tolerance limits. The two most common parameters which may require attention include interstitial salinity and ammonia. Water quality conditions (exclusive of contaminants) should be within the tolerance limits of the test species to remove the impact of their interference on the determination of toxic effects. Depending upon the program, manipulations to the test treatments may be performed to correct any deviations. Unfortunately, these manipulations may also alter the level of contaminants through purging or alter their available chemical state (salinity or pH change). Best professional judgment must be employed when deciding to manipulate the sample treatments and should always involve discussion with the client or regulatory agency. If manipulations are performed to the test treatments, the associated Control and Reference sediment should be treated in the same manner.

Generally, adjustments to the interstitial salinity of the sediments are not desirable. Exceptions to this may be sediments with very low interstitial salinities that are destined for open ocean disposal (~32-35 ppt). Salinity may be adjusted by replacing the overlying water within the test chambers with water of salinity equal to, or slightly greater than (or slightly less than if lowering), the target test salinity. The test chamber water should be removed through siphoning or pumping the water out to a level just above the test sediment. Care should be taken not to remove any sediment during this process. Prepared seawater is gently added up to the 950-mL level. A solid disk attached to a rod is place inside the chamber to limit the suspension of the sediment into the water column by diffusing the water down the inside of the test chamber. The disc should be maintained just above the water surface as the test chamber is filled.

For sediments with pore water ammonia concentrations exceeding those values listed in Table 4, purging may be required to bring the test chambers conditions within acceptable limits. In most cases this should be determined in the pre-test pore water analyses (Section 6.2.1). General procedures for purging of the test chambers are described in further detail in the SMARM clarification paper “Ammonia and Amphipod Toxicity Testing” (SMARM clarification paper: 06/15/02). Additional sacrificial surrogate chambers should be created to monitor pore water ammonia levels during the acclimation process. Overlying water exchanges are conducted in the same manner as the overlying water renewal for salinity adjustment described above. Purging should be conducted twice daily until the pore water ammonia concentrations are below the threshold values. Pore water ammonia levels should be monitored every 1-3 days during the purging process. Overlying ammonia levels should also be measured as part of the monitoring procedure

as it gives an estimate of ammonia reduction without the breakdown of a surrogate chamber. Once the pore water ammonia has been reduced below the threshold values, purging should be terminated and the testing period can commence. Depending upon the program, purging may or may not be continued after test initiation. It may be possible in highly biogenic sediment that ammonia may increase again over the course of the test if renewals are discontinued.

6.2.4 Reference Toxicity Test

During this 96-hour toxicity test with marine amphipods and a test substance, five concentrations of a reference substance (ammonium chloride) with 10 test organisms will be used to assess the health of the test organisms. Three test chambers per reference concentration may be used. One concentration will be the 96-hour LC_{50}. The other four concentrations will be selected to bracket the LC_{50}. The LC_{50} values will be compared with historical data from definitive bioassays with the reference substance. The results of the 96-hour mortality, determined during this study, will be reported and used in combination with control mortality to characterize the health of the test organisms. Table 5 summarizes the test conditions for conducting a 96-hour water-only reference toxicant test.

Table 5. Conditions for Performing 4-Day Water-Only Reference Testing on Marine Amphipods

Test type	Static Non-renewal
Test duration	4 Day
Lighting	Dark and Constant[1]
Test chamber size	250-mL glass beaker (minimum)
Test solution volume	200-mL (minimum)
Renewal of test solution	None
No. of organisms per chamber	10 recommended (minimum of 5)
No. of replicates per treatment	3
Feeding	None
Test solution aeration	None unless needed to maintain DO levels above 60% saturation

[1] In the absence of sediment, amphipods will continue to attempt to bury into the bottom of the chamber. Keeping the amphipods in the dark will lessen this digging behavior thus reducing undue stress on the test organisms.

The results of the ammonia reference-toxicant may be compared to the ammonia concentrations observed within the test samples to assist in correlating any ammonia related effects within a specific batch of organisms. Table 6 summarizes the published threshold ammonia concentrations for each species.

Table 6. Threshold sediment interstitial ammonia levels for triggering ammonia reference toxicant tests.

Interstitial Ammonia (mg/L @ pH 7.7)	*Ampelisca abdita*	*Rhepoxinius abronius*	*Eohaustroius estuarius*	*Leptocheirus plumulosus* [1]
Total	>15	>15	>30	>30
Unionized	>0.2	>0.2	>0.4	>0.2

[1] Direct guidance for *L. plumulosus* is not given under PSEP guidelines; however, test conditions are similar to that of *E. estuarius* and described in other guidance documents (EPA 1991, 1994).

6.2.3 Reference and Control Sediment

During this l0-day toxicity test with marine amphipods on project sediment(s), reference sediment(s) will be used to provide a site-specific basis for comparison of potentially toxic and non-toxic conditions. Control sediment, collected during amphipod collection at the same site, will be used to determine the condition of the amphipods.

6.2.5 Water Quality

During routine test observations, a daily record of test room or water bath temperatures and test chamber aeration should be made.

In order to limit the impact of disturbance on the test organisms, all water quality measurements during the testing procedure will be performed in a surrogate water quality only chamber. In addition to the five test treatment replicates, a minimum of three additional surrogate chambers should also be tested; one for use as a water quality surrogate (WQS), and two to be utilized at test initiation and termination for pore water analyses. Surrogate chambers should be treated in the same manner as the test replicates. This includes randomization among the test treatments and addition of test animals. Additional pre-test surrogate chambers may also be required to monitor pore water salinity, ammonia, or sulfide manipulations.

After one day of acclimation after sediment and overlying water layering (test day 0), an initial set of water quality parameters will be measured in the overlying water of the WQS for each test treatment. The water quality parameters include temperature, dissolved oxygen (DO), pH, salinity, total ammonia, and total sulfides. In addition, a surrogate replicate from each test treatment will be sacrificed in order to extract pore water via centrifugation for subsequent analysis of ammonia and sulfides. Prior to test initiation, these initial water quality measurements must be reviewed to ensure that they are within the testing parameters. Test initiation should be postponed until any deviations are addressed and corrected.

On test days 1 through 9, temperature, DO, pH, and salinity will be measured in the water quality surrogate chamber of each treatment. At test termination (test day 10) the full suite of measurements will be repeated as on day 0.

6.2.6 Test Organism Addition

Amphipods are sieved from the holding sediment (500 µm sieve) and transferred to a sorting tray containing water of the holding temperature and salinity. Active, healthy amphipods are randomly selected from the sorting tray and sequentially distributed among dishes containing approximately 15 mL of dilution seawater until each dish contains 5 individuals. Prior to addition to the test chambers, the number of organisms is verified by recounting the individuals within the dish as well as confirming health and appearance. Unacceptable amphipods are discarded and replaced prior to introduction.

Twenty animals (4 dishes of 5 animals each) are then added to the randomly positioned test chambers. Addition should occur with minimal disruption of the sediment by gently pouring the water and amphipods from the sorting dishes into the test chamber. Any amphipods remaining in the dish should be gently washed into the test chamber. After addition, the test chamber is marked to confirm organism addition, recovered, and aeration restored. Any amphipods that do not bury within 15 minutes will be removed and replaced (*Ampelisca abdita* should be allowed one hour for burial).

6.2.5 Test Initiation

The test is initiated when the test organisms are distributed to each test chamber.

6.2.6 Test Observations

Notes are made on sediment appearance and unusual conditions. This can include fungal and algal growth. The number of amphipods that have emerged from the sediment, either floating on the water surface or lying on top of the sediment is recorded. Amphipods that are floating on the surface can be released from the surface tension by dropping a small drop of water (from the test chamber) with a pipette. Care must be taken not to cross-contaminate beakers. Dead animals either on the water or sediment surface are not removed during the exposure period. A list of observation types and their corresponding codes are detailed in Table 7.

Table 7. Observation Key for Recording Test Observations

Normal	N
No Burrows	NB
Body on surface (mortality). Can indicate a corpse or a molt.	M
Emergence (actively swimming in water column, or walking on sediment surface; not burrowing)	E
Growth. Indicative of fungal, algal, or bacterial mats	G
No Air Flow	D
Floating on surface. Animals caught in surface tension of water.	FOS
Water too cloudy/turbid for observation	TC

6.3 Post-task

The bioassay is terminated on day 10. After final observations are performed, the contents of each test chamber are sieved through a 0.5-mm sieve. A gentle spray of seawater is used to wash the sediment through the sieve. Material retained on the sieve is transferred to a clean sorting vessel containing seawater of a similar salinity and temperature as the test. The numbers of live and dead amphipods are recorded. An amphipod is considered alive if there is any sign of movement (e.g., pleopod twitching or response to gentle prodding). Recoveries may not equal 20 due to the decomposition of dead animals through the test. Although not commonly conducted, there is also a procedure for evaluating the ability of the amphipods (excluding *A. abdita*) to rebury into Control sediment. This sublethal endpoint is discussed in further detail in PSEP 1995.

Results Needed:

- Percent mortality for each treatment
- Mean water quality values by treatment
- LC_{50} and 95% confidence limits (for ref. tox.)
- Reburial

In screening tests, the responses of amphipods in collected test sediments are compared to control and reference site sediments.

6.4 Reporting

The report may include, but will not be limited to, the following:

- Name and address of the laboratory conducting the study, and dates on which the study was initiated and completed.
- The name of the Study Director, other scientists or professionals, and supervisory personnel involved in the study.
- Objectives as stated in the protocol.
- A description of the methods used.

- Transformations, calculations, or operations performed on the data, a summary and analysis of the data, and a statement of the conclusion drawn from the analysis.
- The test substance identified by code number and the date each sample was used.
- The number of organisms used in the study.
- Concentrations of exposure and exposure method.
- Any circumstances that may have affected the quality or integrity of the data, including deviations from test protocols or Standard Operating Procedures.
- The location where raw data and the final report will be stored.
- Additions or corrections to a final report will be in the form of an amendment by the Study Director. The amendment will clearly identify that part of the final report that is being altered and the reason(s) for the alteration(s). The amendment will be signed and dated by the Study Director.

The master copy of the final report will be signed and dated by the Study Director.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Proper laboratory protection, including lab hood or ventilation system, lab coat, closed-toe shoes, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

Refer to the Port Gamble Laboratory's Chemical Hygiene Plan and Health and Safety Plan at S:\Health and Safety for procedures to ensure safe operation in the laboratory and for contingency plans in the event of an accident or emergency.

For specific chemical health and safety information, refer to the Safety Data Sheet log.

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures of the Port Gamble Laboratory which are in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

Usually tests would be unacceptable if the following conditions occurred:

- More than 10% of the organisms die in the Control treatment.

Test data will need to be evaluated and qualified if:

- All test chambers were not identical.
- Treatments were not randomly assigned to test chambers.
- Test organisms were not randomly or impartially distributed to test chambers.
- All test animals were not from the same population, were not all of the same species, or were not of acceptable quality.
- Reference sediment and controls were not included in the test.
- Amphipods were maintained in the laboratory for less than two days or greater than ten days, unless the effect of prolonged maintenance in the laboratory has been shown to have no significant effect on sensitivity.
- Temperature, DO, pH, salinity, and ammonia were not measured, or were not within acceptable range.
- Test organisms were not acclimated at the test temperature and salinity at least 24 hours before they were placed in test chambers.
- Aeration to the test chamber was off for an extended time such that the DO levels dropped below acceptable limits and was associated with mortality.
- Response criteria were not monitored in a blind fashion.

10.0 REFERENCE DOCUMENTS

Puget Sound Water Quality Authority. Revised July 1995. “Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments.” Prepared for U.S. EPA Region 10, Office of Puget Sound. Seattle, W A.

Sediment Management Annual Review Meeting Clarification Paper. Barton, J. “Ammonia and Amphipod Toxicity Testing. “ June 15, 2002.

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Sediment Management Annual Review Meeting Clarification Paper. Warner, L.C. “Reporting Ammonia LC_{50} Data for Larval and Amphipod Bioassays”. October 3, 2001.

Sediment Management Annual Review Meeting Clarification Paper. Michelson, T. “Statistical Evaluation of Bioassay Results”. July 25, 1996.

ASTM E 1367. “Standard Test Method for Measuring the Toxicity of Sediment Associated Contaminants with Estuarine and Marine Invertebrates.” Annual Book of Standards. Volume 11.06 "Biological Effects and Environmental Fate; Biotechnology." American Society of Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA. 2006.

Norberg-King, T.J. 1998. An interpolation estimate for chronic toxicity: The Icp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

USACE/USEPA (U.S. Army Corps of Engineers/U.S. Environmental Protection Agency). 1991. Evaluation of Dredged Material Proposed for Ocean Disposal - Testing Manual." Office of Water, Washington, DC. EPA/503/8-91/001. February, 1991.

USACE/USEPA. 1994. "Methods for Assessing the Toxicity of Sediment-associated Contaminants with Estuarine and Marine Amphipods." Office of Research and Development, Washington, DC. EPA/600/R-94/025.

USACE/USEPA. 1998. "Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. - Testing Manual." Office of Water, Washington, DC. EPA/823/B-98/004. February, 1998.

11.0 APPENDIX OF CHANGE

- 08/20/15 Changed test organism acclimation section to reflect a 10% mortality threshold in assessing the organism's health

- 05/23/16 Added "uncontrolled" statement to SOP and updated Health and Safety section

- 05/09/17 Updated health and safety information, removed branding, added review documentation section. Added "proprietary information" statement to footer.

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1.0 SCOPE

To evaluate the chronic toxicity of marine sediments Sediment testing will be conducted as defined in **Dinnel and Stober (1995), Standard Methods (APHA 1985), ASTM (1989)**, and **Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**.

2.0 SUMMARY OF TEST

2.1 Approach

Number of samples	≥ 1
Number of replicates per test sediment	5
Number of controls	1
Number of replicates per control	5
Number of reference sediments	1
Number of replicates per reference sediment	5
Test chambers	1 L glass beaker or comparable wide mouth glass jar (10 cm internal diameter)
Test sediment volume	18 g of sediment per container
Overlying water	900 mL of 28‰ salinity, clean, filtered, seawater with a maximum holding time of 2 days
Renewal of overlying water	None
Number of test organisms per chamber	20,000-40,000 embryos for Bivalves, 25,000 embryos for Echinoderms
Type of biological observations	Survival, Development
Times of biological observations	Post test
Type of physical observations	Room or bath temperature continuous, light daily
Types of water quality analyses	DO, temperature, salinity, pH; ammonia and sulfides (Program Dependent)
Times of water quality samples	DO, temperature, salinity, and pH measured in a surrogate test chamber daily. Ammonia and total sulfide samples taken at the beginning and end of the test.
Aeration	Gentle aeration is applied to all chambers if Dissolved Oxygen levels fall below 6.0 mg/L.
Sediment holding time	Samples must be stored in the dark at 4 ± 2 º C with no headspace or headspace filled with nitrogen gas.

2.2 Physical Requirements

Species	*Dendraster excentricus*	*Strongylocentrotus purpuratus*	*Mytilus galloprovincialis*	*Crassostrea gigas*
DO (mg/L)*	> 4.8	> 4.8	> 4.8	> 4.6
Temperature (°C)	15 ± 1	15 ± 1	16 ± 1	20 ± 1
Salinity (ppt)	28 ± 1	28 ± 1	28 ± 1	28 ± 1
pH	Ambient	Ambient	Ambient	Ambient
Lighting	14 hours light : 10 hours dark at 50-100 foot-candles	14 hours light : 10 hours dark at 50-100 foot-candles	14 hours light : 10 hours dark at 50-100 foot-candles	14 hours light : 10 hours dark at 50-100 foot-candles
Ammonia	< 0.14 mg/L unionized	< 0.14 mg/L unionized	< 0.13 mg/L unionized	< 0.13 mg/L unionized
Aeration	Gentle, if D.O. falls below 6.0 mg/L	Gentle, if D.O. falls below 6.0 mg/L	Gentle, if D.O. falls below 6.0 mg/L	Gentle, if D.O. falls below 6.0 mg/L

*60 percent saturation at 15ºC and 28 ppt.

2.3 Biological Requirements

Feeding None
Life stage Larval Stage used within 2 hours of fertilization depending on test species.

3.0 TEST ORGANISM

The test organism should be selected based on availability, sensitivity to test materials, tolerance to ecological conditions, ecological importance, and ease of handling in the laboratory. Ideally, organisms with wide geographical distribution should be selected so test results can be compared among laboratories with similar organisms. The organisms for this protocol are *D. excentricus, S. purpuratus, M. galloprovincialis,* and *C. gigas*.

3.1 Test Organism Specifications

Species:	*Dendraster excentricus*	*Strongylocentrotus purpuratus*	*Mytilus galloprovincialis*	*Crassostrea gigas*
Age:	Larval Stage used within 2 hours of fertilization	Larval Stage used within 2 hours of fertilization	Larval Stage used within 2 hours of fertilization	Larval Stage used within 2 hours of fertilization
Source:	In-house collection; Aquatic Toxicology Support, Bremerton, WA; Dave Gutoff, San Diego, CA	Dave Gutoff, San Diego, CA; In-house collection; Aquatic Toxicology Support, Bremerton, WA	Taylor Shellfish, Shelton, WA; Aquatic Research Organisms, Hampton, NH	In-house collection; Taylor Shellfish, Shelton, WA; Aquatic Toxicology Support, Bremerton, WA

3.2 Test Organism Care

Records of the stock shipments will be kept, including original source, feeding regime, and holding water characteristics

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the Port Gamble Laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client.
The test substance is stored at 0 - 6°C in a secure and distinct storage area.

5.0 EQUIPMENT

5.1 Instrumentation/Equipment

Microprocessor-controlled recorder, and a digital thermometer
Light meter
DO meter and probe
Salinity meter and probe
pH meter and probe
Ammonia probe meter and ancillary supplies
Method of measuring total sulfides
1 L test chambers
Clean filtered seawater
Pipets

Miscellaneous labware (wash bottles, tally counters, culture bowls, etc.)
Centrifuge for collecting pore water
20 mL Scintillation or 25 mL shell vials
Syringe (to inject KCl into echinoderms) with 18-22 gauge needle
Pasteur pipets and bulbs
Ice bath or refrigerator
Compound microscope
Neubauer hemocytometer
Sedgwick-Rafter (or equivalent) counting cell (1 mL)
Small siphon hose (2ft. long, 3/16 - 1/4 in diameter)
Laboratory timer
Controlled temperature water bath or room
100-mL graduated cylinder
Perforated plunger

5.2 Reagents

0.5 M KCl
5% Buffered formalin
Copper sulfate
10% hydrochloric acid
Acetone
5% buffered formalin

5.3 Apparatus

5.3.1 Test Area

The test area consists of a room with constant temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.3.2 Lighting

Continuous overhead lighting will be at 50-100 foot-candles (550-1050 Lux).

5.3.3 Test Chambers

l-L glass chambers
20 mL glass scintillation or 25 mL glass shell vials

6.0 PROCEDURE

Prior to use, all glassware and plasticware will be thoroughly cleaned.

6.1 Preparation

6.1.1 Glassware Preparation

Glassware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Glassware will be rinsed three times with running deionized water. Glassware will then be rinsed in 10% hydrochloric acid, rinsed three times with deionized water, rinsed once with reagent grade acetone, and finally rinsed three times with deionized water.

6.1.2 Dilution Water Preparation

Filtered seawater collected from North Hood Canal will be diluted to 28 ± 1 ppt salinity using deionized water. Seawater will be held for a maximum of 2 days.

6.1.3 Test Organism Acclimation

Stock cultures will be acclimated in the same dilution water and at the same temperature as in the test procedures. Short-term culture logs will be maintained throughout the holding period.

6.2 Primary Task

6.2.1 Test Sediment Addition

Test sediment will be prepared using glassware cleaned according to Section 6.1.1, pre-cleaned glassware of a disposable nature, or non-toxic food grade plastic.

Eighteen grams of reference or test sediment is added to each chamber. 900 mL of filtered seawater (28 ppt salinity) is added to each test chamber. Two control series are prepared consisting of clean seawater without sediment. One series is used as a duplicate control in order to monitor embryo development. The sediments are suspended by vigorously shaking for 10 seconds. Test chambers will be randomized, and the mixture will be allowed to settle for four hours prior to embryo induction.

6.2.2 Reference Toxicant Test

Concurrent with this toxicity test, five concentrations of a reference substance are used to assess the health of the test organisms. Three replicates per reference concentration will be used. Five concentrations will be selected to bracket the 48-hour LC_{50}. The LC_{50} values will be compared with historical data from definitive bioassays. The results of this survival and development test, conducted during this study, will be reported and used in combination with control survival and development to characterize the health of the test organisms.

6.2.3 Test Organism Spawning and Addition

To collect gametes for testing with bivalve species, the adult organisms are placed in clean seawater and acclimated to the target test salinity (test dependant) and temperature (16°C for *Mytilus* and 20°C for *Crassostrea*) for approximately 20 minutes. The water bath temperature is then increased 5°C over a period of 15 minutes. Bivalves are maintained at this elevated temperature and monitored for spawning individuals. Spawning animals are removed from the water bath and placed in individual containers with seawater. Gametes from at least two males and two females are used to initiate the test. Once sufficient eggs and sperm had been collected, the eggs are screened though 60-µm mesh to remove any detritus or feces and a homogenized sperm solution added to the egg solutions. Egg-sperm solutions are periodically homogenized with a perforated plunger during the fertilization process. Approximately one hour after fertilization, embryo solutions are checked for fertilization and cell division. Only those embryo stocks with >90% cell division are used to initiate the tests. Density of the embryo stock solution is determined by counting the number of embryos in a subsample of stock solution. For bivalve species, approximately 20,000 - 40,000 embryos will be added to test chambers within 2 hours of fertilization.

To collect gametes required for testing echinoderm species, spawning is induced in the adult organisms by the injection of 0.5 to 1.0 mL of 0.5 M KCl into the coelemic cavity through the perisotomal membrane. The injection is performed while the adult animal is out of water. Females will release orange (*S. purpuratus*) or purple (*D. excentricus*) eggs and males of both species will release cream-colored sperm. Once release has been initiated, each adult is inverted over a 50 to 100 mL beaker with filtered seawater at 15 degrees Celsius and gametes are allowed to accumulate for approximately 15 minutes. Once sufficient eggs and sperm had been collected, the eggs are transferred to a larger beaker with cold filtered seawater and a homogenized sperm solution (taken from several males) is added to the egg solutions. Egg-sperm solutions are periodically homogenized with a perforated plunger during the fertilization process. Approximately one half-hour after fertilization, embryo solutions are checked for fertilization. Only those embryo stocks with >90% fertilization are used to initiate the tests. Density of the embryo stock solution is determined by counting the number of embryos in a subsample of stock solution.

Approximately 25,000 embryos will be added to test chambers within 2 hours of fertilization.

The test is initiated by randomly allocating an aliquot of the embryo stock solution into each test chamber four hours after sediments are shaken and within two hours of egg fertilization. Embryos are held in suspension during initiation using a perforated plunger. The test chambers are covered and incubated for 48 hours or longer under the conditions specified in Section 2.2.

For embryos/larvae test, a perforated plunger is used to mix the embryos/larvae at the test initiation. Approximately 25,000 echinoderm or 20,000-30,000 bivalve embryos will be added to test chambers within 2 hours of fertilization.

In order to determine the initial embryo concentration, five 10-mL samples should be collected from the control culture and preserved using l-mL 5% buffered formalin.

6.2.4 Test Initiation

The test is initiated when the first organism enters a test chamber.

6.2.5 Test Substance Renewal

No test substance renewals are required by this protocol.

6.2.6 Test Measurements

Water Quality. All probes will be cleaned thoroughly before initial use. Data collection will be performed on each samples respective surrogate chamber and recorded. The probes will be rinsed with de-ionized water between each sample. DO, temperature, salinity, and pH will be measured from the overlying water in the surrogate chamber daily. Ammonia and total sulfides should be measured in the overlaying water at least at the beginning of the test.

Biological. Larvae will be scored for normal development according to ASTM guidelines.

6.2.7 Test Termination

For echinoderm species, the test is terminated at 48 hours or when greater than 90% of the embryos in the duplicate seawater control have reached normal development (whichever is later and within 96 hours). For bivalve species, the test is terminated at 48 hours or when greater than 95% of the embryos in the duplicate seawater control have reached normal development (whichever is later and within 60 hours).

The water and the larvae overlying the settled sediment in each container are carefully mixed in order to suspend larvae and prevent disturbance of the sediment. The overlying water and larvae are then placed into a clean, l-L beaker. The water is then mixed, and three l0-mL aliquots of the sample are removed and placed into 20-mL scintillation vials or shell vials. The contents of each vial are preserved with 1.0-mL of 5% buffered formalin, and the caps are securely replaced on the vials.

Preserved samples are examined on Sedgwick-Rafter cells (if using scintillation vials) or in the shell vials. Normal and abnormal larvae are counted to determine the percent normal development. In addition, percent survival is determined using the appropriate method outlined in **Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**.

6.3 Post-task

- PSEP 1995 Recommendations:

Calculate the percent mortality for each replicate:

Mortality = 100 x (l-(No. of surviving test larvae / No. of control larvae))

Calculate the percent abnormality for each replicate:

Abnormality = 100 x (l-(No. of abnormal larvae / No. of normal and abnormal survivors))

Calculate the combined larval mortality/abnormality:

Combined larval mortality/abnormality = 100 x (l-(No. of surviving normal larvae / No. of embryos inoculated))

- Conventional endpoint calculations typically reported for PSEP testing programs:

Endpoint Calculation	Sample Type	
	Control	Reference and Project
Proportion Normal	No. of surviving normal larvae / No. of normal and abnormal survivors	
Proportion Survival	No. of normal and abnormal survivors / No. of embryos inoculated	
Normal Survivorship (Combined Proportion Normal)	No. of surviving normal larvae / No. of embryos inoculated	No. of surviving normal larvae / Mean No. normal in the Control

Results Needed:

- Individual replicate, mean, and standard deviation values for percent survival/mortality, percent normality/abnormality, and combined larval mortality/abnormality
- Plot of dose-response curve at test termination (48 or 72 hours)
- LC_{50} value for mortality, EC_{50} value for abnormality
- 95% confidence limits of LC_{50} value and EC_{50} value
- Tables showing biological, chemical, and physical data

6.3.1 Method

LC_{50} and EC_{50} values and 95% confidence limits will be determined using a computer approach published by Norberg-King (1988) of the U.S. EPA and a commercial statistic software program. The Inhibition Concentration percentage, or ICp, approach to calculating point estimates of toxicity (i.e., LC_{50} and EC_{50}) is based upon a monotonic smoothing technique of biological response versus concentration. Bootstrapped estimates of mean response at each concentration allow for distribution-free estimates of standard error and confidence intervals. The result is a nonparametric statistical test that requires no assumptions of normality or homogeneous variance and is robust enough to accommodate a wide variety of biological responses.

6.4 Reporting

The report may include, but will not be limited to, the following:

- Name and address of the laboratory conducting the study, and dates on which the study was initiated and completed.
- The name of the Study Director, other scientists or professionals, and supervisory personnel involved in the study.
- Objectives as stated in the protocol.
- A description of the methods used.
- Information regarding organisms used.
- All water quality measurements.
- Transformations, calculations, or operations performed on the data, a summary and analysis of the data, and a statement of the conclusion drawn from the analysis.
- The test substance identified by code number and the date each sample was used.
- The number of organisms used in the study.
- Concentrations of exposure and exposure method.

- Any circumstances that may have affected the quality or integrity of the data, including deviations from test protocols or Standard Operating Procedures.
- The location where raw data and the final report will be stored.
- Additions or corrections to a final report will be in the form of an amendment by the Study Director. The amendment will clearly identify that part of the final report that is being altered and the reason(s) for the alteration(s). The amendment will be signed and dated by the Study Director.

The master copy of the final report will be signed and dated by the Study Director.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Proper laboratory protection, including lab hood or ventilation system, lab coat, closed-toe shoes, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

Refer to the Port Gamble Laboratory's Health and Safety Plan at S:\Health and Safety for procedures to ensure safe operation in the laboratory and for contingency plans in the event of an accident or emergency.

For specific chemical health and safety information, refer to the Safety Data Sheet log.

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures which are in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

Test acceptability criteria are:

- ≥ 90% survival of embryos introduced into control test chambers.
- ≥ 70% of embryos demonstrate normal development in the control.

10.0 REFERENCE DOCUMENTS

Dinnel, P.A., J.M. Link, and Q.J. Stober. 1987. Improved methodology for a sea urchin sperm cell bioassay for marine waters. *Arch. Env. Cont. Toxicol.* 16:23-32.

Chapman, G.A., et al. 1995. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms, 1st edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/R-95/136.

Sediment Management Annual Review Meeting Clarification Paper. Warner, L.C. "Reporting Ammonia LC_{50} Data for Larval and Amphipod Bioassays". October 3, 2001.

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Norberg-King, T.J. 1988. An interpolation estimate for chronic toxicity: The ICp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

USACE/USEPA (U.S. Army Corps of Engineers/U.S. Environmental Protection Agency). 1991. Evaluation of Dredged Material Proposed for Ocean Disposal - Testing Manual." Office of Water, Washington, DC. EPA/503/8-911001. February, 1991.

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PTI Environmental Services. 1991. Draft Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments. Prepared for U.S. EPA, PTI Contract C744-12.

Puget Sound Water Quality Authority. Revised July 1995. Recommended Guideline for Conducting Laboratory Bioassays on Puget Sound Sediments. Prepared for U.S. EPA Region 10, Office of Puget Sound, Seattle, WA.

11.0 APPENDIX OF CHANGE

- 04/28/16 Updated logo
- 05/26/16 Added “uncontrolled” statement to SOP and updated Health and Safety section
- 05/09/17 Updated health and safety information, removed branding, added review documentation section. Added “proprietary information” statement to footer. Updated organism suppliers. Added the use of shell vials as an alternative to scintillation vials. Removed reference toxicant and retesting time frames from test acceptability criteria in section 9.0. Added clarification papers from Seattle USACE DMMO. Updated post-task calculation options.

Title: 20-Day Chronic Growth and Survival Test with *Neanthes arenaceodentata*	SOP No.: SED009.08w Effective Date: 11/11/19 Page No.: 1 of 10

1.0 SCOPE

To determine the chronic toxicity of marine sediments on the marine polychaete *Neanthes arenaceodentata*. Sediment toxicity testing will be conducted according to guidelines presented in **ASTM E1611**, **Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**, and the various updates presented during the Annual Sediment Management Review meetings (SMARM).

2.0 SUMMARY OF TEST

Table 1 Test Condition Summary

Sample storage conditions	4°C, dark minimal head space
Recommended Sediment Holding Time:	≤8 weeks (56 days)
Test Species	***Neanthes arenaceodentata***
Age class	Juvenile (2-3 weeks post-emergence)
Test Procedures	ASTM, PSEP 1995 with SMARM revisions
Regulatory program	SMS, DMMP, or other as mandated by the associated program
Test type/duration	20-Day static renewal
Test chamber	1-Liter glass beaker or jar
Exposure volume	175 mL (2cm) sediment/ 775 mL water
Replicates per treatment	5 + 2 surrogate chambers (one used for WQ measurements throughout the test)
Control / Diluent water	North Hood Canal, sand filtered
Test Lighting	Continuous
Aeration	Continuous from test initiation: 100 bubbles per minute
Test temperature	Recommended: 20 ± 1 °C
Test Salinity	Recommended: 28 ± 2 ppt
Test dissolved oxygen	Recommended: > 4.6 mg/L (60% saturation @ 20°C and 28 ppt salinity)[1]
Test pH	Recommended: 7 – 9 [2]
Organisms/replicate	5
Feeding	40 mg/jar every other day (8mg/ind every other day)
Water renewal	Water renewed every third day (1/3 volume of exposure chamber)

[1] PSEP guidance is not specific on dissolved oxygen limits. The value of 60% saturation is based on ASTM 2006.
[2] pH is monitored as a water quality parameter. There are generally no control limits for pH; however measurements of pH may be useful in interpreting results (Ecology 2003).

2.2 Physical Requirements

DO	>4.6 mg/L (60% Saturation)
Temperature	20 ± 1°C
Salinity	28 ± 2 ppt (PSEP); 28 – 36 ppt (ASTM)
pH	7.0 - 9.0
Lighting	Continuous ambient light at approximately 50-100 foot-candles (550-1050 lux)

2.3 Biological Requirements

Feeding	Organisms will be fed ground TetraMin® on an every-other-day basis. The amount of food provided will be approximately 8 mg (dry weight) per juvenile *N. arenaceodentata*
Life stage	Juvenile worms (2-3 weeks, 0.25-1.0 mg),

3.0 TEST ORGANISM

The test organism should be selected based on availability, sensitivity to test materials, tolerance to ecological conditions, ecological importance, and ease of handling in the laboratory. Ideally, organisms with wide geographical distribution should be selected so test results can be compared among laboratories with similar organisms. The organism for this protocol is *Neanthes arenaceodentata*.

3.1 Test Organism Specifications

Species:	*Neanthes arenaceodentata*
Source:	Aquatic Toxicology Support, Bremerton, WA
Age:	Juvenile Worms (2-3 weeks, 0.25-1.0 mg), laboratory cultured

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the Port Gamble Laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 - 6°C in a secure and distinct storage area.

5.0 EQUIPMENT

5.1 Instrumentation/Equipment

Thermometer
Light meter
DO meter and probe
Salinity meter and probe
pH meter and probe
Ammonia probe meter and ancillary supplies
Microbalance capable of measuring weights to the nearest 0.0001 g
Environmental test chamber or water bath capable of maintaining 20 ± 1°C
1000 mL test chambers
Clean filtered seawater
Deionized water
Pipets
Brushes
Miscellaneous labware (wash bottles, tally counters, culture bowls, etc.)
500 µm stainless steel sieves
Aluminum weigh boats
Holding cups (food grade plastic is acceptable)
Stir plate and teflon stir bars
Finely ground TetraMin®
Centrifuge and centrifuge Teflon® tubes for collecting pore water
Drying oven capable of maintaining 60°C
Muffle furnace capable of 550°C
Desiccator

5.2 Apparatus

5.2.1 Test Area

The test area consists of a water bath or a room with constant temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Continuous overhead lighting will be at 50-100 foot-candles (550-1050 Lux).

5.2.3 Test Chambers

1000 mL glass beakers with a 10 cm internal diameter covered with a petri dish.

6.0 PROCEDURE

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware will also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

Natural seawater will be obtained from North Hood Canal, sand filtered, and filtered to 0.45µm. Seawater will be adjusted as necessary to maintain a target test salinity. Salinity should be lowered with the addition of high purity deionized water or increased with the addition of bioassay grade sea salts or brine.

6.1.3 Test Organism Care and Acclimation

Upon receipt, salinity and temperature of water in shipping containers should be measured. If salinity is more than 2 ppt different from the target test salinity of 28 ppt then the salinity should be adjusted (no more than 3 ppt daily). If salinity is outside the range of 15 to 35 ppt, then test animals may be possibly stressed and the supplier should be notified to provide a new batch of test organisms. Temperature should be allowed to equilibrate to test temperature prior to removing animals from shipping containers. If temperature of shipping containers is outside the range of 15 to 25°C then a new batch of test organisms may be required. Animals should be held for at least 24 hours prior to testing and may be fed during holding period.

If animal health is suspect upon receipt (e.g. over 10% of number received dead, animals behaving strangely or diseased), notify the laboratory manager who will assess whether to notify the supplier and order replacements. If more than 10% of the organisms die in the 48h prior to testing, the entire batch is discarded, and a new batch is ordered. If the acclimation process is repeated with a new group of test organisms and excessive mortality occurs, an alternative source of dilution water should be used.

6.2 Primary Task

6.2.1 Test Sediment Addition

Test sediment will be prepared using labware cleaned according to Section 6.1.1, pre-cleaned labware of a disposable nature, or non-toxic food grade plastic.

If pre-sieving of sediment is required to exclude large material or potential predators they may be press sieved (no water) through a clean stainless steel sieve (2 mm mesh).

One day prior to test initiation test sediment, reference, and control sediment should be added to the test chambers. Sediment should be thoroughly homogenized prior to addition to the test chambers. A subsample should be analyzed for pore water ammonia. Approximately 2 cm of sediment should be added to each of the 5 replicate containers and applicable surrogate chambers. Once sediment has been added, clean filtered seawater should be added up to the 950-mL mark at a salinity of 28 ppt. Water should be added to ensure minimal disturbance of test sediments. Test chambers should be aerated at approximately 100 bubbles/minute under test temperature and photoperiod regime. The system should be left overnight with gentle aeration to allow suspended particles to settle and an equilibrium to be established between sediment and overlying water before the organisms are added.

6.2.2 Reference and Control Sediment Test

During this 20-day toxicity test with *Neanthes arenaceodentata* and a test sediment, a reference substance will be used to provide a site-specific basis for comparison of potentially toxic and non-toxic conditions.

6.2.3 Test Organism Addition

For test initiation, worms should be selected at random from a large culture dish(es) that contains all of the shipped animals. Animals should be added in order of replicate number, not treatment, to ensure an equal distribution of selected animals across treatments (i.e., so that animals selected initially aren't all in a single treatment and animals selected at the end aren't all in a single treatment). Transfer of animals to the test chambers is accomplished by gently drawing one worm into the wide end of a Pasteur pipette and adding the organism directly to the test chamber just above the water’s surface to prevent cross-contamination. The number of animals added will be tracked by a cell counter operated by the person adding the worms. As animals are added to the test chamber, test chambers should be marked. Test chambers should be observed within one hour of addition. Worms demonstrating non-burrowing behavior may be replaced, if the observer believes the behavior results from factors other than sediment toxicity.

During test initiation, five worms should be assigned to an additional 3 holding cups for initial calculated individual weight measurements. Worms for these measurements should be selected at random from the culture dish and should be collected at regular intervals during initiation of the test so as not bias the initial size measurements.

6.2.4 Test Initiation

The test is initiated when test organisms are distributed completely to each test chamber.

To make initial weight measurements, individual animals should be gently scooped onto a small brush, rinsed briefly in deionized water, blotted dry on a Kimwipe and transferred onto a pre dried, pre weighed, pre marked (number etched into pan prior to pre weighing) aluminum pan (2x2 cm piece of aluminum foil). All five worms from one holding cup should be placed onto a foil weigh boat. Fold pans over to prevent loss of animals over the course of drying. Oven dry worms and pans at 60°C for 24 hours prior to weighing. Remove pans/worms from the oven and place in a desiccator for approximately 1 hour to cool to room temperature. All weight measurements must be made on a balance that can be measured to the nearest 0.01 mg.

An initial ash-free dry weight (AFDW) measurement may also be desired on the worms if this endpoint is included in the final test weight determinations. After obtaining the dry weight data, each of the weigh boats is then dried in a muffle furnace heated to 550°C for 2 hours in order to determine ashed weights. The ashed boats are again weighed to 0.01 mg and the ashed weight is subtracted from the dry weight to calculate the AFDW.

6.2.5 Test Maintenance

Feed worms every 48 hours. TetraMin® should be provided at approximately 8 mg (dry weight) per juvenile *Neanthes* (40 mg per test chamber).

Overlying water should be renewed every three days (total of six renewals). Approximately one third of the overlying water volume should be exchanged at each renewal.

6.2.6 Test Measurements

Data are recorded on data sheets.

Water Quality. A daily record of test room or water bath temperatures and test chamber aeration should be made. Water quality measurement should be made prior to renewals. Record temperature, salinity, dissolved oxygen, and pH in one randomly selected test chamber per treatment or a designated water quality surrogate chamber.

Biological. Response criteria indicating toxicity of test sediment include mortality, sublethal and chronic effects. A sublethal effect is the emergence from highly toxic sediment during the course of the test. Chronic effects are monitored by comparing the differences in dry weight or AFDW between test sediments and reference sediments (or control treatment when appropriate). Response criteria will be monitored in a "blind" fashion, that is, the observer will have no knowledge of the treatment of the sediment in the test chambers.

Mortality. At test termination (Day 20), all sediment from each individual chamber should be sieved through a 500 µm sieve to collect surviving organisms. Gently rinse sediment through sieve using 26 - 30 ppt salinity seawater. Gently remove animals from the sieve using a camel hair brush taking care not to damage the animal. Once removed, the animal should be placed into a labeled holding container containing clean filtered seawater (26 - 30 ppt) at room temperature. Record whether animal recovered from each test chamber is surviving, dead, or missing (for purposed of calculations all missing animals are assumed to be dead).

Growth (Dry Weight). Growth is measured by the dry weight of the surviving test worms within a replicate. The results are compared with the weight of the worms at the beginning of the test and with the control(s) and the test concentrations of sediment. Each surviving animal is removed from its holding cup, rinsed briefly in deionized water (< 5 seconds) blotted dry on a Kimwipe, and then placed onto a pre dried, pre weighed, pre labeled weigh boat. The aluminum foil boat should be folded over to prevent the loss of the animal during drying. Note weigh boats should be handled with forceps only. Oven dry animals at 60°C for 24 hours, remove animals and boats from oven and allow to come to room temperature in a desiccator prior to weighing on a microbalance to the nearest 0.01 mg. Subtract boat weight from total weight to obtain measured dry weight value of surviving worms.

Growth Modification (Ash-Free Dry Weight). The purpose of this modification is to account for the weight of sediment contained in the gut of the worms during the drying process. Worms reared under similar conditions and life history, but exposed to different grain size sediment, may express significantly different dry weights due to the contribution of heavier gut material of the worms maintained in sandy (heavier particles) sediment. This discrepancy has the potential to lead to Type II errors, where significant differences are found between test treatments, when none actually exist. The procedure below is a tool to estimate the actual contribution of gut content to the overall weight of the animals. A procedure defined as “ashing” is employed to heat the worm tissue at high temperatures until all that is left behind is solid inorganic material.

At the termination of the 20-day survival and growth test, sediment from each test chamber is sieved through a 0.5-mm screen and all recovered polychaetes are transferred into a plastic cup. Survival is recorded and worms are rinsed with deionized water and placed in pre-ashed, pre-weighed aluminum boats and dried in a gravimetric

oven at 60°C for at least 24 hours. Each weigh-boat is removed from the oven, cooled in a desiccator for approximately 30 minutes, and then weighed on an analytical microbalance to 0.01 mg. Each of the weigh boats is then dried in a muffle furnace heated to 550°C for 2 hours in order to determine ashed weights. The ashed boats are again weighed to 0.01 mg and the ashed weight is subtracted from the dry weight to calculate the AFDW. Both the dry weight and the AFDW are used to determine individual worm weight and growth rates.

The 20-day average individual dry weight (or AFWD) in each exposure chamber is recorded and the mean and standard deviation calculated for each treatment.

6.3 Post-task

Results Needed:

- Percent mortality for each treatment
- Mean dry weight per individual for each treatment
- Ash-Free dry weight (AFDW) per individual for each treatment (program specific, if desired)
- Mean water quality values by treatment
- LC_{50} and 95% confidence limits (for ref. tox.)
- Tables showing biological, chemical, and physical data

In screening tests, the responses of worms in collected test sediments are compared to control and reference site sediments.

6.4 Reporting

The report may include, but will not be limited to, the following:

- Name and address of the laboratory conducting the study, and dates on which the study was initiated and completed.
- The name of the Study Director, other scientists or professionals, and supervisory personnel involved in the study.
- Objectives as stated in the protocol.
- A description of the methods used.
- Transformations, calculations, or operations performed on the data, a summary and analysis of the data, and a statement of the conclusion drawn from the analysis.
- The test substance identified by code number and the date each sample was used.

- The number of organisms used in the study.
- Concentrations of exposure and exposure method.
- Any circumstances that may have affected the quality or integrity of the data, including deviations from test protocols or Standard Operating Procedures.
- The location where raw data and the final report will be stored.
- Additions or corrections to a final report will be in the form of an amendment by the Study Director. The amendment will clearly identify that part of the final report that is being altered and the reason(s) for the alteration(s). The amendment will be signed and dated by the Study Director.

The master copy of the final report will be signed and dated by the Study Director.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Proper laboratory protection, including lab hood or ventilation system, lab coat, closed-toe shoes, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

Refer to the Port Gamble Laboratory's Health and Safety Plan at S:\Health and Safety for procedures to ensure safe operation in the laboratory and for contingency plans in the event of an accident or emergency.

For specific chemical health and safety information, refer to the Safety Data Sheet log.

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures which are in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

Usually tests would be unacceptable if one or more of the following occurred:

- More than 10% of the control organisms die.
- All test chambers were not identical.

- Treatments were not randomly assigned to test chambers.
- Test organisms were not randomly or impartially distributed to test chambers.
- All test animals were not from the same population, were not all of the same species, or were not of acceptable quality.
- Reference sediment and controls were not included in the test.
- Temperature, DO, pH, salinity, and ammonia were not measured, or were not within acceptable range.
- Aeration to the test chamber was off for an extended time such that the DO levels dropped to less than 4.6 mg/L.
- Response criteria were not monitored in a blind fashion.

10.0 REFERENCE DOCUMENTS

ASTM. 2012. Guide for conducting Sediment Toxicity Test with Marine and Estuarine Polychaetous Annelids. Standard Guide #E-1611-00(Reapproved 2007). American Society for Testing and Materials, Philadelphia, P A.

Puget Sound Water Quality Authority. Revised July 1995. “Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments.” Prepared for U.S. EPA Region 10, Office of Puget Sound. Seattle, W A.

11.0 APPENDIX OF CHANGE

- 08/20/15 Hand-written change to reflect criteria: if >5% mortality 48hrs preceding test, organisms should be replaced

- 11/12/15 Updated logo, corrected microbalance to nearest gram, and changed test organism acclimation section to reflect a 10% mortality threshold when assessing the organism’s health during rounds

- 05/23/16 Added “uncontrolled” statement to SOP footer and updated Health and Safety section

- 05/09/17 Updated health and safety information, removed branding, added review documentation section. Added “proprietary information” statement in footer. Updated information on animal health upon receipt in section 6.1.3.

STANDARD OPERATING PROCEDURE
SPT AND SPLIT SPOON SAMPLING

Introduction

Split spoon sampling is generally used to collect disturbed soil samples of 18 or 24 inches in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling, providing samples at discrete depth intervals. During discrete sampling, the split spoon is driven to its sampling depth through the bottom of the augured hole and the core extracted. A split-spoon sample is ideal for collecting subsurface geotechnical data, including relative soil strength information through the standard penetration test (SPT). When split spoon sampling is performed to gain geologic information, all work should be performed in accordance with ASTM D1586, "Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils". This SOP describes the SPT and collection of soil samples using the split spoon.

Standard Penetration Test

The SPT is an approximate measure of soil density and consistency. To be useful, the results must be used with engineering judgment in conjunction with other tests. The SPT (ASTM D1586) is used to obtain disturbed soil samples. This test employs a standard 2-inch outside diameter[1] split-spoon sampler. Using a 300-pound hammer, free-falling 30 inches, the sampler is driven into the soil for 18 inches. The number of blows required to drive the sampler the last 12 inches only is the Standard Penetration Resistance. This resistance, or blow count, measures the relative density of granular soils and the consistency of cohesive soils. The blow counts are plotted on the boring logs at their respective sample depths.

Soil samples are recovered from the split-barrel sampler, field classified, and placed into watertight jars or double bagged in ziplock bags. They are then shipped to the geotechnical laboratory for further testing.

In the Event of Hard Driving

Occasionally very dense materials preclude driving the total 18-inch sample. When this happens, the penetration resistance is entered on logs as follows:

[1] Different sized samplers may be used, including oversized split spoons where sample volume requirements dictate collecting more soils. In all cases, the size of the split spoon sampler shall be recorded in field records so that SPT blowcounts can be corrected, if necessary, for non-standard split spoon sizes.

Penetration less than six inches. The log indicates the total number of blows over the number of inches of penetration.

Penetration greater than six inches. The blow count noted on the log is the sum of the total number of blows completed after the first 6 inches of penetration. This sum is expressed over the number of inches driven that exceed the first 6 inches. The number of blows needed to drive the first 6 inches are not reported. For example, a blow count series of 12 blows for 6 inches, 30 blows for 6 inches, and 50 (the maximum number of blows counted within a 6-inch increment for SPT) for 3 inches would be recorded as 80/9.

Required Information on Boring Logs

Logs shall include the following information, at a minimum, to describe the drilling work:

1. The sample station identification
2. Names of field personnel collecting and handling the samples
3. Type of sampling equipment used (i.e. split spoon inside and outside diameter; hammer weight; free fall height; hammer deployment method)
4. Date and time at the start and completion of each boring location
5. Total depth of boring penetration below ground surface or mudline
6. Depth of water and time of measurement for barge-based drilling
7. Date and time of collection of each sample
8. Driller observations regarding changes in subsurface conditions, and depth of drilling equipment at the time of observation (e.g. gravelly drill action, hard penetration, etc.)
9. Observations made during sample collection, including weather conditions, complications, and other details associated with the sampling effort
10. Length and depth intervals of each sample and measured recovery
11. Qualitative notation of apparent resistance during driving
12. Any deviation from the approved SAP

Split Spoon Sample Collection and Processing

The following procedures are used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of barrel and then screwing the drive shoe (with catcher) on the bottom and the head piece on top.
2. Place the sampler in a perpendicular position on the sample material. Where a drill rig is used, this step is performed by the drilling contractor.

3. Use the SPT hammer to drive the tube. Do not drive past the bottom of the sample length. Where a drill rig is used, this step is performed by the drilling contractor.
4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain this depth, in 6-inch depth intervals
5. Withdraw the sampler, and open by unscrewing the bit and head and splitting the barrel. The amount of recovery and soil type should be recorded on the boring log.
    a. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally.
    b. The split spoon sampler is typically available in 2- and 3-1/2-inch diameters. A larger barrel may be necessary to obtain the required sample volume.
6. Record soil description on the field log, and place samples in labeled, watertight containers.
7. Store sample in a dry location outside of direct sunlight.

Split Spoon Sample Logging

Split spoon samples will be logged on-site by an experienced field geologist or geotechnical engineer. Prior to sub-sampling, a description of each sample will be recorded on a standard boring log. The following parameters will be noted:

1. Sample recovery
2. Physical soil description in accordance with the Unified Soil Classification System (includes soil type, moisture, density/consistency of soil, color)
3. Odor (e.g., hydrogen sulfide, petroleum)
4. Visual stratification, structure, and texture
5. Vegetation and debris (e.g. woodchips or fibers, concrete, metal debris)
6. Biological activity (e.g., detritus, shells, tubes, bioturbation, live or dead organisms)
7. Presence of oil sheen

Standard terminology for field logs is attached to this SOP.

Sample Description Key

Classification of soils in this report is based on visual field and laboratory observations which include density/consistency, moisture condition, grain size, and plasticity estimates and should not be construed to imply field nor laboratory testing unless presented herein. Visual-manual classification methods of ASTM D 2488 were used as an identification guide.

Soil descriptions consist of the following:
Density/consistency, moisture, color, minor constituents, MAJOR CONSTITUENT, additional remarks.

Density/Consistency

Soil density/consistency in borings is related primarily to the Standard Penetration Resistance. Soil density/consistency in test pits is estimated based on visual observation and is presented parenthetically on the test pit logs.

SAND or GRAVEL Density	Standard Penetration Resistance (N) in Blows/Foot	SILT or CLAY Consistency	Standard Penetration Resistance (N) in Blows/Foot	Approximate Shear Strength in PSF
Very loose	0 - 4	Very soft	0 - 2	< 250
Loose	4 - 10	Soft	0 - 4	250 - 500
Medium dense	10 - 30	Medium stiff	4 - 8	500 - 1,000
Dense	30 - 50	Stiff	8 - 15	1,000 - 2,000
Very dense	>50	Very stiff	15 - 30	2,000 - 4,000
		Hard	>30	> 4,000

Moisture

Dry	Little perceptible moisture
Damp	Some perceptible moisture, probably below optimum
Moist	Probably near optimum moisture content
Wet	Much perceptible moisture, probably above optimum

Minor Constituents

	Estimated Percentage
Not identified in description	0 - 5
Slightly (clayey, silty, etc.)	5 - 12
Clayey, silty, sandy, gravelly	12 - 30
Very (clayey, silty, etc.)	30 - 50

Legends

Sampling Test Symbols

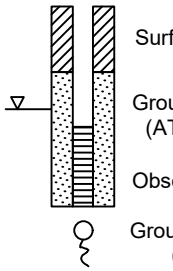
BORING SAMPLES

- Split Spoon
- Shelby Tube
- Cuttings
- Core Run
- ✳ No Sample Recovery
- P — Tube Pushed, Not Driven

TEST PIT SAMPLES

- Grab (Jar)
- Bag
- Shelby Tube

Groundwater Observations



Surface Seal

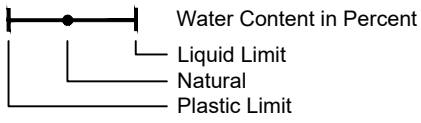
Groundwater Level on Date (ATD) At Time of Drilling

Observation Well Tip or Slotted Section

Groundwater Seepage (Test Pits)

Test Symbols

GS	Grain Size
Comp	Composite
Chem	Chemistry
VST	Vane Shear Test
BD	Bulk Density
UU	Triaxial Unconsolidated Undrained
TCU	Triaxial Consolidated Undrained
TCD	Triaxial Consolidated Drained
QU	Unconfined Compression
DS	Direct Shear
K	Permeability
PP	Pocket Penetrometer - Approximate Compressive Strength in TSF
TV	Trovane - Approximate Shear Strength in TSF
AL	Atterberg Limits



PID	Photoionization Detector Reading
Note:	additional observation modifiers to be added as appropriate, including approximate amount (e.g. trace debris) at depth interval where encountered

Nov 22, 2019 4:30pm jlaplante K:\Standards\Geotech\KEY TO EXPLORATIONS geotechnical.dwg 1

ANCHOR QEA

Figure 1
Key to Explorations

STANDARD OPERATING PROCEDURE

THIN WALL SAMPLING

Introduction

Undisturbed[1] soil sampling is performed using a thin wall (a.k.a. Shelby tube) sampler advanced by hand, or hydraulically pushed from a land- or water-based drill rig. Thin wall sampling is generally used to collect undisturbed soil cores of 24 to 36 inches in length. A series of consecutive cores may be extracted with a thin wall sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling for a discrete sample interval. In the case of discrete interval sampling, the thin wall sampler is pushed to its sampling depth through the bottom of the augured hole and the core extracted. A thin wall sampler is ideal for collecting relatively undisturbed subsurface geotechnical samples for advanced geotechnical laboratory testing. When thin wall sampling is performed to gain geologic information, all work should be performed in accordance with ASTM D1587, "Thin-Walled Tube Sampling of Soils for Geotechnical Purposes". This SOP describes the collection of soil samples using the thin walled sampler.

Thin Wall Sample Collection and Processing

The following procedures are used for collecting soil samples with a thin-walled sampler:

1. Assemble the sampler by attaching the driving head to the sampling tube.
2. Place the sampler in a perpendicular position on the sample material. Where a drill rig is used, this step is performed by the drilling contractor.
3. Use a smooth continuous push to advance the tube. Do not drive past the bottom of the sample length. Where a drill rig is used, this step is performed by the drilling contractor.
4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, as well as the detailed information described in this SOP.
5. Withdraw the sampler and remove the drive head. The amount of recovery and soil type should be measured recording the depth to soil from both the top and bottom of the sample tube. Note any aberrations such as rocks or other objects visible in the drive end of the sampler, or any visible damage to the sample tube.
6. Fill any voids in the sample tube with packing material such as bubble wrap or wax.
7. Tightly seal both ends of the sample tube, and visually indicate the top of the tube with markings on the outside of the tube.

[1] The term "undisturbed" is relative for soil sampling. All soil sampling induces some disturbance to the sample. Thin-walled sampling induces the least disturbance, compared to other methods such as standard penetration test (SPT) split-spoon sampling.

8. Store sample upright in a protected and dry location outside of direct sunlight.

Required Information on Boring Logs

Logs shall include the following information, at a minimum, to describe the sampling work:

1. The sample station identification
2. Names of field personnel collecting and handling the samples
3. Type of sampling equipment used
4. Date and time at the start and completion of each boring location
5. Total depth of boring penetration below ground surface or mudline
6. Depth of water and time of measurement for barge-based drilling
7. Date and time of collection of each sample
8. Driller observations regarding changes in subsurface conditions, and depth of drilling equipment at the time of observation (e.g. gravelly drill action, hard penetration, etc.)
9. Observations made during sample collection, including weather conditions, complications, and other details associated with the sampling effort
10. Length and depth intervals of each sample and measured recovery
11. Qualitative notation of apparent resistance during driving
12. Any deviation from the approved SAP

Thin Wall Sample Handling

Thin wall tube samples do not allow for direct observation or logging in the field. When recovered from the boring, the tubes will be measured for amount of recovery and checked to ensure the tube was not dented or damaged while driving or removing. The tubes will then be quickly cleaned, sealed with a plastic cap and duct tape on both ends, and labeled with boring name, sample name, date, approximate depth, and the location of the top of the sample with respect to the orientation it was removed from the subsurface. Every effort will be made to store and transport the thin wall sample tubes with minimal disturbance in the upright, vertical position.

Standard terminology for field logs is attached to this SOP.

Sample Description

Classification of soils in this report is based on visual field and laboratory observations which include density/consistency, moisture condition, grain size, and plasticity estimates and should not be construed to imply field nor laboratory testing unless presented herein. Visual-manual classification methods of ASTM D 2488 were used as an identification guide.

Soil descriptions consist of the following:
Density/consistency, moisture, color, minor constituents, MAJOR CONSTITUENT, additional remarks.

Density/Consistency

Soil density/consistency in borings is related primarily to the Standard Penetration Resistance. Soil density/consistency in test pits is estimated based on visual observation and is presented parenthetically on the test pit logs.

Density SAND or GRAVEL	Standard Penetration Resistance (N) in Blows/Foot	SILT or CLAY Consistency	Standard Penetration Resistance (N) in Blows/Foot	Approximate Shear Strength in TSF
Very loose	0 - 4	Very soft	0 - 2	<0.125
Loose	4 - 10	Soft	2 - 4	0.125 - 0.25
Medium dense	10 - 30	Medium stiff	4 - 8	0.25 - 0.5
Dense	30 - 50	Stiff	8 - 15	0.5 - 1.0
Very dense	>50	Very stiff	15 - 30	1.0 - 2.0
		Hard	>30	>2.0

Moisture

Dry	Little perceptible moisture
Damp	Some perceptible moisture, probably below optimum
Moist	Probably near optimum moisture content
Wet	Much perceptible moisture, probably above optimum

Minor Constituents

	Estimated Percentage
Not identified in description	0 - 5
Slightly (clayey, silty, etc.)	5 - 12
Clayey, silty, sandy, gravelly	12 - 30
Very (clayey, silty, etc.)	30 - 50

Legends

Sampling Test Symbols

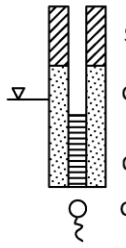
BORING SAMPLES

- ☒ Split Spoon
- ⧅ Shelby Tube
- ▥ Cuttings
- ◫ Core Run
- ✳ No Sample Recovery
- P Tube Pushed, Not Driven

TEST PIT SAMPLES

- ☒ Grab (Jar)
- ⧄ Bag
- ⧅ Shelby Tube

Groundwater Observations



Surface Seal

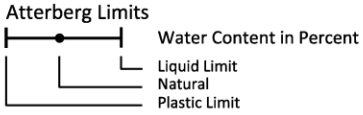
Groundwater Level on Date (ATD) At Time of Drilling

Observation Well Tip or Slotted Section

Groundwater Seepage (Test Pits)

Test Symbols

GS	Grain Size
Comp	Composite
Chem	Chemistry
NS	No Sheen
SS	Slight Sheen
MS	Moderate Sheen
HS	Heavy Sheen
TCD	Triaxial Consolidated Drained
QU	Unconfined Compression
DS	Direct Shear
K	Permeability
PP	Pocket Penetrometer Approximate Compressive Strength in TSF
TV	Torvane Approximate Shear Strength in TSF
CBR	California Bearing Ratio
MD	Moisture Density Relationship
AL	Atterberg Limits
PID	Photoionization Detector Reading
CA	Chemical Analysis
DT	In Situ Density Test



STANDARD OPERATING PROCEDURE
CONE PENETROMETER TESTING

Introduction

Cone Penetrometer Testing (CPT) is generally used to develop a continuous profile of subsurface soil/sediment geotechnical characteristics. CPT penetration tip resistance, side friction, and pore water pressure are continuously measured as the instrumented probe is advanced into the subsurface. These three parameters are further processed to develop a range of geotechnical engineering soil classification parameters using industry-standard protocols for interpreting CPT data. This SOP describes subsurface data collection using the CPT.

CPT Data Collection and Processing

The electric piezocone penetrometer test procedure involves hydraulically pushing in instrumented cylindrical rod into the subsurface at a constant rate of two centimeters per second and subsequently monitoring soil and pore fluid response near the conical tip. The cylindrical rod houses a pressure transducer and load cells which, during probing, measure the parameters indicated above. The results are used with engineering judgment in conjunction with other tests, preferably the SPT procedure, which allows soil sample collection for direct comparison purposes. CPT tests are performed in general accordance with procedures outlined in ASTM D 5778, Standard Test Method for Electronic Friction Cone and Piezocone Penetration Testing of Soils.

The cone system is mounted on heavy equipment to provide the necessary reaction for the applied loads. The cone tip has a surface area of about 10 square centimeters (cm^2) and an angle of 30 degrees from the axis. The friction sleeve has a surface area of about 150 cm^2. Prior to testing, a plastic filter element, which has been saturated under vacuum in glycerin, is placed behind the cone tip. This filter element transmits pore pressures to the transducer. Load cells measure end resistance on the tip and frictional resistance on the friction sleeve. As the cone penetrates the soil, measurements are continuously recorded on a portable computer at depth increments of about 5 centimeters.

The classification method used to develop an interpreted soil profile is based on normalized parameters provided by the piezocone, as there are no soil samples collected with a penetrometer system of this type. The relationship between the cone tip resistance and friction ratio, which has been normalized for soil overburden stresses, can be established to predict soil behavior (e.g. Sabatini et. al. 2002).

Commercial software is often used to process raw CPT data and to provide geologic and geotechnical engineering interpretations of subsurface conditions. Some CPT contractors provide a complete report, with data interpretation as part of their deliverable. In other cases, CPT contractors may provide interpreted data and raw data for independent interpretation.

Independent interpretation of raw CPT data can be performed by commercial software programs. At Anchor QEA, the software package CPeT-IT by Geologismiki is used for raw CPT data interpretation, and CLiq by Geologismiki is used for liquefaction evaluations of CPT data.

Where commercial software is not used to process raw CPT data, the methods described in Sabatini et. al. (2002) will be used to process CPT data for use in geotechnical engineering evaluations.

References

Sabatini, P.J., Bachus, R.C., Mayne, P.W., Schneider, J.A., and Zettler, T.E., 2002. *Geotechnical Engineering Circular No. 5, Evaluation of Soil and Rock Properties, Report No. FHWA-IF-02-034*. U.S. Department of Transportation, Federal Highway Administration, Washington, D.C.

STANDARD OPERATING PROCEDURE
DYNAMIC CONE PENETROMETER TESTING

Introduction

Dynamic Cone Penetrometer (DCP) testing is generally used to develop a continuous profile of subsurface blowcounts indicating relative density of soils, using handheld equipment for locations with difficult access. DCP blowcounts can be correlated to standard penetration test (SPT) blowcounts for further use in classifying site subsurface soils. This SOP describes subsurface data collection using the DCP.

DCP Data Collection and Processing

DCP data collection entails advancing a 10-square-centimeter field point fixed to the end of a drive rod that is driven continuously through a series of hammer blows. The blows are delivered to the top of the 1-meter-long drive rod through the raising and dropping of a 35-pound weight at a consistent fall height of 15 inches. The number of blows is recorded for each 10-centimeter interval for the full drive length. Additional 1-meter drive rods are added as needed until refusal or the desired investigation depth is reached. The blow count data obtained are then correlated to an equivalent SPT N-value for each 10-centimeter interval. The SPT N-values are then used to estimate the geotechnical engineering properties of interest.

EQUIPMENT AND SUPPLIES REQUIRED

- 10-square-centimeter field points (sacrificial)
- 1-meter drive rods with marks at 10-centimeter intervals and thread connections
- Driver hammer attachment with 35-pound weight with minimum 15 inches of throw
- Driving head (threaded connection)
- Mechanical drive rod extractor
- Base plate for drive rod extractor
- Equipment carrying case
- Field logbook, surface soil field collection form, and pens
- Project-specific Field Sampling Plan (FSP) and Health and Safety Plan (HASP)
- Personal protective equipment (safety glasses, steel-toed boots, work gloves, and any other items required by the project-specific HASP)
- Decontamination equipment

PROCEDURES

Performing the Exploration

1. Expose the soil surface by clearing an approximately 1-square-foot area at the sampling site of any surficial detritus that may otherwise create an obstruction
2. Ensure the driving head is threaded onto a 1-meter drive rod
3. Fix the field point to the driving head
4. Place drive rod and field point unit on the ground with field point resting on the desired location of the exploration
5. Connect the driver attachment with the 35-pound hammer
6. Seat the field point by raising and dropping the driver until the field point is fully embedded in the subsurface
7. Begin raising and dropping the driver and count the number of blows required for 10 centimeters of advancement
    a. Record the blows for each 10-centimeter drive interval; manual adjustments may be needed to maintain verticality of the drive rods
    b. Record any obstructions/zones of difficult driving or apparent changes in substrate that occur within the 10-centimeter interval, if applicable, on the field data collection form
8. Connect additional drive rods as needed until refusal or the desired drive depth is achieved
    a. Refusal is assumed to be 50 blows per 10 centimeters or less
    b. Leave approximately 0.5 meters of stickup of the last rod for extraction
9. After the target depth or refusal is reached, place the base plate near the rod and fix the extractor and begin retrieving the rods
    a. The drive hammer may need to be removed to allow for extraction of drive rods
    b. Care must be applied when extracting the rod so as to not drop loose rods back down the hole
10. Decontaminate equipment, if necessary

Data Processing

1. Input the data obtained for each exploration into the data processing spreadsheet, which was developed based on methods described in Triggs and Simpson (1991), attached.
2. The depth, field recorded blow count, and equivalent SPT N-value are reported for the processed data

Quality Assurance and Quality Control

1. Complete all pertinent field quality assurance (QA)/quality control (QC) documentation, logbooks, sample labels, and field data sheets
    a. Record any deviations from the specified sampling procedures or any obstacles encountered
2. Record actual exploration locations with field measurements from landmarks or a Differential Global Positioning System (DGPS) recording device
3. Photograph the sample location and document it in the logbook
4. Decontaminate all sampling equipment as appropriate

References

Triggs and Simpson, 1991. *A Portable Dynamic Penetrometer for Geotechnical Investigations*. 34th Annual Meeting, Association of Engineering Geologists. Chicago, IL.

Attachment

A PORTABLE DYNAMIC PENETROMETER FOR GEOTECHNICAL INVESTIGATIONS

J. Fred Triggs, P.E.,
Triggs Technologies, Inc., Willoughby Hills, OH 44094

Paul D. Simpson, P.E.,
University of Akron, Akron, OH 44325

INTRODUCTION

Most of us are frustrated by our human inability to "see" into the ground. Without special instruments, we can only see, probe, or squeeze the very surface of the ground. Such looks, probes, and squeezes give little reliable information about its ability to support loads because its supporting properties depend upon the soils' strength, deep within the ground.

The authors have developed and tested a lightweight dynamic cone penetrometer which one person can carry to remote locations where he can readily test for strength properties to deep within the soil. A means of injecting fluid into the cone path annulus to reduce parasitic friction dynamic energy loss is described. A logging program which quickly reduces the penetrometer's blow count data to dynamic cone resistances, plots these resistances, and interprets them, is described and illustrated.
Calibration of this dynamic cone penetrometer has been accomplished by the authors' correlations of side-by-side dynamic cone resistances with Standard Penetration Test N values in various soil types. This paper proposes correlations between this penetrometer's dynamic cone resistances and SPT N values.

THE NEED FOR A PORTABLE SOIL EVALUATION INSTRUMENT

The normal commercial structure needs and generally receives a subsurface exploration including test borings with SPT N values and laboratory strength testing of soil samples. But it is often impractical to use test borings to:

a. preliminarily explore the subsurface in densely wooded, building covered, swampy, or steep terrain sites.

b. explore the subsurface for single-family residences.

c. evaluate earth fill compaction.

d. verify footing bearing capacities during construction.

REQUIREMENTS FOR A PORTABLE PENETROMETER

For such a penetrometer to be most useful, it must be usable by a single person; portable, in that it can be carried to test locations; small enough to travel in the trunk of a

car; versatile enough to test any soil type; sensitive enough to differentiate between weak, medium, and strong soils; and simple to interpret.

DESIGN OF THIS DYNAMIC PENETROMETER

The authors followed these specifications to develop and test a light dynamic cone penetrometer with the characteristics of:

a. An unmotorized (hand-raised) hammer with a 35 lb weight and a 15 inch drop, to provide the energy for driving a 10 cm^2 projected area cone. This can be transported in a car trunk, carried by one person, and worked by one person to test all but the most consolidated soils. As testing progresses below the first meter, additional 1 meter long sounding rods are screwed onto the rod string.

b. A fluid injection system, pumps a cellulose/water mixture into the annulus between the 1.4" diameter cone path and the 1.1" diameter rods, minimizing parasitic friction on the rods. Consequently, undiminished hammer energy is transmitted to the cone, allowing confident use of the Dutch Formula to calculate cone resistance (q_d). The rods slip out of the "lost point" cones to be pulled from the slurry- filled hole by hand. Cellulose slurry biodegrades.

c. A simple spread-sheet computer program logs the hammer blows per 10 cm; calculates, plots, and tabulates dynamic cone resistances (q_d); and tabulates consistency adjectives.

Unfortunately, this penetrometer, like other dynamic cone penetrometers, does not ascertain the grain size of the tested soils. Consequently, although the data tells much about soils' relative densities, the data does not indicate whether the soils are clay, silt, or sand. Where determination of soil grain sizes is important, that information must be found by some method other than by dynamic cone testing.

REDUCTION AND LOGGING OF DYNAMIC PENETROMETER DATA

In this paper, dynamic cone resistance, q_d, is the cone resistance pressure in Kg/cm^2, calculated by the "Dutch Formula". In that formula,

$$q_d = \frac{M^2 \times H \times N_d}{A_p(M + M' + P_a)10}$$

where,

M= Mass of the hammer = 35# x 0.453 = 15.89 Kg
H= Height of Drop = 15" x 2.54 = 38.1 cm
N_d= Number of blows per 10 cm of drive
A_p=Projected area of the cone = 10 cm2
M' = Mass of the driven portion of the hammer = 2.49 Kg
P_a= Mass of the rod string = 3.26 Kg x the number of rods.

This means that the dynamic cone resistance, in Kg/cm^2, is:

4.44 x N_d for 1 sounding rod
3.86 x N_d for 2 sounding rods
3.42 x N_d for 3 sounding rods
3.06 x N_d for 4 sounding rods
2.77 x N_d for 5 sounding rods

2.54 x N_d for 6 sounding rods
2.33 x N_d for 7 sounding rods
2.16 x N_d for 8 sounding rods
2.01 x N_d for 9 sounding rods
1.89 x N_d for 10 sounding rods

The program for logging a dynamic cone penetration test is illustrated in figure 1. The hammer blows per 10 cm are entered. A spread sheet program tabulates these figures, and calculates, tabulates, and plots the dynamic cone resistances. The program also tabulates three columns of consistency adjectives: one for sand, one for silt, and one for clay.

PENETROMETER CALIBRATION BY CORRELATIONS WITH SPT N VALUES

Since many of us in North America are most comfortable evaluating soil strengths from Standard Penetration Test in-situ test results, we have correlated dynamic cone resistance of the dynamic penetrometer with SPT N values by using both test types in close proximity. In the reduction of the correlation test data, we compared the average of three 10 cm long dynamic cone resistances with the corresponding 12 inch SPT N value.

Soil samples are a byproduct of SPT testing, so we took the opportunity to either visually estimate or test for the mean soil particle size of each SPT test sample. These determinations of d_{50} in mm were used in our q_d/N versus d_{50} plot of Figure 2.

(Robertson, Campanella, and Wightman, 1983) in correlating static cone resistances, q_c with SPT N, found that q_c/N increased from approximately 1 for clays to approximately 8 for sands. We have not found a similar increase of q_d/N to be characteristic of dynamic cone resistances. Perhaps because the dynamic cone penetrometer and the Standard Penetration Test both employ a dynamic penetration force, their relationships are more linear than the relationship of static cone and dynamic SPT.

Figure 3 plots our currently available q_d versus N correlations. Each plotted point indicates whether it is a clay, silt, or sand soil type. By plotting q_d directly, rather than the ratio of q_d/N, one can see how at higher blow counts, the q_d/N values increase. We believe that this is caused by the relatively low energy of the dynamic penetrometer, compared to the higher energy of SPT.

CONCLUSIONS

We do believe that this dynamic cone penetrometer, as developed, is a valid instrument for estimating approximate strengths of nearly all soils to reasonable depths. it correlates well with N values of SPT borings. With q_d values up to 90 Kg/cm^2, q_d/N ratios are approximately 3.5.

Two technical reservations of this penetrometer should be understood. The first reservation is that this penetrometer tells nothing about whether a soil is clay, silt, or sand. The second reservation is that when the q_d values of the cone exceed approximately 90 Kg/cm^2, SPT N values exceed 25, but are indeterminate.

Most soil evaluation concerns focus on soils with SPT N values less than 15. This penetrometer provides a continuous stream of accurate soil strength data through the entire 0 to 25 range of SPT N values. Consequently, the penetrometer is both usable and most valuable in the soils that require the most concern.

TRIGGS TECHNOLOGIES, INC.
33977 CHARDON ROAD
WILLOUGHBY HILLS, OHIO 44094

SHEET #: 1
FILE #: 1
STARTED: 4/27/90
COMPLETED: 4/27/90

****
WILDCAT DYNAMIC

CONE PENETROMETER LOG
****

CREW: ACT
TEST #: DEMO
PROJECT: NONE
LOCATION: HAYES DRIVE

SURFACE ELEVATION:
HAMMER WEIGHT: 35 LBS.
CONE AREA: 10 SQ. CM
HAMMER DROP: 15"

DEPTH FT	DEPTH M	BLOWS PER 10 CM	RESISTANCE KG/CM^2	TESTED CONSISTENCY SAND	SILT	CLAY
	0.1	3.0	13.1	LOOSE	LOOSE	MEDIUM
	0.2	4.0	17.4	LOOSE	LOOSE	MEDIUM
1	0.3	55.0	239.8	COMPACT	DENSE	HARD
	0.4	14.0	61.0	FIRM	DENSE	VERY STIFF
	0.5	26.0	113.4	COMPACT	DENSE	HARD
2	0.6	19.0	82.8	FIRM	DENSE	HARD
	0.7	15.0	65.4	FIRM	DENSE	VERY STIFF
	0.8	13.0	56.7	FIRM	MEDIUM	VERY STIFF
3	0.9	10.0	43.6	FIRM	MEDIUM	VERY STIFF
	1.0	10.0	43.6	FIRM	MEDIUM	VERY STIFF
	1.1	9.0	33.7	FIRM	MEDIUM	STIFF
4	1.2	9.0	33.7	FIRM	MEDIUM	STIFF
	1.3	8.0	30.0	LOOSE	LOOSE	STIFF
	1.4	9.0	33.7	FIRM	MEDIUM	STIFF
5	1.5	7.0	26.2	LOOSE	LOOSE	STIFF
	1.6	7.0	26.2	LOOSE	LOOSE	STIFF
	1.7	7.0	26.2	LOOSE	LOOSE	STIFF
6	1.8	8.0	30.0	LOOSE	LOOSE	STIFF
	1.9	9.0	33.7	FIRM	MEDIUM	STIFF
	2.0	7.0	26.2	LOOSE	LOOSE	STIFF
7	2.1	6.0	19.7	LOOSE	LOOSE	STIFF
	2.2	6.0	19.7	LOOSE	LOOSE	STIFF
	2.3	10.0	32.9	FIRM	MEDIUM	STIFF
8	2.4	8.0	26.3	LOOSE	LOOSE	STIFF
	2.5	8.0	26.3	LOOSE	LOOSE	STIFF
	2.6	12.0	39.5	FIRM	MEDIUM	STIFF
9	2.7	9.0	29.6	LOOSE	LOOSE	STIFF
	2.8	10.0	32.9	FIRM	MEDIUM	STIFF
	2.9	7.0	22.8	LOOSE	LOOSE	STIFF

DYNAMIC CONE RESISTANCE PLOT

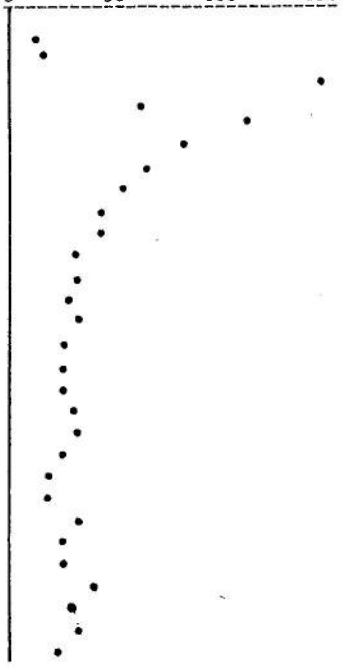


FIGURE 1

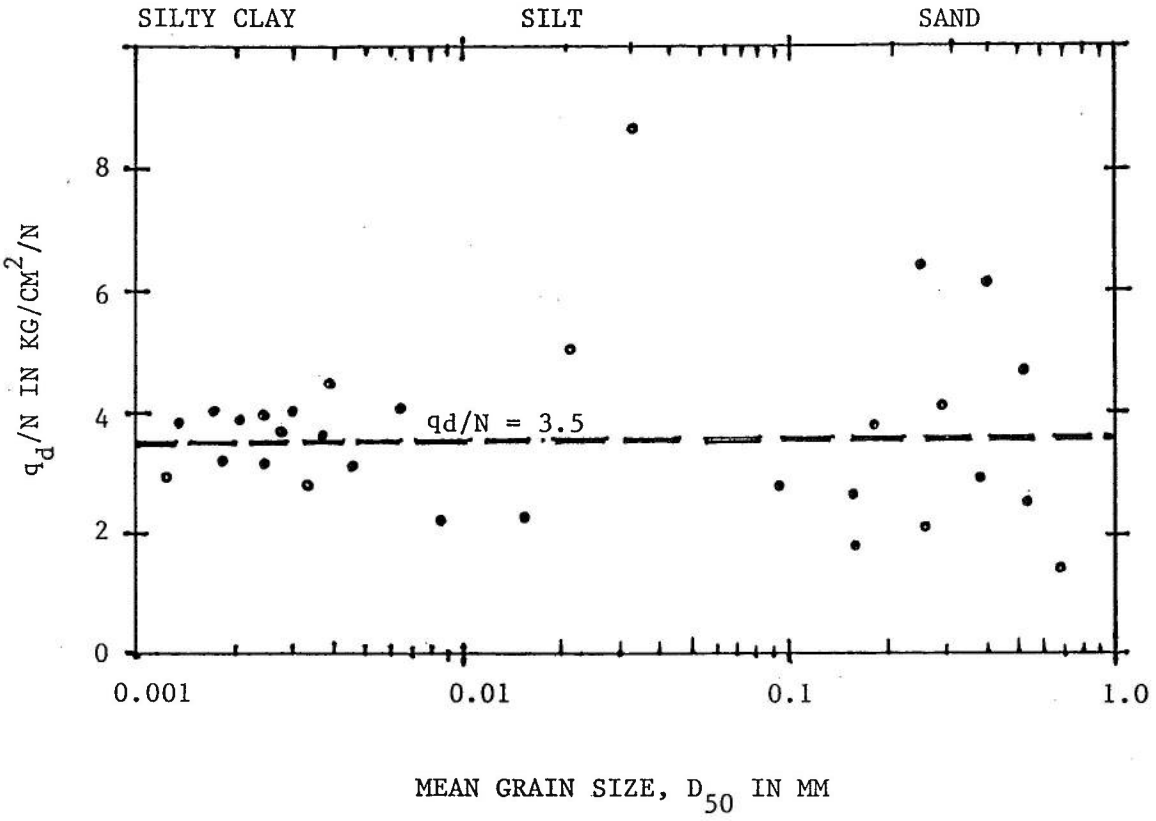

SILTY CLAY
SILT
SAND
8
6
4
2
0
qd/N = 3.5
0.001
0.01
0.1
1.0
q_d/N IN KG/CM^2/N
MEAN GRAIN SIZE, D_{50} IN MM

FIGURE 2

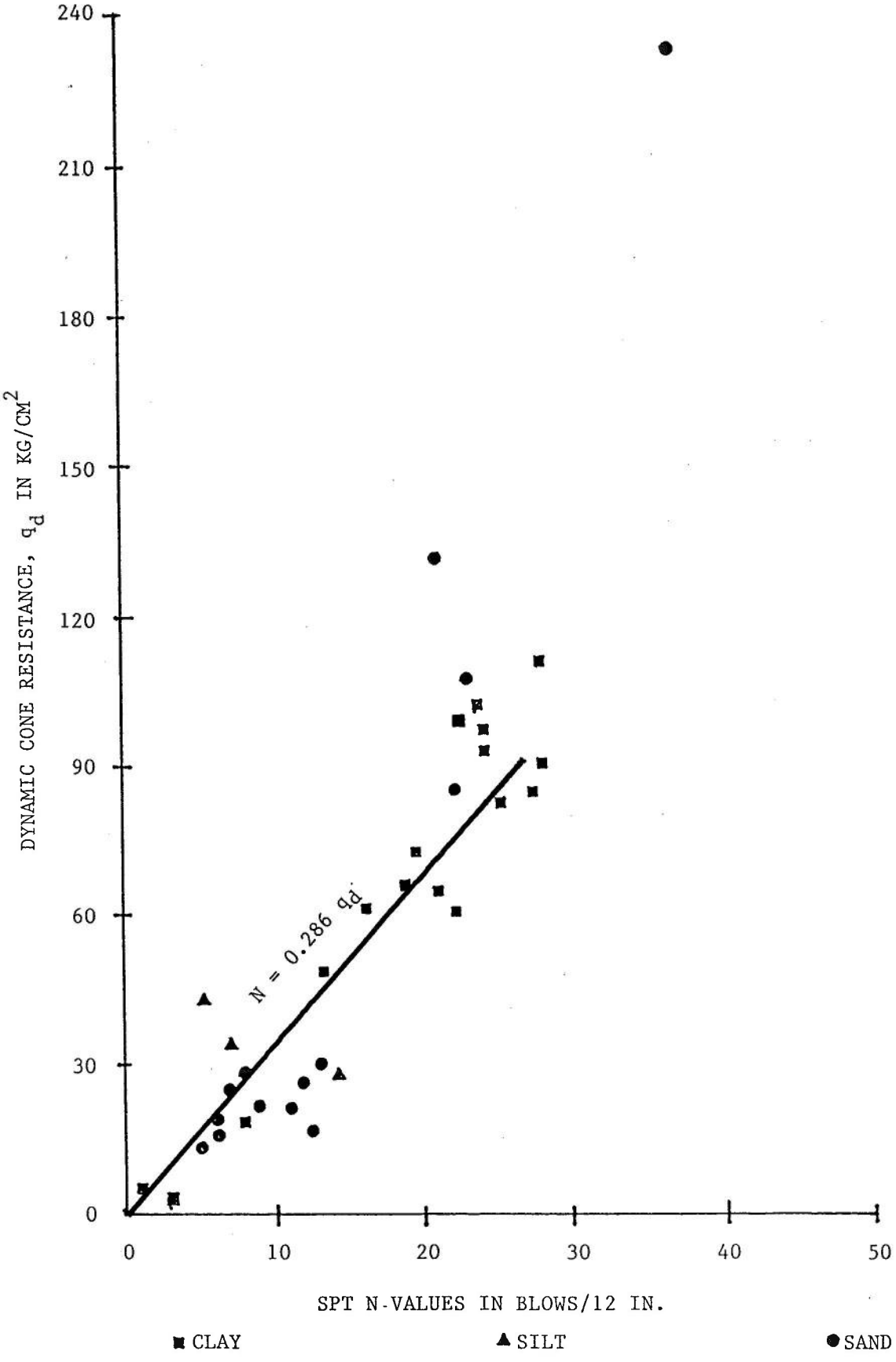

240
210
180
150
120
90
60
30
0
DYNAMIC CONE RESISTANCE, q_d IN KG/CM^2
N = 0.286 q_d
0
10
20
30
40
50
SPT N-VALUES IN BLOWS/12 IN.
CLAY
SILT
SAND

FIGURE 3

REFERENCE

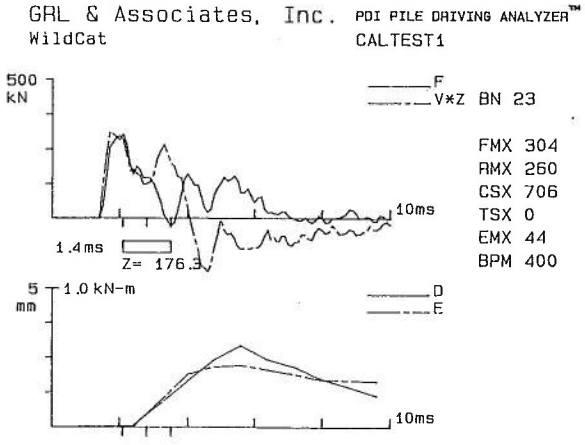
Robertson, P.K.; Campanella, R.G.; and Whitman, A., "SPT-CPT Correlations," Journal of Geotechnical Engineering, Vol. 109, No. 11, (Nov. 1983), 1449-1459.

The information below was presented to the 34th Annual AEG Meeting, but was not included in the Proceedings.

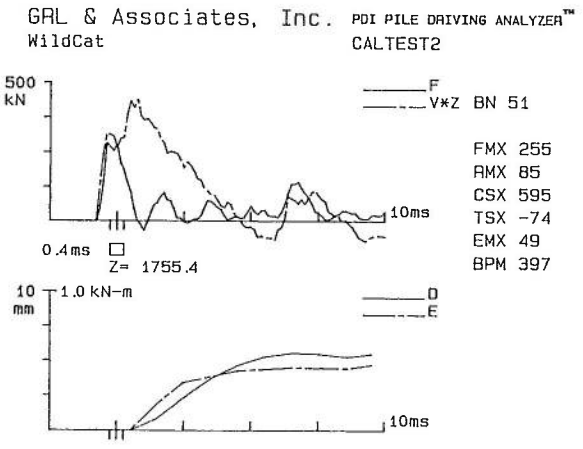
HOW MUCH ENERGY REACHES THE CONE?

ASTM D 4633-86 specifies a method for measuring the portion of a dynamic penetrometer's kinetic energy that is available to drive the tip. GRL and Associates, Inc. instrumented a WILDCAT DYNAMIC CONE PENETROMETER with two accelerometers and two strain transducers and used a pile driving analyser and their CAPWAP program to estimate the effective energy during both easy and hard driving. For easy driving (N_d = 7 blows/10 cm), 82 percent of the kinetic energy was found to be effective. For hard driving (N_d = 130 blows/10 cm), the effective energy was measured as 73 percent. In the arena of dynamic penetrometers, these effective energy percentages show the WILDCAT to be exceptionally efficient. The Force, Velocity, and Energy plots of both the hard and easy driving typical blows, and a photograph of the instrumented penetrometer are shown below.

HARD DRIVING
N_d = 130/10 cm



EASY DRIVING
N_d = 7/10 cm



$$\frac{E\ max}{E\ KE} = \frac{44}{60} = 73\%$$

$$\frac{E\ max}{E\ KE} = \frac{49}{60} = 82\%$$

INSTRUCTION MANUAL

FIELD INSPECTION VANE TESTER

Model H-60

Tel.: 1.450.465.1113 • 1.877.ROCTEST (Canada, USA) • 33 (1) 64.06.40.80 (Europe) • www.roctest.com • www.telemac.fr

E10136-051014

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1 APPLICATIONS

The inspection vane borer is used to measure in situ undrained shear strength in clays. It is primarily intended for use in trenches and excavations at a depth not influenced by drying and excavation procedure.

When different sizes of vanes are used, the instrument range is from 0 to 260 kPa. The accuracy of the instrument should be within 10% of the reading.

Figure 1: H-60 vanes in three different sizes

2 PRODUCT

2.1 DESCRIPTION

The vane tester consists in two parts: the vane with its shaft and the measurement part with its handle.

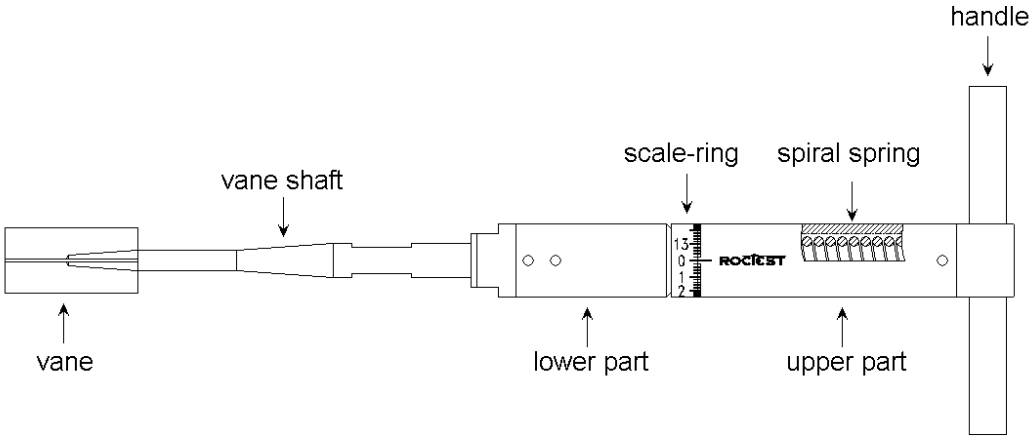

Figure 2: H-60 vane borer

The scale-ring is graduated from 0 to 130 kPa.

Three sizes of four-bladed vanes can be used:

- small: 16 x 32mm
- medium: 20 x 40mm (standard)
- large: 25.4 x 50.8mm

They make it possible to measure shear strength of 0 to 260, 0 to 130 and 0 to 65 kPa respectively.

2.2 OPERATION PRINCIPLE

The measurement part of the instrument is a spiral spring. When the handle is turned, the spring deforms. The upper part and the lower part of the instrument get a mutual angular displacement which depends on the torque applied. The shear strength of the soil is obtained by means of a scale-ring.

The lower and upper halves of the instrument are connected by means of threads. The scale is also supplied with threads and follows the upper part of the instrument by means of two lugs. The zero-point is indicated by a line on the upper part. When torque is applied, the scale-ring follows the upper part of the instrument, and when failure in the soil is obtained, the scale-ring will remain in its position due to the friction in the threads.

3 OPERATION AND READING PROCEDURES

3.1 GENERALITIES

The vane blades are soldered to a shaft which again is extended by one or more 49 cm long rods. The connection between the shaft-rods and the instrument is made by threads. To make the connections as straight as possible, the rods have to be screwed tight together and threads cleaned for dirt.

In clays with shear strength of 260 kPa, a force of about 40 to 50 kilos is required to press the vane down into the soil. The shaft is designed to take this force, but if extension rods are used, precautions against buckling are required.

3.2 GENERAL PROCEDURES

1. Connect required vane and extension rods to the inspection vane instrument.

Note: While screwing vane or rods to instrument, hold onto lower part.

2. Push vane into the ground to the required position.

Note: Do not twist inspection vane during penetration.

3. Make sure that the scale-ring is set to zero-position.

4. Turn handle clockwise.

Note: Turn as slowly as possible with constant speed.

Be careful not to turn the handle over 360°, otherw ise the spring inside the instrument may be permanently damaged.

5. When the lower part follows the upper part around or even falls back, failure and maximum shear strength is obtained in the soil at the vane.

6. Holding handle firmly, allow it to return to zero-position.

Note: Do not allow the handle to spring back uncontrolled.

7. Note the reading on the graduated scale.

Note: Do not touch or in any way disturb the position of the graduated ring until the reading is taken.

8. Write down the reading together with position of hole and depth.

9. Turn the graduated scale anti-clockwise back to zero-position.

10. To determine the remoulded shear strength, the following procedure is used:

    - Turn the vane quickly at least 25 revolutions. Do not turn using handle. Turn using wrenches provided.
    - Zero the scale and take at least two measurements by turning the instrument as slowly as possible.
    - The minimum value is considered the correct one.

11. Push the vane down to next position. If necessary, screw on another extension rod.

12. Repeat the above measurement procedure (steps 3 to 10).

13. When the last reading is taken, pull the vane up. If soil is comparatively soft, this can be done by hand, gripping the handle. In harder soils, some mechanical device might be necessary. It is then advisable to connect this device directly to the connection rods (not to the instrument).

3.3 SPECIAL PROCEDURES

When measuring the shear strength at greater depths, the friction between soil and extension rods can be appreciable, and must be taken into consideration.

To measure the friction, extension rods and a vane-shaft without vane (dummy) are pushed into the ground to the depths required for shear force measurements. The torque due to friction is then measured in the same way as when using vanes (steps above from 3 to 9). The friction torque thus obtained is used to evaluate the actual shear strength from the measured shear strength.

To penetrate through firm layers a pre-boring using a rod with the same diameter as the vane may be helpful.

4 CONVERSION OF READINGS

The shear strength depends on the size of vane the instrument is used with. Multiply the reading of the scale-ring by the correct factor in the table below.

Shear strength (kPa) = α . Reading

Vane size in mm	Multiplicative factor α
16 x 32	2
20 x 40	1
25.4 x 50.8	0.5

Table 1: Factors to use for conversions

Note: If a correction on the shear strength should be applied because of friction on the shafts, do the correction on the reading before applying the vane coefficient by subtracting the torque friction. Please refer to the ASTM standard D2573 (volume 04.08) for more information.

5 MAINTENANCE

The H-60 vane borer is simply designed, and does not require much attention. But it is most important to keep it as clean as possible. Periodically, the instrument should be sent back to factory for verification.

6 CONVERSION FACTORS

	To Convert From	To	Multiply By
LENGTH	Microns	Inches	3.94E-05
	Millimetres	Inches	0.0394
	Meters	Feet	3.2808
AREA	Square millimetres	Square inches	0.0016
	Square meters	Square feet	10.7643
VOLUME	Cubic centimetres	Cubic inches	0.06101
	Cubic meters	Cubic feet	35.3357
	Litres	U.S. gallon	0.26420
	Litres	Can–Br gallon	0.21997
MASS	Kilograms	Pounds	2.20459
	Kilograms	Short tons	0.00110
	Kilograms	Long tons	0.00098
FORCE	Newtons	Pounds-force	0.22482
	Newtons	Kilograms-force	0.10197
	Newtons	Kips	0.00023
PRESSURE AND STRESS	Kilopascals	Psi	0.14503
	Bars	Psi	14.4928
	Inches head of water*	Psi	0.03606
	Inches head of Hg	Psi	0.49116
	Pascal	Newton / square meter	1
	Kilopascals	Atmospheres	0.00987
	Kilopascals	Bars	0.01
	Kilopascals	Meters head of water*	0.10197
TEMPERATURE	Temp. in °F = (1.8 x Temp. in °C) + 32 Temp. in °C = (Temp. in °F – 32) / 1.8		

* at 4 °C

E6TabConv-990505

Table 2: Conversion factors

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Mercury
Cold Vapor Analysis

SOP 547S
Version 001

Revision Date: 3/27/19
Effective Date: 3/27/19

Prepared by:

Eric Larson / Tyler Hightower

Approvals:

Eric Larson, Inorganics Division Manager

David R. Mitchell, Quality Assurance Manager

Annual Review

SOP Number: _____

Title: Mercury Analysis using Cold Vapor Analysis

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 cold vapor atomic absorption instrumental analysis of mercury in

digested water, soil, and tissue samples plus the extracts generated from the TCLP and SPLP procedures. The instrument used is a Leeman Labs Hydra II AA.

1.2. This method, with modifications to accommodate the use of the Hydra instrument, is consistent with USEPA Methods SW-846 7470A, 7471A and 245.1 and 245.5.

1.3. All samples must be digested with the appropriate method prior to analysis. Refer to SOPs 511S and 532S for solids and 535S for waters and aqueous extracts.

1.4. The analytical range of this procedure is 0.1 to 10 µg Hg/L. This range can be extended with sample dilution or by increasing or decreasing the sample size.

2. Summary of the Procedure

2.1. Cold vapor atomic absorption spectroscopy (CVAAS) is a method based on the absorption of radiation at 253.7 nm by atomic mercury vapor.

2.2. The samples are digested then further treated with stannous chloride to reduce the mercury in the samples to the elemental state. The mercury is aerated from the solution to the analyzer by a carrier gas. The vapor passes through the light path of a mercury emission source, absorbing some of the light as it passes. The absorbance is measured and related to the mercury concentration in the sample. Unknown samples are run against a calibration curve generated by standards of known concentration

3. Definitions

3.1. CVAAS - Cold Vapor Atomic Absorption Spectroscopy

3.2. Detection Limit (DL) - As defined in DoD QSM 5.0; the smallest concentration that can be demonstrated to be different from zero or a blank concentration with 99% confidence.

3.3. Limit of Detection (LOD) - As defined in DoD QSM 5.0; the smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence.

3.4. Limit of Quantitation (LOQ) - As defined in DoD QSM 5.0; the smallest concentration that produces a quantitative result with known and recorded precision and bias. Often referred to as the reporting limit (RL).

3.5. SD - Standard Deviation

3.6. RSD - Relative Standard Deviation - The SD divided by the mean, multiplied by 100.

3.7. RPD - Relative Percent Difference - The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.

3.8. %R - Percent Recovery - The difference between the spike concentration and the original sample concentration divided by the concentration of the spike added multiplied by 100.

3.9. LIMS (Element) - Laboratory Information Management System - ARI's computerized sample data and analytical data system.

4. Interferences

4.1. Several interferences have been reported for samples containing sulfide, chloride and high amounts of organic material which have a broad absorbance band around 253.7 nm. Because effects from these interferants are difficult to quantitate the sample preparation and quality control procedures must be followed.

4.2. Contamination during the preparation and analysis of low-level mercury samples can be very problematic. Proper care should be taken to ensure that all reagents, glassware and equipment are free of mercury sources and samples are not subjected to environmental sources of mercury such as airborne dust.

5. Safety

5.1. The mercury samples and reagents contain strong oxidizing and reducing compounds. The mercury reagents are made in excess; that is, the concentration of the reagents is very high to drive the reaction equilibrium equation to one side or the other. Therefore, the solutions must be handled with care and proper safety equipment must be worn at all times. Gloves, safety goggles, and a lab coat for protection are a must.

5.2. Mercury compounds are known to be highly toxic if swallowed, inhaled, or absorbed through the skin. Acidification of samples may release toxic gases such as cyanides or sulfides requiring that all sample preparation must be performed in a fume hood.

5.3. The work area must be kept clean to eliminate the possibility of contamination, and also as a safety issue to protect the analyst from the hazards of the reagents, as described in section 5.1.

5.4. Safety data sheets are available to all employees in hardcopy format located in the file cabinet by the main copier or electronically as linked on the ARI Intranet homepage.

6. Equipment and Supplies

6.1. Leeman Labs Hydra II AA, interfaced with a controlling computer running Version 2.1 Software.

6.2. Compressed nitrogen gas, “High Purity” grade (99.998% purity), with regulator.

6.3. Adjustable air displacement pipettes with disposable tips that have been calibration checked.

7. Reagents and Supplies

7.1. Deionized water, ASTM Type I, that is produced with the in-house water system.

7.2. 14% Hydroxylamine hydrochloride/sodium chloride solution - Dissolve 144 grams of hydroxylamine hydrochloride (or 144 grams of hydroxylamine sulfate) and 144 grams of sodium chloride in deionized water and dilute to 1000 mL with deionized water. Use reagents that have been certified to be low in mercury. Label the solution bottles with the date of preparation, batch number, and initial.

7.3. 10% Stannous chloride solution – To approximately 500 mL of deionized water, with mixing, add 70 ml of concentrated Trace Metal Grade HCl. Add 100 grams of stannous chloride and mix until dissolved. Dilute to 1000 mL with deionized water. Use reagents that have been certified low in mercury. Label the solution bottle with the date of preparation, batch number, and initial. When not in use cap tightly and store in the refrigerator. This solution will need to be made approximately every week. Check bottle for precipitate (cloudy appearance or white layer on the bottom). If solution has precipitated, prepare a fresh batch.

7.4. 1% HNO_3/HCl rinse solution – To a clean 2000 mL polybottle add approximately 1000 mL of deionized water. Add, with mixing, 20 mL HNO_3 and 20 mL of HCl. Use only concentrated Trace Metal Grade acids that have been lot certified. Bring to a final volume of 2000 mL. This reagent is non-quantitative, and the volume measurements do not need to be exact but should be consistent.

7.5. 30% HNO_3 rinse solution – To a clean 500 mL polybottle add approximately 250 mL of deionized water. Add, with mixing, 150 mL of concentrated Trace Metal Grade HNO_3 that has been lot certified. Bring to a final volume of 500 mL. This reagent is non-quantitative, and the volume measurements do not need to be exact but should be consistent.

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 28 days prior to sample preparation.

8.3. All samples received for dissolved metals analysis that have not been field filtered should be unpreserved at the time of receipt. They should be filtered through a 0.45µm filter prior to preservation to a pH<2 with trace metal grade HNO_3.

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 1008S includes procedures for handling shared samples for the Metals Lab.

9. Quality Control

9.1. Documentation: The CVAA summary logbook is filled out during the run. Any event or observation or action that is worth noting should be recorded in the appropriate logbook and on the raw data. When the analytical data is complete, a data package for review consisting of all

raw data, and copies of all related logbook pages, is scanned to the calibration in Element. A text file generated during the run, the name of which is based on the date of analysis, should be included for use in the data loading process.

9.2. Initial Demonstration of Performance.

9.2.1. Before any samples can be analyzed by this method the instrument and analysts' performance must be evaluated. This will require the determination of the instrument calibration range, quantitation limits and the analysis of quality control samples to assess the accuracy and precision of the method.

9.2.2. Quantitation limits (DL, LOD and LOQ) must be established initially according to SOP 1018. Quantitation limits must be verified at least quarterly or whenever major changes are made to the instrument or method. Quantitation data will be maintained by the Quality Assurance Department and analyzed according to SOP 1018.

9.2.3. To demonstrate the initial performance of the instrument and the ongoing ability of each analyst a series of quality control samples must be analyzed. For each new analyst a minimum of four samples of known concentration must be processed and analyzed with calculated recoveries within 10% of the true values. This data will be maintained in individual training records and by the Quality Control Officer.

9.3. Calibration Verification (ICV ICB CCV CCB) – Immediately following calibration the ICV standard must be analyzed followed by the ICB with CCV, CCB repeated after every ten samples and at the end of the analytical run. The ICV must be within 10% of the true value whereas the CCV must be within 20%. The ICB and CCB must be less than the reporting limit. If out of control the analysis should be stopped the problem corrected and all samples not bracketed with in control standards reanalyzed. **Note: For drinking water samples, EPA 245.1 the control limit for the ICV is 5% and the CCV 10%.**

9.4. Detection Limit Standard (CRA): The first sample of the analytic run, immediately following the first CCV/CCB set should be a CRA. The true concentration is 0.1 μg/L and should be recovered within 70-130%. If the standard falls outside of these limits the CRA shall be reanalyzed immediately. If the analysis of the reanalysis is in control no further corrective action is required. If the result is again outside the limits the problem should be corrected and the instrument recalibrated.

9.5. Method Blank (MB / BLK) – At least one method blank / reagent blank will be analyzed for each batch of 20 or fewer prepared samples for each matrix type. The values will be used to determine if contamination exist. The value of the MB should be less than 0.1 μg/L (<1RL) or less than ½ the RL for DOD samples.

9.6. Matrix QC Samples – For each batch of 20 or fewer prepared samples of each matrix type at

least one matrix spike and one laboratory duplicate must be analyzed. The matrix spike is a separate aliquot of a client sample that has been spiked with a known amount of analyte. The calculated recovery should be within 75 - 125% of the true value. The matrix duplicate is a separate aliquot of a client sample that is prepped and analyzed at the same time. The calculated RPD should be less than 20%. If the concentration of the sample is < 5X RL, then the difference must be <1RL.

9.7. Method Blank Spike or Laboratory Control Sample (MBSPK / LCS / BS): Laboratory control samples are analyzed with each batch of 20 or less samples. The true value is 2.0 μg/L with control limits of 80 – 120%. If the control limits are not met, all samples in that batch will need to be re-digested and re-analyzed. A corrective action form needs to be filled out.

10. Calibration and Standardization

10.1. Calibration:

10.1.1. A new calibration is performed with a blank and a minimum of 5 standards at different concentrations each day samples are analyzed, for each Hg prep code, and for all samples requiring extra permanganate additions.

10.1.2. The calibration standards are prepared as described in the individual preparation SOPs. The calibration range is 0.1 to 10 µg/L.

10.1.3. In the “Method” tab, under “Calibration”, select “Clear Calibration” to remove the previous calibration results.

10.1.4. To begin calibration, in the “Sequence” tab right-click “Cal 1 – Blank" and select “Start from here”.

10.1.5. After the calibration has been run, it can be viewed in the “Calibration” section of the “Method” tab. Click “Stop” in the instrument software toolbar before reviewing the calibration.

10.1.6. Review the calibration for precision (<5% SD), and for linearity (Rho > 0.995). One Cal standard may be dropped if its RSD is > 10%, or 30% for the lowest standard, by deselecting all 3 reps for the Cal standard. If more than one standard’s RSD or SD is high, or Rho < 0.995, the instrument should be recalibrated, possibly with different standards.

10.1.7. In the “Calibration Data” box click “Accept” and then print the calibration to include with the data.

11. Procedure

11.1. Instrument and sample setup:

11.1.1. Turn on the instrument and wait 20 minutes for warm-up.

11.1.2. Take 10% $SnCl_2$ solution (section 7.3) out of the refrigerator and check for precipitate

(cloudy appearance or white layer on the bottom). If the solution has precipitate, prepare fresh solution. Replace the rinse solution with fresh 1% HNO_3 /HCl solution (section 7.5). You will want to make about 2000 mL of this solution for a normal analytic day.

11.1.3. Check the waste carboy level; if more than 80% full, dispose.

11.1.4. On the peristaltic pump, check the peristaltic pump tubing for flatness, indicating the need to change tubing; if tubing change is necessary, change all 5 tubing as a group. Attach the pump tubing as indicated in the Operator Manual. Clamp the pump tubing in place; no adjustment is usually necessary on the tension.

11.1.5. Open the Hydra II software by clicking on Hg Analysis Icon. In the “Method” tab, click open and select “ARI 10ppb”

11.1.6. Connect the green “sample gas out” connector to the top of the gas liquid separator (GLS).

11.1.7. Open the valve on the nitrogen tank; it is not necessary to adjust the regulator (leave at 25 PSI).

11.1.8. Turn on the pump by pressing the “Startup” button in the software toolbar. Put the SnCl2 line in DI water and check that liquid has begun moving through the pump tubing and the autosampler. In the ”Method” tab under “Instrument Control”, move the autosampler tip to “Air”.

11.1.9. Check that liquid and gas are moving through the GLS and draining properly.

11.1.10. Check the drain line for good flow.

11.1.11. Place the SnCl2 line in the 30% HNO3 solution (Section 7.5) and let the system rinse for 10 minutes.

11.1.12. After the HNO3 rinse, rinse for an additional 10 minutes with DI water before placing the line in the SnCl2 solution. Let aspirate for about 3 minutes, until the solution has moved completely through the instrument.

11.1.13. Look for the Hg lamp current on the instrument control page and record this value in the Hydra II Hg Analyzer Instrument Logbook.

11.1.14. Prepare the samples and standards for analysis. To each sample and standard add the appropriate amount of hydroxylamine hydrochloride/sodium chloride solution (section 7.1). For water samples prepared in 50 ml HotBlock tubes add 1.05 mL of the solution and for soil samples prepared in 100 ml HotBlock tubes add 2.5 mL. Swirl the tube intermittently. The KMnO4 will be reduced first to MnO2, a brown solid, and then will dissolve into solution. The sample is ready for analysis when all the MnO2 has been dissolved. Make sure no KMn04 is left on the lid of the Hot Block tube. This step should be performed just prior to analysis. After the KMn04 is reduced the samples should be analyzed within 24 hours.

11.1.15. Starting with the first prep code, label 50 mL centrifuge tubes as follows: S0, S0.1, S0.5,

S1.0, S2.0, S5.0, S10.0, CB, CCV (4.0 □g/L), ICV (8.0 □g/L). Fill them with the appropriate solution and place in the autosampler standards rack in the designated positions. A diagram of the Cal standard rack can be found under the "Sequence" tab. Note: A separate calibration and sample run is performed for each Hg prep code, and for all samples requiring extra permanganate additions.

11.1.16. On the "Analysis" tab, select "New" and name the analysis as the prep code and analysis date (ex. TWM 01-01-18). Click "View" and select "Latest Chapter".

11.2. Analysis:

11.2.1. To begin initial QC checks, under the "Sequence" tab right-click the "ICV" and select "Start from here". Review the CVs, CBs, and CRL for results outside control limits (See section 15). Failing QC samples must be reanalyzed before continuing and recalibration may be necessary.

11.2.2. Type the sample labels into the "Sample ID" column in the "Sequence" tab using the element format: 16A0001-01 (Note: the instrument must be stopped prior to typing in the first sample ID). Sample dilutions are typed into the "Vol." column. Once finished, click "Update" to add the samples to the run list on the left-hand side. CCVs and CCBs are added automatically to the run list every 9 samples. No more than 10 samples may be run consecutively without a CCV and CCB. More samples can be added to the run list at any time.

11.2.3. Pour the samples into labeled test tubes and load autosampler rack in the positions designated in the run list; take care to avoid particulates--filter with syringe filters if necessary. Note: The autosampler tip has a screen that clogs easily. All soils and any particulate filled liquids should be filtered.

11.2.4. Begin sample analysis by right-clicking the desired sample in the run-list and selecting "Start From Here". Analysis may be paused at any time by clicking "Stop" in the toolbar.

11.2.5. In the "Analysis" tab, check the run periodically for QC control limits of CCVs, CCBs, MBs, MBSPKs, REFs, DUPs and Matrix Spikes. At the same time check the sample precision, the RSD should be <5% for all samples ≥5 RL. Also check for samples over the calibration range; these can be diluted and rerun.

11.2.5.1. NOTE: Samples are diluted using the calibration blank for the diluent. An example would be, for a 10X dilution, add 1 part sample and 9 parts calibration blank. All dilutions will be made with QC checked pipettes.

11.3. To Print the Run:

11.3.1. After the sample run has been completed for a prep code group, go to the "Report" tab within the "Analysis" tab. Click "Clear All" to clear the previous report data. Select "Statistics",

then under “Report Spec” click “Load” and select “Hg Report Temp” from the pop-up window. Click the checkbox next to the analytical run chapter on the left-hand side. Under “Output”, click “Report”, then click “Printer”. Name the file as prep code and date (ex. TWM 01-01-18). Then click “CSV File” and name the file with the same format.

11.3.2. Make notes on the printout of %R, RPD, REF mg/kg, prep dilution, etc.

11.3.3. Shutdown: Move the autosampler tip to “Air” in the “Instrument Control” screen under the “Method” tab and remove the rinse solution line from the rinse container.

11.3.4. Put the SnCl2 uptake line in 30% HNO3 (section 7.5) for 10 minutes of rinsing.

11.3.5. Remove the uptake line from the 30% HNO3 an place in deionized water for 10 minutes of rinsing.

11.3.6. Remove the SnCl2 uptake line and allow it to aspirate air until the uptake and drain lines run dry.

11.3.7. Turn off the peristaltic pump by clicking the “Stop” button on the toolbar.

11.3.8. Release the pump tubing clamps. Turn off the instrument main power using the switch on the back of the instrument.

11.3.9. Close the valve on the nitrogen gas tank.

11.3.10. Disconnect the green “Sample gas out” connector from the top of the GLS.

11.3.10.1. Dispose standards and samples.

11.3.11. All maintenance should be noted in the mercury maintenance logbook. If any maintenance needs to be made during a run, observe the following requirements:

11.3.12. For In house CLP runs, the instrument must be recalibrated before continuing with analysis.

11.3.13. For Routine runs a CV/CB pair should be run before and after any minor maintenance done during an analytic run. If this cannot be done, the instrument must be recalibrated before continuing with analysis.

12. Data Analysis and Calculations

12.1. The data is reviewed by the analyst during the sample analysis run. For each sample, the instrument operating software graphically displays the peak and prints the mean μAbs, concentration and %RSD. The analyst reviews the data for high samples, high RSDs, baseline changes, QC samples in or out of control limits, and method blank contamination.

12.1.1. Raw data review

12.1.1.1. Note on the raw data and/or an Analyst Notes Sheet any comments on instrument problems, delays, unusual occurrences, etc. Check for any potential problems and especially check the instrument QC checks (CV %R), matrix duplicates RPD, matrix spike

%R, and reference recoveries, as described in section 13.

12.2. CVAA sample logbook review

12.2.1. Copy the appropriate CVA sample logbook pages that correspond with the raw data. Check every sample label and dilution factor. Highlight the client sample edits and sample analysis deletions so they are not missed during the data loading process. Scan the logbook pages and analysis run pages to the calibration in Element.

12.3. Fill out corrective action forms and analyst notes forms where applicable. Note samples requiring corrective action with "w/CAF" in the log.

13. Method Performance

13.1. Quantitation limit studies are performed for all analytes as described in SOP 1018.

13.1.1. The detection limit must be lower than the limit of quantitation (LOQ) for each analyte. If not, the LOQ will need to be changed or the study replicated.

13.1.2. Quantitation limits shall be re-determined annually or following any change to the sample preparation procedure.

13.2. An Instrument Quantitation Limit Verification Study is performed once each quarter to verify the LOQ and LOD. Summaries are maintained by ARI's QA Section and available for review upon request.

13.3. Analytical accuracy is determined using LCS/MBSPK, SRM or MS analyses. 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.

13.4. Laboratory precision is measured by performing replicate analyses. Replicates (sample or matrix spike) acceptance limits are ± 20%.

13.5. 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. The primary Pollution Prevention Opportunity for this procedure is to limit the quantity of chemicals purchased and stored on site. Smaller volumes of commercially prepared reagents are being purchased in lieu of in-house preparation from stock salts or crystals. Quantities of reagents purchased and prepared will more closely reflect anticipated usage and stability.

14.2. Wastes known to contain high concentrations of heavy metals are collected and disposed of in the metals solids or aqueous waste streams.

14.3. Corrosive acidic solutions are neutralized prior to sink disposal.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. The correlation coefficient for the calibration, r should be greater than 0.995 (coefficient of determination, r^2 >0.990). Each standard should return a regressed value within 10% of its prepared concentration except for the low standard which should be within 30%

15.2. Calibration Verification Standards (ICV/CCV): At the beginning of the mercury run, after every 10 samples, and at the end of the run, a CV standard must be analyzed. Immediately following calibration an ICV must be analyzed. The true concentration of the ICV standard is 8.0 μg/L and must be recovered within 10%. A CCV standard must be analyzed before and after each set of 10 samples and at the end of the run. The true concentration of the CCV standard is 4.0 mg/L and has a control limit of 20%. **Note: For drinking water samples, EPA 245.1 the control limit for the ICV is 5% and the CCV 10%.** If the ICV is out of range, the instrument should be recalibrated. If a CCV is out of control, the problem should be corrected, a new CCV analyzed and all the previous samples run since the last good CCV should be reanalyzed.

15.3. Continuing Calibration Blank Standard (ICB/CCB): Immediately after every CV standard, a CB standard must be run. The result of the analysis should be between ±0.1 mg/L (1 RL). If a CB is outside of these limits, the problem should be corrected, and all previous samples run since the last good CB should be reanalyzed.

15.4. Detection Limit Standard (CRA): The first sample of the analytic run, immediately following the first CCV/CCB set should be a CRA. The true concentration is 0.1 μg/L and should be recovered within 70-130 %. If the standard falls outside of these limits the CRA shall be reanalyzed immediately. If the analysis of the reanalysis is in control no further corrective action is required. If the result is again outside the limits the problem should be corrected and the instrument recalibrate.

15.5. Spike Recovery (%R): The spike amount for mercury in the digests is equal to 1.0 μg/L. To calculate the spike recovery, subtract the background sample result (if the sample is undetected, ±0.1 μg/L, do not subtract anything) from the spiked sample result, divide by the spike added, and multiply by 100:

$$\%R = \left(\frac{spike\ sample\ result - background\ sample\ result}{spike\ added} \right) * 100$$

EXAMPLE: Sample 1-SPK has a result of 1.67 μg/L. Sample 1 has a result of 0.85 μg/L. The spike amount is 1.0 mg/L. The formula to calculate the %R is

$$\%R = \left(\frac{1.67\ \mu g/L - 0.85\ \mu g/L}{1.0\ \mu g/L} \right) * 100 = 82.0\%$$

If the background sample result is 4X greater than the spike added, the %R result has no control limits, otherwise the %R should be between 75-125%. If the spike is out of control a corrective action form must be filled out and the results will be evaluated based on the clients specific project plan. Re-preparation and analysis may be required.

15.6. Duplicates (RPD-Relative Percent Difference): The RPD between a background sample and its duplicate should be no greater than 20%, provided the analysis results are above 0.5 μg/L (5X the RL). The formula to calculate the RPD of a background sample and its duplicate is

$$RPD = \left[\frac{(background\ result - duplicate\ result)}{(background\ result + duplicate\ result)/2} \right] * 100$$

EXAMPLE: Sample 1 has a result of 0.86 μg/L. Sample 1-DUP has a result of 0.99 μg/L. The RPD is:

$$RPD = \left[\frac{(0.86\ \mu g/L - 0.99\ \mu g/L)}{(0.86\ \mu g/L + 0.99\ \mu g/L)/2} \right] * 100 = 14.1\%$$

If either result is less than 0.5 μg/L (5X the RL), then the difference between the background sample result and the duplicate result should be no greater than the RL (0.1 μg/L), and the RPD is not used for quality control. If the duplicate is out of control a corrective action form must be filled out and the results will be evaluated based on the client's specific project plan. Re-preparation and analysis may be required.

15.7. Method Blank (MB / BLK): A Method Blank is prepared and analyzed with each job or batch of samples of 20 or less. The blank is used to monitor for possible contamination. The blank results should be < 0.1 □g/L (<1RL). The DoD-QSM requires that the MB contain ≤ ½the RL. If the blank is detected a corrective action form must be filled out and evaluated based on the clients specific project plan. Re-preparation and analysis of the entire batch may be required if the sample concentrations are less than 10X the blank concentration.

15.8. Method Blank Spike or Laboratory Control Sample (MBSPK / LCS / BS): Laboratory control samples are analyzed with each batch of 20 or less samples. The true value is 2.0 μg/L with

control limits of 80 – 120%. The % Recovery is calculated the same as a matrix spike except there is no "background sample result" to subtract (see 8.3). If the control limits are not met, all samples in that batch will need to be re-digested and reanalyzed. A corrective action form needs to be filled out.

15.9. Reference Materials (SRM): Reference materials are soil samples that have independently certified concentrations of the analytes of interest. The certificate of analysis accompanying the particular reference material sets the control limits. If the control limits are no met, all samples in that batch will need to be re-digested and reanalyzed. A corrective action form needs to be filled out.

15.10. Any sample with a value above the high calibration standard must be diluted and reanalyzed, see section 11.3.5.1.

16. Corrective Actions For Out of Control Events

16.1. Calibration. If the calibration does not meet the criteria in sections 15.1, then corrective action may need to be taken before proceeding with re-calibration. In these cases all that is required is to recalibrate the instrument again. Instrument problems that require corrective action before recalibration could include gas leaks, worn pump tubing, light source failure, cell misalignment, or incorrect calibration standards preparation.

16.2. The ICV, CCV, ICB, and CCB are considered QC solutions. If a QC solution result is out of control limits, corrective action must be taken before proceeding with analysis. If the ICV is out of range, the instrument should be recalibrated. If a CCV is out of control, the problem should be corrected, a new CCV analyzed and all the previous samples run since the last good CCV should be reanalyzed. A corrective action form must be filled out.

16.3. Instrument malfunctions. When instrument malfunctions occur, consult with other experienced CVAA operators or the supervisor for guidance. Record the event in the mercury instrument maintenance logbook. The maintenance logbook and the service manual could be helpful for troubleshooting.

17. Contingencies for Handling out of Control or Unacceptable Data

17.1. In the event of significant batch QC failure, analysis will stop and the analyst will perform corrective action as discussed above.

17.2. In general, sample data associated with out-of-control batch QC sample results (Method blanks, calibration verification and Laboratory Control Samples) will not be reported. Re-runs will be conducted based upon availability of sample volume. If insufficient sample remains or the remaining sample has been compromised by other withdrawals from the sample bottle or by holding time, the client will be notified to determine an appropriate course of action.

17.3. Batch analysis is not controlled by Matrix Specific QC and failing matrix QC does not reflect a failure in the analytical protocol. Failing matrix QC will be reported to the client along with supporting information as may be available to qualify the result.

17.4. All corrective actions will be clearly and completely documented on a corrective action form. All maintenance and instrument repairs will be clearly documented in the maintenance log.

17.5. In the event of a major instrument failure immediately inform the project managers so all critical samples can be subcontracted if necessary.

18. Waste Management

18.1. ARI's Laboratory Chemical Hygiene Plan (CHP) describes internal hazardous waste handling procedures. All analysts must be familiar with these requirements.

18.2. ARI properly profiles and disposes all hazardous waste using an EPA registered TSD (Treatment, Storage and Disposal) facility.

18.3. Aqueous corrosive waste is neutralized following Elementary Neutralization Procedures in SOP 1201S.

18.4. Solid and aqueous samples designating as hazardous for Metals are collected in the "Metals Waste Solids Drum" and the "Metals Waste Solutions Drum", respectively, in the Central Accumulation Area.

19. Method References

19.1. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Method 7470A, September 1994

19.2. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Method 7471A, September 1994

19.3. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Method 7000A, July 1992

19.4. USEPA, ILM04.0, Exhibit D, Methods 245.1M and 245.5M

19.5. Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Rev 3 May 1994), Method Number 245.1, Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry

19.6. Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Rev 3 May 1994), Method Number 245.5, Determination of Mercury in Solids by Cold Vapor Atomic Absorption Spectrometry

19.7. DOD Quality Systems Manual for Environmental Laboratories, Version 5.0, July, 2013

20. Appendices

20.1. Not Applicable.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Metals Analysis

Nexion ICP-MS with Universal Cell Technology

SOP 545S
Version 001

Revision Date: 2/8/16
Effective Date: 2/8/16

Prepared By:

Jay Kuhn / Eric Larson

Approvals:

Eric Larson, Inorganics Division Manager

David R. Mitchell, Quality Assurance Manager

Annual Review

SOP Number: 545S

Title: Metals Analysis – Nexion ICP-MS with UCT

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 the Nexion® 300D and 350D ICP-MS according to EPA Method 200.8 Version 5.4 and SW-846 Method 6020, 3rd Edition- Final Update IV. 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® 300D and 350D ICP-MS may be found in the Nexion® manuals provided by the instrument manufacturer.

1.4. Detailed instructions on the use of the Nexion® ICP-MS operating software may be found in a PDF version of 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) using Universal Cell Technology (UCT™). 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 polyatomic 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. UCT (Universal Cell Technology): Refers to the different analysis modes of the Nexion 300D and 350D which include KED, DRC, or Standard (STD).

3.2.1. DRC (Dynamic Reaction Cell): This mode utilizes ammonia, a reactive gas (NH_3), to carry out gas phase chemical reactions. Interferants are altered (e.g., by proton/electron transfer, oxidation, or dissociation) which causes them to be unstable within the system and eliminated. Analytes of interest do not interact with the NH_3 and thus make it to the detector. It is important to make sure that the analyte of interest/internal standard does not react with the reaction gas (NH_3).

3.2.2. KED (Kinetic Energy Discrimination): This mode utilizes helium, an inert gas (He), to collide with interferants to reduce their kinetic energy. A “KED barrier” in the instrument allows only ions with sufficient kinetic energy to pass through it and reach the quadrupole. Care needs to be taken when selecting analytes to monitor in KED mode; common interferants on the analyte of interest should be known and analytes that have a similar cross sectional size as its interferants (i.e. the interferant should be larger than the analyte it interferes with) should not be analyzed in KED.

3.3. 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).

3.4. 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 40 CFR Appendix E Part 136.

3.6. CRDL (Contract Required Detection Limit): Contract specified minimum level of detection.

3.7. ICV (Initial Calibration Verification): A mid-range second source standard, run immediately after calibration to verify the accuracy of the calibration.

3.8. 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.

3.9. ICB (Initial Calibration Blank): A calibration blank run, immediately after the ICV to verify the baseline and to check for carry-over.

3.10. CCB (Continuing Calibration Blank): A calibration blank, run immediately after every CCV to verify the baseline and to check for carry-over.

3.11. 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.

3.12. 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.

3.13. 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.

3.14. CRI (Low Check Standard): This low level standard is at 1 RL.

3.15. SD: Standard Deviation

3.16. RSD (Relative Percent Standard Deviation): The SD divided by the mean, multiplied by 100.

3.17. RPD (Relative Percent Difference): The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.

3.18. %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.

3.19. Analytical Batch: An analytical batch shall consist of no more than 20 samples.

3.20. MB (Method Blank): An aliquot of analyte-free matrix taken through the sample preparation procedure with each analytical batch.

3.21. 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 LCS's.

3.22. 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.

3.23. 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.

3.24. 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.

3.25. MD (Matrix Duplicate): A second replicate matrix sample prepared and analyzed with a sample batch to measure precision with respect to a given matrix.

3.26. 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.

3.27. 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, nebulizer, spray chamber, cones, or in the torch. The lower concentration sample that follows may show successively decreasing concentrations, which could suggest 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.

3.28. Set-up (Tuning) Solution: A solution that is used to determine acceptable instrument performance prior to calibration and sample analyses.

3.29. 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).

3.30. Analysis Protocols:

3.30.1. 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.

3.30.2. 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., ^{98}Mo and ^{98}Ru). 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. Correction equations are listed in Appendix 9.

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 interferences are minimized by implementing KED/DRC modes in analytical methods

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. Depending on the method, five or six 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 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 300D is fully interlocked to protect the user from dangers such as high voltages, radio frequency generators, and intense ultraviolet light. At no time should the operator attempt to disable these interlocks or operate the Nexion 300D if any safety interlock is 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® NT software, a printer, and an ESI FAST autosampler.

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: 1.0 mm id sample probe (gray marker), internal standard and carrier solution probes (0.5mm id); sample loops (size varies according to method); and spare valve parts including a stator, rotor, and 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 (HNO_3), concentrated. Trace Metal Grade HNO_3 that has Lot QC documentation to verify that it is acceptable for trace metals use.

7.1.3. Hydrochloric acid (HCl), concentrated, Trace Metal 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, ^{6}Li, Ce, U and Pb in 1% HNO_3):

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 HNO_3. Dilute to 100 mL with DI water and mix well (see Appendix 1 Section 2).

7.2.2.2. Setup Solution (1 μg/L Be, Mg, Fe, In, ^{6}Li, Ce, U and Pb in 1% HNO_3): Prepare by pipetting 0.10 mL of Standard Mode Setup 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.

7.2.3. Internal Standard Solution:

7.2.3.1. Solution Preparation (0.15 mg/L ^{6}Li; 0.6 mg/L Ge; 0.12 mg/L Sc; 0.1 mg/L Ga; 0.05 mg/L Y, In, Tb, and 0.2 mg/L Bi): Prepare by pipetting 0.15mL ^{6}Li, 0.6mL Ge, 0.12mL Sc, 0.1mL Ga, 0.2mL Bi, and 0.05 mL each Y, In, Tb of the 1000 mg/L individual stock standards into a 1000 mL volumetric flask containing 800 mL DI water and 10 mL concentrated HNO_3. Dilute to 1000 mL with DI water and mix well (see Appendix 1 Section 1).

7.2.3.2. Internal Standard Solution is pumped to all standards and samples via a mixing "T" prior to being introduced into the nebulizer.

7.2.4. Calibration Standard Stocks (see Appendix 2):

7.2.4.1. Calibration Stock 1 (100 mg/L): Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, Th, U, V, and Zn.

7.2.4.2. Calibration Stock 2 (100 mg/L): Mo and Sb.

7.2.4.3. Individual Stock Standards (10,000 mg/L): Al, Ca, Fe, K, Mg, and Na

7.2.5. Calibration Intermediate Standard (Appendix 3) is prepared, as needed, by adding 10.0 mL of each of the Calibration 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 HNO_3. Bring to volume with DI water and mix well.

7.2.6. 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.)

7.2.7. QCS: The QCS, typically an ERA or NIST (National Institute of Standards and Technology) 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).

7.2.8. Initial Calibration Verification (ICV) 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 HNO_3. Dilute to 1000 mL with DI water and mix well.

7.2.9. 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.

7.2.10. 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 HNO_3. Dilute to 100 mL with DI water and mix well.

7.2.11. 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 HNO_3. Dilute to 200 mL with DI water and mix well.

7.2.12. Continuing Calibration Verification: Standard 4 (50 μg/L non-minerals and 5000 μg/L minerals), the mid-range calibration standard, is used.

7.2.13. Calibration Blank: A solution containing 1% (v/v) concentrated HNO_3 in DI water. Fill a 1L volumetric flask with approximately 900 mL of DI water. Pipette 10 mL of concentrated HNO_3 into the flask, dilute to 1000 mL with DI water and mix well. NOTE: Cal. Blank is also used as the "carrier solution".

7.2.14. Dual Detector Calibration Solution: contains 200 ug/L each of Al, As, Be, K, Mg, Na, Ni, Pb, Th, Tl, U, Zn, 6Li, Sc, Ge, Y, In, Tb, Bi and 100 ug/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).

7.2.15. Dual Detector Calibration Intermediate Solution: 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 HNO3 . 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.

7.2.16. Dual Detector Calibration Supplementary Elements for Nexion: Prepare by adding 0.01 mL each of 1000 mg/L of V, Cr, Co, Mn; 0.09 mL of Ca and 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 HNO_3. Dilute to 200 mL with DI water and mix well.

7.2.17. Interference Check Solutions (ICSA, ICSAB): These solutions are made from Inorganic Ventures multiple element stock standards (see Appendix 8). Prepare as needed.

7.2.18. ICSA: Prepare by pipetting 20.0 mL of Inorganic Ventures AR-6020ICS-OA10 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.

7.2.19. 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.

7.2.20. 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); after every 10 samples and at the end of the analytical run, a Continuing Calibration Verification Standard (CCV) must be run. 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 and 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. 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 verified quarterly 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 five calibration standards before analysis. The high concentration standard will contain 100 □g/L of all analytes except for the minerals, which are 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 7.2.6.

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. Before commencing calibration, open a “Blanks” sample table, and run three to five blank samples to ensure the loop is thoroughly rinsed and that the internal standards are stable.

10.3. Load the calibration blank and the calibration standards into the autosampler positions specified on the Sampling page of the analytical method.

10.3.1. 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.

10.3.2. 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 tab in the Method Dialog Box., Under Report View, browse to select “**arical.rop**” for the Report Options Template. Click on the Dataset Icon, highlight the latest calibration standard row (rinse sample) and click Reprocess. The method file does not need to be saved at this point, but save the calibration with the name of that run, i.e. mmddyy and A, B… for the 1st, 2nd, etc. calibration if re-calibration or re-zeroing is necessary. To reset the usual report options template, click on the Report page, and under Report View, click browse to select “**ariquant.rop**” for the Report Options Template and save the method.

10.3.3. Review the r-values for any that are <0.998

10.3.4. If poor curve fit and/or poor r-value are found, rerun a standard or recalibrate (also see Section 1.1).

10.4. Analyze Required QC Samples

10.4.1. 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. If these conditions are not satisfied the analysis must stop, the problem corrected, the instrument recalibrated and the Initial Standards

rerun.

10.4.2. 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.

10.4.3. 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.)

10.4.4. 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 before using this method. Detection limits established shall be less than or equal to the MDL.

11.1.1.1. Calibrate the Instrument, and then run the usual QC sample sequence.

11.1.1.2. Run the blank solution as a series of 10 sequential samples with rinsing in between each sample.

11.1.1.3. Calculate the standard deviation of the 10 blanks for each isotope.

11.1.1.4. IDLs shall be determined whenever the following occurs:

11.1.1.4.1. When placing a new instrument into service, and before using this method.

11.1.2. Method detection limits (MDLs) shall be established for all analytes by the method outlined in 40 CFR Part 136.

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 following 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 cone access button on the outside of the instrument. Check the condition of the cones for deposits and clean the outside of the sampler cone using a small amount of DI water on a Kimwipe® or cotton swab. When deposits are severe, change or clean the cones.

11.2.1.2. Attach the three pump tubings to the peristaltic pump. Relative to the instrument, green-orange Tygon® tubing is on the inside channel and is used for the internal standard; black-black Tygon® tubing is located on the second channel from inside and is used for the sample line; gray-gray Santoprene® tubing is used for the spray chamber drain line and is on the outermost channel. Make sure the tubing is not flattened or showing visible signs of wear, otherwise change to new tubing for optimum performance. Place the internal standard probe (green tape) and the carrier probe (blue tape) in a DI container.

11.2.1.3. Initiate the plasma and place the internal standard and carrier probes into a 2% HNO_3 rinse solution and allow instrument to warm-up for 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_UCT.wrk** workspace to perform the necessary optimization procedures. Verify the active folders and Dataset in use are correct (month and year can be used for the Dataset name).

11.2.3. Open the SmartTune™ window and load the appropriate SmartTune™ wizard file (**aridaily_UCT.swz**). If using KED mode, the KED Autolens® needs to be calibrated (KED

optimize.swz). It is possible to optimize all the parameters at once by clicking “optimize” in the SmartTune™ window, or individually by right clicking (“quick optimize”) on the individual files listed in the SmartTune™ window.

11.2.3.1. Manually aspirate (without the autosampler) the 1 μg/L setup solution by placing the Internal Standard and Carrier Solution probes in the solution. This solution will be continuously aspirated for the torch alignment, mass calibration, 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.**

11.2.4. Right Click the Daily Performance button to perform the daily performance check.

11.2.4.1. . Continue to aspirate the 1 μg/L setup solution.

11.2.4.2. . Click on the Analyze Sample button in Sample window to start analysis.

11.2.4.3. . 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%).

11.2.4.4. Monitor the daily performance measures (as recommended by Perkin Elmer) of Be, Mg, In, Pb and U sensitivity, background, % double charged and % oxide levels:

11.2.4.4.1. Be > 3000 cps, Mg > 20,000 cps, In > 50,000 cps, Pb >20,000cps, and U > 40,000 cps.

11.2.4.4.2. Background at mass 220 < 5 cps

11.2.4.4.3. Ce^{+2} <0.030 (% double charged < 3.0%)

11.2.4.4.4. CeO <0.025 (% oxides < 2.5%).

11.2.5. Right click on **Torch Alignment**. Record the x and y results**.**

11.2.6. Right Click on the **Calibration and Resolution** button in the SmartTune™ window.

11.2.6.1. After the tuning (mass calibration) has been completed, a tuning report for each of the runs performed will be automatically sent to the printer. Check that the mass calibration for each of the measured masses is ± 0.05 AMU (0.1 AMU ideally) of the true mass. (Methods 6020 and 200.8 require +/- 0.1 AMU).

11.2.6.2. 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.

11.2.6.3. . If both the resolution and mass calibration are acceptable a report of acceptability will be automatically printed.

11.2.6.4. If any of the tuning parameters do not meet method specifications and the instrument requires adjustment, the instrument will automatically rerun the tuning routine (# of retries

can be set in the method). It is typical to run several tunings to get all 5 elements within specifications.

11.2.7. Right click on the **AutoLens®** button to perform the AutoLens® calibration.

11.2.7.1. Continue to aspirate the 1 μg/L setup solution.

11.2.7.2. Print an Interactive Graph (add all elements) and save the AutoLens® Calibration.

11.2.7.3. Review the AutoLens® calibration graphs.

11.2.8. Right Click the Daily Performance button to perform the final daily performance check.

11.2.8.1. . Continue to aspirate the 1 μg/L Set-up solution.

11.2.8.2. 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%).

11.2.8.3. Monitor the daily performance measures (as recommended by Perkin Elmer) of Be, Mg, In, Pb and U sensitivity, background, % double charged and % oxide levels:

11.2.8.3.1. Be >3000 cps, Mg > 20,000 cps, In > 50,000 cps, Pb >20,000cps, and U > 40,000 cps.

11.2.8.3.2. Background at mass 220 < 5 cps

11.2.8.3.3. Ce^{+2} <0.030 (doubly charged < 3.0%)

11.2.8.3.4. CeO <0.025 (oxides < 2.5%)

11.2.8.3.5. Oxides and doubly 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 nebulizer flow.

11.2.8.3.6. Other optimization routines are available in the SmartTune™ window by clicking on the Edit button.

11.2.8.3.7. After the Optimization sequence has passed, place the probes in the 2% HNO_3 for 5-10 minutes, and then place the carrier probe (blue tape) and the internal standard probe (green tape) in the appropriate solutions.

11.3. Sample Analysis

11.3.1. Open the ariquant workspace (aridaily_UCT.wrk)and load the applicable method for the analytes required (see the method list at the instrument). In the method window, click on the

report tab. Change the report filename to reflect the run date **mxyymmdd.rep**, where m is the analysis method and x is the instrument number, 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% HNO_3 diluent as the calibration blank and standard 50 □g/L non-minerals (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" dialog box 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. Ten 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".

11.3.4. 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. (This should all be set and not needed to be done every day.)

11.3.4.1. Check the autosampler positions.

11.3.4.2. Rinse 15 mL polypropylene tubes in groups of five. Rinse with 10% HNO_3 followed by DI water. Prepare the sample dilutions according to sample prep method and knowledge of sample analyte levels. Cap and mix the samples using the small vortexer.

11.3.4.3. Load the samples into the autosampler positions specified in the sample table. Save the sample file (mmdd).

11.3.4.4. Select the samples to be analyzed by highlighting the rows.

11.3.4.5. Click on Analyze Batch. A Pop-up window will ask if you wish to clear the current calibration – Click NO unless you wish to recalibrate. Clicking on Yes will clear the current calibration.

11.3.5. 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.

11.3.6. Analytical Run Order

11.3.6.1. 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.

11.3.6.2. 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.

11.3.7. Monitoring the Analysis

11.3.7.1. 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 and waste levels. 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.

11.3.7.2. 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.

11.3.7.3. Monitoring High Levels and carryover: If any sample level within 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.

11.3.8. Recalibrating the Calibration Blank: (It is possible to recalibrate the Blank and re-set the internal standards during a run):

11.3.8.1. Stop the run and insert a CV/CB pair in the AS table

11.3.8.2. 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.**

11.3.9. Shut Down

11.3.9.1. Run 5% HNO_3 as a sample 3-4 times followed by DI water 3-4 times. Move the carrier solution and I.S. probes to air to drain the uptake lines and the spray chamber. When the spray chamber drain line is empty, extinguish the plasma by clicking “Stop” in the Instrument window. Loosen the peristaltic pump tubing and turn off the Peltier cooler.

11.3.9.2. Auto-shutdown (unattended shutdown) requires adding a 5% HNO_3 sample (use autosampler position 9) and a DI water sample (use autosampler position 10) to the last autosampler sequence (in the sample window). 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.

13.1.1. The MDLs must be lower than in-house RLs. If not, the RLs will need to be changed or the MDL study replicated.

13.1.2. MDLs shall be re-determined following any change to the sample preparation procedure.

13.2. Analytical accuracy is determined using LCS/MBSPK, SRM or MS analyses. 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.

13.3. Laboratory precision is measured by performing replicate analyzes. Replicates (sample or matrix spike) acceptance limits are ± 20%.

13.4. 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. 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.

15.3.3. 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. QCS analysis should be performed when new standards are prepared to verify the accuracy of the calibration standards.

15.4.1.1.1. 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 >2x 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 μg/L minerals) and LR300 (300 μg/L non-minerals, 30,000 μg/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

15.4.2.1.1. Method Blank (MB): A method blank (MB) should be run with every 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 to the MB.

15.4.2.1.2. MB values greater than the RL indicate laboratory or reagent contamination.

15.4.2.1.3. The method blank concentration should be <1RL for all requested elements. If a requested element is detected in the method blank at >1RL, 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.

15.4.2.2. Laboratory Control Sample, Reference Sample or Method Blank Spike (LCS / REF / MBSPK)

15.4.2.2.1. One LCS, REF or MBSPK (of the same matrix type as the samples), should be analyzed with each batch of samples of the same preparation procedure.

15.4.2.2.2. For an aqueous LCS, a REF sample or an MBSPK, 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.

15.4.2.2.3. 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

15.4.2.2.4. The Percent Recovery for the aqueous LCS, 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.

15.4.2.2.5. 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.

15.4.2.3. Matrix Spike/Matrix Spike Duplicate.

15.4.2.3.1. . A matrix spike should be run with every 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.

15.4.2.3.2. 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

15.4.2.3.3. 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 projects require a post digestion spike for out of control analytes.

15.4.2.4. Laboratory Duplicate

15.4.2.4.1. A laboratory duplicate should be run with every 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.

15.4.2.4.2. 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

15.4.2.4.3. 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 300D Hardware Manual, Perkin-Elmer Corporation

18.3. Nexion 350D ICP-MS Software Manual, 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
Ga	1000	0.1	0.100

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 200mL	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
^{78}Se	77.917	-0.030461*Kr83
^{82}Se	81.917	-1.007833*Kr83
^{98}Mo	97.906	-0.109613*Ru101
^{111}Cd	110.904	-1.073*(MoO 108-(0.712*Pd106))
^{114}Cd	113.904	-0.027250*Sn118
^{115}In	114.904	-0.014038*Sn118
^{123}Sb	122.904	-0.125884*Te125
^{208}Pb	207.977	Pb206+Pb207

Appendix 10

ANALYTICAL ISOTOPES AND ADDITIONAL MONITORED ISOTOPES

1. ANALYTICAL ISOTOPES			2. ADDITIONAL ISOTOPES	
ELEMENT	ISOTOPE(S)	MODE	ELEMENT	ISOTOPE
Li	6	STD	Ru	101
Be	9	STD	Pd	106
Sc	45	STD	Sn	118
Al	27	STD	Te	125
V	51	DRC		
Cr	52, 53	DRC		
Fe	54, 57	KED		
Mn	55	DRC		
Co	59	KED		
Ge	72	KED		
Ni	60, 62	KED		
Cu	63, 65	KED		
Zn	66, 67, 68	KED		
Ga	71	DRC		
As	75	KED		
Se	78, 82	DRC		
Mo	98	KED		
Y	89	STD		
Kr	83	STD		
Ag	107	STD		
Cd	111, 114	KED		
In	115	KED/STD		
Sb	121, 123	STD		
Ba	135, 137	STD		
Tb	159	STD		
Tl	205	STD		
Pb	208	STD		
Bi	209	STD		
Th	232	STD		
U	238	STD		

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 of all 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.

1.5 Check the 6-port Valve. **Aspirate DI water, then air until all water is removed from the sample introduction system. Turn off the Plasma.**

1.5.1 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).

1.5.2 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 display should be 14-16°C. The temperature can be adjusted using the knob below the display (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), if not, fill with appropriate coolant. The pressure gauge on the front panel should be between 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

Semi-Volatile Organic Analysis
Gas Chromatography/Mass Spectrometry
EPA Method 8270E

SOP 804S
Version 018

Revision Date: 6/06/19
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Prepared by:

Van Spohn

Approvals:

Brian N. Bebee, Laboratory Section Manager

Bob Congleton, Quality Assurance, Manager

Annual Review

SOP Number: 804S

Title: Semi-Volatile Organic Analysis – Gas Chromatography/Mass Spectrometry – EPA Method 8270E

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. Method 8270E is used to determine the concentration of semivolatile 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). The procedures described also meet the requirements of EPA Method 625.1 (Reference 19.5). The requirements outlined in Appendix 20.7 are used when analyzing samples using EPA Method 625.1. Some text is directly from the referenced documents. The table in Appendix 20.1 outlines ARI's routine procedure. 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 may be used to analyze for most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted from a gas-liquid chromatographic system. Such compounds include hydrocarbons, polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, resin acids, phthalate esters, organophosphates, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. Appendix 20.3 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. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration, and its chromatography is poor. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine and pyridine are difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 4-Chloroaniline; 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are active analytes and

subject to erratic chromatographic behavior, especially if the GC system is contaminated.

1.6. Method Reporting Limits

Extraction Type	Extraction Parameters	MRL
In House Soil Extraction	7.5g to 0.5mL	67 to 330µg/Kg
DUAL SCAN Soil Extraction	10g to 1mL	20 to 200µg/Kg-Full scan 5 to 100µg/Kg-Sim scan
Water Extraction	500mL to 0.5mL	1 to 10µg/L
1,4-Dioxane Water Extract	500ml to 1.0ml	0.2µg/L

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 RLs and MDLs, see the ARI website.

2. Summary of Procedure

2.1. For example, an aliquot of sample (water or soil) is extracted by a matrix appropriate technique. Typically, this will be either continuous liquid-liquid or separatory funnel extraction for aqueous samples and sonication or microwave extraction for solid samples. The extracted sample is subjected to any appropriate cleanup and then concentrated. The extract is then delivered to the 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. 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. Initial Calibration Verification (ICV): A process used to verify that the current instrument calibration is acceptable 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 during or at the end of an analytical sequence.

3.3. Decafluorotriphenylphosphine, (DFTTP): used to demonstrate acceptable tuning parameters.

3.4. Method Detection Limit (MDL): The lowest result that can reliably be distinguished in a matrix from a blank. Also referred to as Detection Limit (DL)

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

3.6. Second Source Verification (SCV): A process used to verify that the current instrument verification is acceptable.

3.7. 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.

3.8. 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.

3.9. 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.

3.10. 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.

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

3.12. Method Reporting Limit (MRL): The lowest result that may be reported unqualified based upon the lowest curve point.

3.13. 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.

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

3.15. Method Blank (MB): A sample of a matrix like 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.

3.16. 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.

3.17. Method detection Limit Spike (MDL): A matrix spike prepared at the reporting limit and used for preparing MDL studies to calculate the MDL.

3.18. Reconstructed Ion Current (RIC): A plot of the total instrument response versus time

3.19. Relative Retention Time (RRT): The elution time of an analyte relative to the elution time of its associated internal standard

3.20. 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.

3.21. 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.

3.22. Target software (TARGET): Chromatographic analysis software from Thermoquest Thru-Put version 4.14

3.23. Dual scan (DS): Dual scan is the synchronous acquisition of both full scan and sim data used to achieve lower reporting limits for all matrices.

3.24. Low level calibration verification (LCV): Lowest calibration standard used for an initial calibration.

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 450 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, water washing or gel permeation chromatography. See the appropriate extractions SOPs for clean-up applicability to matrices or target analytes.

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 using nitrile gloves, safety glasses, and laboratory coats.

5.3. Standard solutions should be handled in the fume hoods to avoid exposure to fumes.

5.4. All GC-MS split vents and vacuum exhaust are connected to an exhaust vent or charcoal filter.

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 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.msdshazcom.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 coated with cross bonded 5% diphenyl/95% dimethylpolysiloxane stationary phase (Phenomonex ZB-5msi or equivalent).

6.1.3. Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less. The mass spectrometer must be capable of producing 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 (COA).

7.3. Stock Standard Preparation

7.3.1. 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 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 replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

7.3.6. Stock standard solutions must be replaced 1 year after being de-ampullated.

7.3.7. 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.

7.4. Internal Standard Stock Solution - The internal standards employed are 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, di-n-octylphthalate-d4 and perylene-d12. Other compounds may be used as internal standards if the method requirements are met. Dissolve 0.250g 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.

7.4.1. Each 0.1mL aliquot of the sample extract undergoing analysis should be spiked with 2µL of the internal standard solution, resulting in a concentration of 20ng/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). Dual Scan internal standard is at 200µg/mL and is spiked at 4µg/ml.

7.5. Surrogate Stock Standards - The surrogate standards employed are phenol-d5, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluorobiphenyl, 2-chlorophenol-d4, 1,2-dichlorobenzene-d4, and p-terphenyl-d14.

7.5.1. Prepare a stock solution containing all the acid surrogates (d5-phenol, 2-fluorophenol, d4-2-chlorophenol, and 2,4,6-tribromophenol) by adding 250mg of each into a 50mL volumetric flask. Bring the solution up to volume with methylene chloride. The resulting solution will contain the acid surrogates at 5000µg/ml.

7.5.2. Prepare a stock solution containing all the base surrogates (d4-1,2-dichlorobenzene, d5-nitrobenzene, 2-fluorobiphenyl, and d14-p-terphenyl) 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 base surrogates at 5000 µg/ml.

7.6. Working solutions- working standards are prepared from stock standards or purchased as commercially certified mixtures.

7.6.1. 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 at this time.

7.6.2. Working standard solutions must be replaced 1 year after being de-ampullated.

7.6.3. Working standards must be stored at >0 to 6°C and protected from light.

7.6.4. Working standards should be checked frequently for signs of concentration or degradation.

7.6.5. 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.

7.7. Surrogate working standards

7.7.1. Surrogate calibration standard- the surrogate calibration standard is prepared by diluting the acid and base surrogate stocks in methylene chloride such that the concentration of each analyte is 500µg/ml. This solution is used to calibrate the instrument to quantitate surrogate concentrations.

7.7.2. Surrogate spiking standard- the surrogate spiking standard is prepared by diluting the acid and base surrogate stocks such the concentrations of the acid surrogates are 150µg/mL and the concentrations of base surrogates are 100µg/ml. This solution is prepared in methanol. This solution is used to spike all extracted samples and QC samples with surrogates.

7.8. Matrix spike working standards- the matrix spiking standards are used to prepare MS/MSD sets as well as BS/BSDs.

7.8.1. The matrix spiking solution is purchased commercially and contains all the analytes in an acetone/methylene chloride mixture. The concentration of each analyte is 100µg/ml.

7.8.2. 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. 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 to 1000µg/ml.

7.9.1. Benzoic acid; 2,4-dinitrophenol; and 4,6-dintro-2-methylphenol are augmented in the working calibration solutions such that the concentration of each analyte is 100 to 2000µg/ml.

7.9.2. A selected number of acids and bases are augmented for the Dual Scan working solution from 100 to 225µg/ml.

7.10. GC/MS working tuning standard- a tuning standard should be prepared containing 500µg/mL each of DFTPP (Decafluorotriphenylphosphine); p,p'-DDT, Pentachlorophenol, and Benzidine.

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 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 -10ºC to -20ºC 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 and update the location 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. 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. 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. In order 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. In order 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. 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.

9.6. Duplicate Analysis

9.6.1. 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.

9.6.2. The RPDs between the Sample and Sample duplicate must be measured and reported.

9.6.3. Evaluate the Sample and Sample duplicate RPD and note any deviation >30% in the reviewer checklist.

9.6.4. When mandated by project-specific requirements, an SRM (Standard Reference Material) sample will be analyzed as an independent assessment of method performance.

9.6.5. 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.

9.7. 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 the samples/associated batch QC and the ICV.

9.8. 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 in order to assess data quality and any possible need for corrective actions. Current control limits may be found in the Element.

9.9. 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 0.2 (1,4-dioxane-full scan), 1, 5, 10, 25, 40, 60 and 80µg/mL

10.1.3.1. Dual Scan Calibration standards are prepared from the working calibration solutions at concentrations of 0.05 to 20µg/mL

10.1.3.2. Concentrations of specific acids and bases are varied in the Dual Scan calibration standards and tailored to the reporting limits.

10.1.4. The concentrations of Benzoic Acid; 2,4-Dinitrophenol; and 4,6-Dinitro-2-Methylphenol are doubled in the calibration standard solutions, hence their concentrations are 2, 10, 20, 50, 80, 120 and 160 µg/mL

10.1.5. The calibration curve standards are made as needed and the internal standard solution is added prior to analysis.

10.1.6. Each standard must contain all analytes requested for a specific project, and no target analyte may be quantitated without first being calibrated.

10.1.7. 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.

10.1.8. 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 (In House) at 80, 60, 40, 25, 10, 5, and 1µg/mL		
Phenol	Naphthalene	Carbazole
Bis (2-Chloroethyl)ether	Hexachlorobutadiene	Di-n-butylphthalate
2-Chlorophenol	2-Methylnaphthalene	Fluoranthene
1,3-Dichlorobenzene	4-Bromophenyl-phenylether	Pyrene
1,4-Dichlorobenzene	2-Chloronaphthalene	Phenanthrene
1,2-Dichlorobenzene	Dimethylphthalate	Butylbenzylphthalate
2-Methylphenol	Acenaphthylene	Benzo(a)anthracene
2,2'-oxybis(1-Chloropropane)	Acenaphthene	Chrysene
4-Methylphenol	Dibenzofuran	Di-n-octylphthalate
Hexachloroethane	Fluorene	Benzo(b)fluoranthene
Nitrobenzene	Diethylphthalate	Benzo(k)fluoranthene
Isophorone	4-Chloropheny-phenylether	Benzo(a)pyrene
Bis (2-Chloroethoxy)methane	N-Nitrosodiphenylamine	Indeno(1,2,3-cd)pyrene
1,2,4-Trichlorobenzene	Hexachlorobenzene	Dibenzo(a,h)anthracene
Anthracene	Benzo(g,h,i)perylene	1-methylnaphthalene
Azobenzene(1,2-DP-Hydrazine)	Butylatedhydroxytoluene	Tributyl phosphate
1,4-Dioxane (0.2)	Benzyl Alcohol	Triphenyl phosphate
Butyl diphenyl phosphate	Dibutyl phenyl phosphate	Bis(2-ethylhexyl)phalate

Compounds that are routinely calibrated (In House) at 80, 60, 40, 25, 10, and 5µg/mL		
All Tetrachlorophenols	Hexachlorocyclopentadiene	2,4-Dinitrotoluene
1,4-Dioxane-d8	2,4,6-Trichlorophenol	4-Nitroaniline
N-Nitroso-Di-N-Propylamine	2,4,5-Trichlorophenol	Pentachlorophenol
2-Nitrophenol	2-Nitroaniline	3,3-Dichlorobenzidine
2,4-Dimethylphenol	2,6-Dinitrotoluene	N-Nitrosodimethylamine
2,4,-Dichlorophenol	3-Nitroaniline	Benzidine
4-Chloroaniline	4-Nitrophenol	Pyridine
4-Chloro-3-Methylphenol	Aniline	1,2-Dichlorobenzene-d4
2-Fluorophenol	2-Fluorobiphenyl	Nitrobenzene-d5
Phenol-d5	Terphenyl-d14	
2-Chlorophenol-d4	2,4,6-Tribromophenol	

Compounds that are routinely calibrated (In House) at 160, 120, 80, 50, 20 and 10µg/mL		
Benzoic Acid	2,4-Dinitrophenol	4,6-Dinitro-2-methylphenol.

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 should also be 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 for procedures on how to bring the instrument into compliance for tuning, DDT breakdown, or peak tailing factors.

10.2.3. The mid-level standard ABN may be used as the tuning standard as it contains DFTPP, DDT, pentachlorophenol, and benzidine at 25µg/ml. Providing that the requirements in Section 10.2 are met, the analysis of 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 * Cs)

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.

10.4. 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

$RRFav = \frac{\sum RRFi}{n}$
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

$RSD = \frac{100 * SD}{RFav}$	$= 100 * ((\sum(RRFi - RRFav)^{2)}/(n-1))^{1/2}/RRFav$
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 quadradic 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 (25 ng/µL), 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 Section 20.2 If the minimum relative response factors are not met, the system must be evaluated, and corrective action should 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 similar to 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:

10.9.2.4.1. Relative retention times change.

10.9.2.5. 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/µl) from the most recent initial calibration as the reference.

10.9.2.6. 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), a number of 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.

10.9.2.6.1. Reported values for the analytes failing the acceptance criteria must be flagged with a “Q” qualifier and noted in the Reviewer checklist.

10.9.2.7. 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.

10.9.2.8. (CCV criteria) If the percent difference for each analyte is less than or equal to 50% the continuing calibration verification (CCV) is valid. Problems similar to those listed under the minimum response factors could affect this criterion. See Section 16.6 for procedures for dealing with %D failure.

10.9.2.9. (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.

11. Procedure

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

11.2. Sample Preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580
Tissue	3540, 3545, 3550

11.3. Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640
Anilines and aniline derivatives	3620
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640

Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

11.4. The recommended GC/MS operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration).

Mass range:	**35-500 amu**
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 3.5 minutes
Temperature program:	40-320°C at 12/15C°/min
Final temperature:	320°C, hold until benzo[g,h,i]perylene is eluted
Injector temperature:	250°C
Transfer line temperature:	300°C
Source temperature:	According to manufacturer's specifications(230-250°C for MSD)
Injector:	Grob-type, splitless/split
Sample volume:	1-2 µL
Carrier gas:	Helium at 30 cm/sec.

11.5. Dual Scan Analysis requires a 5975C XL Inert GC/MS with synchronous sim/scan mode which allows for selective SIM acquisition while also acquiring full scan data.

11.6. 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 in Sections 10.3 and 10.4.

11.7. Prior to sample analysis the initial calibration verification must be analyzed, and this ICV must meet the criteria found in Sections 10.9.2. 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 ICV provided it meets the requirements found in Section 10.9.2.

11.8. 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.

11.9. GC/MS analysis

11.9.1. It is highly recommended that the extract be screened on a GC/FID or GC/PID 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. Highly concentrated samples should be extracted using a medium/high level extraction.

11.9.2. 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 20µg/mL (4µg/mL for dual scan) of each standard in the sample. This aliquot should be prepared in an amber glass autosampler vial and sealed with a PFTE crimp cap.

11.9.3. Analyze the 0.3ml aliquot by GC/MS. The volume to be injected should ideally contain 25µg/mL (5µg/mL dual scan) of base/neutral and 37.5µg/mL (7.5µg/mL dual scan) of acid surrogates. 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.

11.9.4. When the response for any target analyte exceeds the high point of the initial calibration curve, then extract dilution must take place. See section 16.12 for guidance on dilutions.

11.10. 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 Teflon® 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 and the standard component mass spectrum.

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

12.5. The relative intensities of ions specified in Appendix 20.2 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).

12.6. 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 50% of the average of the two peak heights. Typically, structural isomers not meeting the 50% resolution requirement are identified and integrated as a whole peak and reported as a total analyte. (Total Benzofluoranthenes)

12.7. 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.

12.8. Tentatively Identified Compounds (TICS)

12.8.1. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the 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 qualitative identification are:

12.8.1.1. Relative intensities of major ions in the reference spectrum (ions >10 % of the most abundant ion) should be present in the sample spectrum.

12.8.1.2. The relative intensities of the major ions should agree within ± 30%.

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

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

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

12.8.1.6. Sample spectrum will be searched against the unknown spectral library with the top three matches identified for each TIC. The spectra is reviewed and assigned a general chemical classification in the following style: Unknown Hydrocarbon, Unknown PNA, Unknown Acid Ester, etc. The general classification prevents the assignment of a specific CAS number when importing into the ELEMENT database. Sample TIC spectrum that does not appear to be of any general chemical classification may be presented simply as “Unknown”.

12.9. Quantitative analysis

12.9.1. 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 continuing calibration. The report for the continuing 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 quantitation using the primary characteristic ion (when free of interference). All quantifications 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.

12.9.2. Calculate the concentration of each identified analyte in the sample as follows:

12.9.3. Water

Concentration (µg/L) =	$\frac{(Ax)(Is)(Vt)(D)}{(Ais)(RRF)(Vo)(Vi)}$

where:
D = Dilution Factor
A_X = Area of characteristic ion for compound being measured
Is = Amount of internal standard injected (ng)
Vt = Total volume of the 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)

12.9.4. 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, taking into account dilutions (i.e. for a 1 to 10 dilution of a 1 ml extract Vt = 10,000 µL)	
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	

12.9.4.1. Where applicable, an estimate of concentration for tentatively identified compounds (TICS) in the sample should be made. The formula given above should be used with the following modifications: The area Ax and Ais should be from the total ion chromatograms (RIC) and the RRF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration.

12.9.4.2. Use the nearest internal standard free of interferences. Free of interferences means <10% of internal standard RIC is from any co-eluting interferences present in the sample matrix.

12.9.4.3. Quantitation is performed using the total ion chromatograms (RIC) for both the internal standard and the TICs.

12.9.4.4. In cases where all the internal standards show RIC interference >10% contribution from

the sample matrix the internal standard showing the least amount of interference shall be used to quantify all the unknowns

12.9.4.5. TICS that elute before the first target 1,4-Dioxane or N-Nitrosodimethylamine will not be included as their identifications are more appropriately made from the GC/MS volatile analysis.

12.9.4.6. TICS that are less than 10% area of the closest internal standard free of interferences are discarded.

12.9.4.7. A maximum of 20 TICS for any individual sample are quantified.

12.9.4.8. The method blank associated with the samples is also evaluated for TICS and any unknowns found are compared to those quantified in the samples and "B" flagged when the spectra and retention times match closely. The analyst will use their best judgment to make this determination.

12.9.4.9. Project specific requirements may require more (or less) TICS to be quantified for each individual sample.

12.9.5. Quantitation of multi-component compounds (e.g. Toxaphene, Aroclors) is beyond the scope of this method. Normally, quantitation is performed using a GC/ECD by Method 8081 or 8082. However, this SOP may be used to confirm the identification of these compounds, when the sample extract concentrations are 10µg/mL or greater.

12.9.6. Manual Integration – see SOP 1021S for guidance when manual integration is required.

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 and charcoal filter.

14.4. All MS vacuum pumps will be connected to an exhaust vent.

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 Quality Control Measures

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 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 samples internal standard EICP areas following the ICV must meet the technical acceptance criteria listed in Section 9.1

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. Surrogate recoveries are considered unacceptable when:

15.4.1.1. Any surrogate has a recovery less than 10.0 percent

15.4.1.2. More than one base/neutral surrogate or more than one acid surrogate have recoveries outside of the applicable surrogate acceptance windows.

15.4.1.3. Note: ARI uses a surrogate solution containing 8 surrogates rather than the method recommended six.

15.4.1.4. Recoveries outside of the In-House QC limits should not necessarily be used to reject batch data but will require corrective action.

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

15.4.3. Project specific recovery limits may be applied to surrogate recoveries. 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 or the recoveries meet in house criteria.

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.

15.4.6. 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)

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.

15.5.2.1. 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.

15.5.2.3. 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.

15.6.1.1. The RPDs between the MS/MSD samples must be measured and reported.

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

15.6.1.3. 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 will document this in the analytical notes accompanying the data so that it may be included in the reviewer checklist.

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. 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). 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 25µg/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 actions 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 analysis, 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)

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/Matrix Spike Duplicates

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 20µg/mL 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 and internal standard 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.

16.14.1.1. 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)

16.14.1.2. 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.

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 blank spikes 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 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 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. 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 8000D, (SW-846), Revision 5, March, 2018.

19.4. "Department of Defense (DOD) Department of Energy (DOE) Consolidated Quality Systems Manual for Environmental Laboratories", Version 5.3, 2019.

19.5. "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.

20. Appendices

20.1. Appendix 20.1: ARI Acceptance Criteria

20.2. Appendix 20.2: 8270E target analyte list

20.3. Appendix 20.3: DFTPP Key ion and ion abundance criteria

20.4. Appendix 20.4: Chromatogram of calibration standard - Acid/Base/Neutral

20.5. Appendix 20.5: Example pages from GC/MS semivolatile organics virtual logbook

20.6. Appendix 20.6: Peak tailing factor calculations

20.7. Appendix 20.7 Method 625.1 requirements

20.8. Appendix 20.8 SIM 1,4-dioxane analysis

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., BS 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 standard	RRT of each target analyte in each calibration standard within ± 0.06RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.	After maintenance is performed which may affect relative retention times the RRT may be updated based on the ICV
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^2 limits 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.

Appendix 20.1. ARI ACCEPTANCE CRITERIA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
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 the 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. Average RRFs for analytes 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. 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.	
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. Perform corrective action from section 16.1	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.	

Appendix 20.1. ARI ACCEPTANCE CRITERIA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
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 analytes if acceptance criteria are not met to BS results.	
Blank spike duplicate (BSD)	Project specific	RPD ≤ 30% (between BS and BSD or sample and sample duplicate)	Perform corrective action from section 16.1	Apply *-flag to the specific analytes 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 analytes 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 analytes 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 (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, 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 analytes if acceptance criteria are not met to surrogate results.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Results reported between MDL and MRL	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
ARI's Routine Method 8270E 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
1,4-Dichlorobenzene-d4 (IS)[1]	106-46-7	152	150,115	--	--	--
1,4-Dioxane	123-91-1	88	58,57	NA	15	20
d8-1,4-Dioxane (SS)	17647-74-4	64	96,62	NA	15	20
Aniline [2]	62-53-3	93	66,65	NA	15	20
Benzyl alcohol [2]	100-51-6	108	79,77	NA	15	20
bis(2-chloroethyl) ether	111-44-4	93	63,95	0.7	15	20
bis(2-chloroisopropyl) ether	108-60-1	45	77,121	0.01	15	20
2-Chlorophenol	95-57-8	128	64,130	0.8	15	20
1,3-Dichlorobenzene	541-73-1	146	148,111	NA	15	20
1,4-Dichlorobenzene	106-46-7	146	148,111	NA	15	20
1,2-Dichlorobenzene	95-50-1	146	148,111	NA	15	20
2-Fluorophenol (SS) [1]	367-12-4	112	--	NA	15	20
d4-2-chlorophenol (SS) [1]	93951-73-6	132	134	NA	15	20
d4-1,2-dichlorobenzene (SS) [1]	2199-69-1	152	150	NA	15	20
Hexachloroethane	67-72-1	117	201,199	0.3	15	20
2-Methylphenol	95-48-7	108	107,77,79, 90	0.7	15	20
4-Methylphenol	106-44-5	108	107,77,79, 90	0.6	15	20
N-Nitrosodimethylamine [2]	62-75-9	74	42	NA	15	20
N-Nitroso-di-n-propylamine	621-64-7	70	42,101, 130	0.5	15	20
Phenol	108-95-2	94	65,66	0.8	15	20
Phenol-d5 (SS)	108-95-2	99	42,71	NA	15	20
Pyridine [2]	110-86-1	79	52	NA	15	20
Naphthalene-d8 (IS)[1]	91-20-3	136	68	--	--	--
Benzoic acid [2]	65-85-0	122	105,77	NA	15	20
Bis(2-chloroethoxy)methane	111-91-1	93	95,123	0.3	15	20
4-Chloroaniline [2]	106-47-8	127	129,65,92	0.01	15	20
4-Chloro-3-methylphenol	59-50-7	107	144,142	0.2	15	20
2,4-Dichlorophenol	120-83-2	162	164,98	0.2	15	20
2,4-Dimethylphenol	105-67-9	107	121,122	0.2	15	20
Hexachlorobutadiene	87-68-3	225	223,227	0.01	15	20
Isophorone	78-59-1	82	95,138	0.4	15	20

Internal Standard Associated Analyte[1]	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
2-Methylnaphthalene	91-57-6	142	141	0.4	15	20
1-Methylnaphthalene	90-12-0	142	141,143	NA	15	20
Naphthalene	91-20-3	128	129,127	0.7	15	20
Nitrobenzene	98-95-3	77	123,65	0.2	15	20
Nitrobenzene-d5 (SS) [1]	98-95-3	82	128	NA	15	20
2-Nitrophenol	88-75-5	139	109,65	0.1	15	20
1,2,4-Trichlorobenzene	120-82-1	180	172,145	NA	15	20
Acenaphthene-d10 (IS)[1]	83-32-9	164	162,160	--	--	--
Acenaphthene	83-32-9	154	153,152	0.9	15	20
Acenaphthylene	208-96-8	152	151,153	0.9	15	20
2-Chloronaphthalene	91-58-7	162	127,164	0.8	15	20
4-Chlorophenyl Phenyl Ether	7005-72-3	204	206,141	0.4	15	20
Dibenzofuran	132-64-9	168	139	0.8	15	20
Diethyl phthalate	84-66-2	149	177,150	0.01	15	20
Dimethyl phthalate	131-11-3	163	77,164	0.01	15	20
2,4-Dinitrophenol	51-28-5	184	63,154	0.01	15	20
2,4-Dinitrotoluene	121-14-2	165	63,89	0.2	15	20
2,6-Dinitrotoluene	606-20-2	165	63,89	0.2	15	20
Fluorene	86-73-7	166	165, 167	0.9	15	20
2-Fluorobiphenyl (SS) [1]	321-60-8	172	171	NA	15	20
Hexachlorocyclopentadiene	77-47-4	237	235,272	0.05	15	20
2-Nitroaniline [2]	88-74-4	138	65,92	0.01	15	20
3-Nitroaniline [2]	99-09-2	138	65,92	0.01	15	20
4-Nitroaniline [2]	100-01-6	138	65,92	0.01	15	20
4-Nitrophenol	100-02-7	139	109,65	0.01	15	20
1,2,4,5-Tetrachlorophenol		232	230,234	NA	15	20
2,3,5,6-Tetrachlorophenol	935-95-5	232	230,234	NA	15	20
2,4,6-Tribromophenol (SS) [1]	118-79-6	330	332	NA	15	20
2,4,6-Trichlorophenol	88-06-2	196	198,200	0.2	15	20
2,4,5-Trichlorophenol	95-95-4	196	198,200	0.2	15	20
Phenanthrene-d10 (IS)[1]	85-01-8	188	94,80	--	--	--
Anthracene	120-12-7	178	176,179	0.7	15	20
4-Bromophenyl phenyl ether	101-55-3	248	250,141	0.1	15	20
Di-n-butyl phthalate	84-74-2	149	150,104	0.01	15	20
4,6-Dinitro-2-methylphenol [2]	534-52-1	198	51,105	0.01	15	20
1,2-Diphenylhydrazine	122-66-7	77	105,182	NA	15	20
Fluoranthene	206-44-0	202	101,200	0.6	15	20
Hexachlorobenzene	118-74-1	284	142,249	0.1	15	20
N-Nitrosodiphenylamine	86-30-6	169	168,167	0.01	15	20
Pentachlorophenol	87-86-5	266	264,268	0.05	15	20
Phenanthrene	85-01-8	178	179,176	0.7	15	20

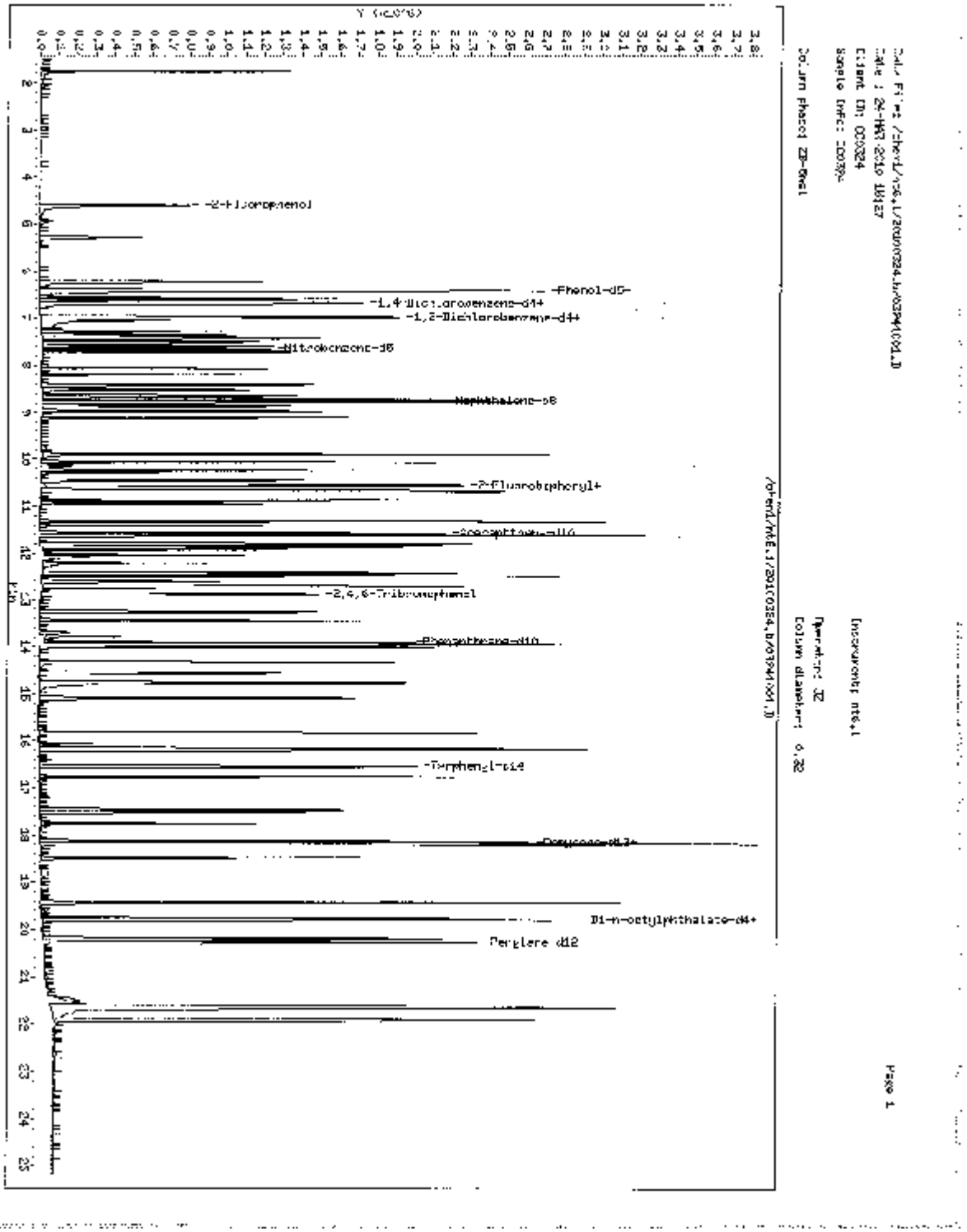
Internal Standard Associated Analyte[1]	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
Chrysene-d12 (IS)[1]	218-01-9	240	120,236	--	--	--
Benzidine [2]	92-87-5	184	92,185	NA	15	20
Benzo(a)anthracene	56-55-3	228	229,226	0.8	15	20
Butyl benzyl phthalate	85-68-7	149	91,206	0.01	15	20
Chrysene	218-01-9	228	226,229	0.7	15	20
3,3'-Dichlorobenzidine [2]	91-94-1	252	254,126	NA	15	20
Pyrene	129-00-0	202	200,101	0.6	15	20
Terphenyl-d14 **(SS)[1]**	84-15-1	244	122,243	NA	15	20
Di-n-octylphthalate-d4 (IS)[1]	117-84-0			--	15	20
Bis(2-ethylhexyl) phthalate	117-81-7	149	167,279	0.01	15	20
Di-n-octylphthalate	117-84-0	149	167,279	0.01	15	20
Perylene-d12 (IS)[1]	198-55-0	264	260,132	0.01	15	20
Benzo(b)fluoranthene	205-99-2	252	253,126	0.7	15	20
Benzo(k)fluoranthene	207-08-9	252	253,126	0.7	15	20
Benzo(g,h,i)perylene	191-24-2	276	138,277	0.01	15	20
Benzo(a)pyrene	50-32-8	252	253,126	0.7	15	20
Dibenz(a,h)anthracene	53-70-3	278	139,279	0.5	15	20
Benzo(g,h,i)perylene	191-24-2	276	138,274	0.5	15	20
Indeno(1,2,3-cd)pyrene	193-39-5	276	138,227	0.5	15	20

1 – Compound designations: IS = Internal Standard, SS = Surrogate Standard; 2 – Active analytes

Appendix: 20.3
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR METHOD 8270E

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

Appendix 20.4
Chromatogram of calibration standard - Acid/Base/Neutral



Appendix 20.5
GC/MS Semivolatile Organics Logbook

Analytical Resources, Incorporated
Analytical Chemists and Consultants

ANALYSIS SEQUENCE

SPA0030

Printed: 1/13/2017 9:58:25AM

Inst. Used: NT11 Element Column ID: E006480
Calibration ID: Z100C81 Tune File: 161216 Q
EM Voltage: 2352

Lab Number	Sample Name	Analysis	Container	Order	STD ID	IS ID	Comments
SPA0088-TUN1	DFTPP	QC		1	E007446		
SPA0088-ICV1	Initial Cal Check	QC		2	E006517	E002370	
BRA0131-BLK1	Blank	QC		3		E002370	
BRA0131-BS1	LCS	QC		4		E002370	
[illegible]-01	[illegible]-122016	SIM PAH Low (0.01 ug/L - 0	E 01	5		E002370	
[illegible]-02	[illegible]-122016	SIM PAH Low (0.01 ug/L - 0	E 01	6		E002370	
SPA0088-CCV1	SIM PAH [illegible]	QC		7	[illegible]	[illegible]	

INTERNAL STANDARD SUMMARY FOR DATABATCH - \\target\share\chem3\nt11.i\20170110.b

[illegible]

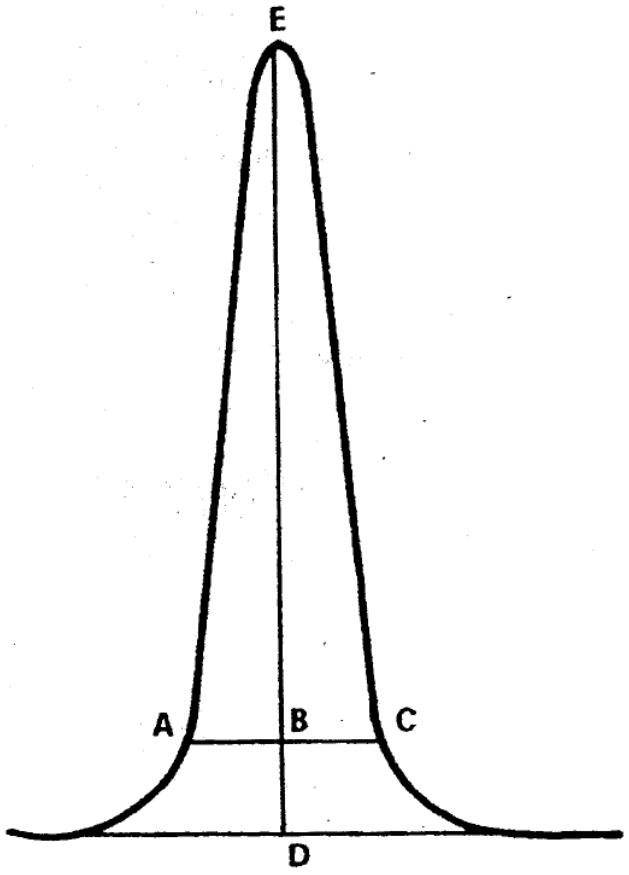
MANUAL INTEGRATION SUMMARY FOR DATABATCH - \\target\share\chem3\nt11.i\20170110.b

ARI Job No.: SPA0 Method: DFTPP.m Instrument: nt11.i Date: 10-JAN-2017

[illegible]

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

20.7 Modification Required for EPA Method 625.1 (These modifications are only implemented when specifically requested by a client, otherwise Method 625.1 is analyzed as described in previously in this SOP)

20.7.1 The following DFTPP key ions and ion abundance criteria for Method 625.1 are substituted for those listed in Appendix 20.3 used for Method 8270E.

Mass	Ion Abundance Criteria
51	30 – 60 % of mass 198
68	< 2 % of mass 69
70	< 2 % of mass 69
127	40 – 60 % of mass 198
197	< 1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	> 1% of mass 198
441	Present, but < mass 443
442	40 -100% of mass 198
443	17-23 % of mass 442

20.7.2 The Initial Calibration for Method 625.1 is a minimum of 5 points for averaged fit and 6 points for a quadratic fit.
20.7.3 Initial calibration RSD for Method 625.1 must be RSD< 35% or R^2 <.990 with no exceptions.
20.7.4 ICV/CCV %D for Method 625.1 must be fall within the limits shown in appendix 20.7.6. Note that these limits are not in Element as shown on table 6 -QC acceptance criteria for method 625.1-and must be evaluated manually.
20.7.5 Blank spike and matrix spike recoveries verification %D for Method 625.1 must be fall within the limits shown in appendix 20.7.6. Note that these limits are not in Element as shown on table 6 -QC acceptance criteria for method 625.1-and must be evaluated manually.
20.7.6 Table 6 as shown below includes control limits for the ICV/CCV (%Q), the blank spike/blank spike duplicate (X), and matrix spike/matrix spike duplicate (P_1P_2). Note that these limits are not in Element as shown in table 6 and must be evaluated manually for quality control.

Table 6 – QC Acceptance Criteria – Method 625[1]					
Analyte	Range for Q (%)[2]	Limit for s (%)[3]	Range for $\bar{X}$ (%)[3]	Range for P_1, P_2(%)[3]	Limit for RPD (%)
Acenaphthene	70-130	29	60-132	47-145	48
Acenaphthylene	60-130	45	54-126	33-145	74
Aldrin	7-152	39	7-152	D-166	81
Anthracene	58-130	40	43-120	27-133	66
Benzo(a)anthracene	42-133	32	42-133	33-143	53
Benzo(b)fluoranthene	42-140	43	42-140	24-159	71
Benzo(k)fluoranthene	25-146	38	25-146	11-162	63
Benzo(a)pyrene	32-148	43	32-148	17-163	72
Benzo(ghi)perylene	13-195	61	D-195	D-219	97
Benzyl butyl phthalate	43-140	36	D-140	D-152	60
beta-BHC	42-131	37	42-131	24-149	61
delta BHC	D-130	77	D-120	D-120	129
bis(2-Chloroethyl)ether	52-130	65	43-126	12-158	108
bis(2-Chloroethoxy)methane	52-164	32	49-165	33-184	54
bis(2-Chloroisopropyl) ether	63-139	46	63-139	36-166	76
bis(2-Ethylhexyl) phthalate	48-137	50	29-137	8-158	82
4-Bromophenyl phenyl ether	70-130	26	65-120	53-127	43
2-Chloronaphthalene	70-130	15	65-120	60-120	24
4-Chlorophenyl phenyl ether	57-145	36	38-145	25-158	61
Chrysene	44-140	53	44-140	17-168	87
4,4'-DDD	D-135	56	D-135	D-145	93
4,4'-DDE	19-130	46	19-120	4-136	77
4,4'-DDT	D-171	81	D-171	D-203	135
Dibenz(a,h)anthracene	13-200	75	D-200	D-227	126
Di-*n*-butyl phthalate	52-130	28	8-120	1-120	47
3,3'-Dichlorobenzidine	18-213	65	8-213	D-262	108
Dieldrin	70-130	38	44-119	29-136	62
Diethyl phthalate	47-130	60	D-120	D-120	100
Dimethyl phthalate	50-130	110	D-120	D-120	183
2,4-Dinitrotoluene	53-130	25	48-127	39-139	42
2,6-Dinitrotoluene	68-137	29	68-137	50-158	48
Di-*n*-octyl phthalate	21-132	42	19-132	4-146	69
Endosulfan sulfate	D-130	42	D-120	D-120	70
Endrin aldehyde	D-189	45	D-189	D-209	75
Fluoranthene	47-130	40	43-121	26-137	66
Fluorene	70-130	23	70-120	59-121	38
Heptachlor	D-172	44	D-172	D-192	74
Heptachlor epoxide	70-130	61	71-120	26-155	101
Hexachlorobenzene	38-142	33	8-142	D-152	55
Hexachlorobutadiene	68-130	38	38-120	24-120	62
Hexachloroethane	55-130	32	55-120	40-120	52

Table 6 – QC Acceptance Criteria – Method 625 [1]					
Analyte	Range for Q (%) [2]	Limit for s (%) [3]	Range for $\bar{X}$ (%) [3]	Range for P_1, P_2(%) [3]	Limit for RPD (%)
Indeno(1,2,3-cd)pyrene	13-151	60	D-151	D-171	99
Isophorone	52-180	56	47-180	21-196	93
Naphthalene	70-130	39	36-120	21-133	65
Nitrobenzene	54-158	37	54-158	35-180	62
N-Nitrosodi-n-propylamine	59-170	53	14-198	D-230	87
PCB-1260	19-130	77	19-130	D-164	128
Phenanthrene	67-130	24	65-120	54-120	39
Pyrene	70-130	30	70-120	52-120	49
1,2,4-Trichlorobenzene	61-130	30	57-130	44-142	50
4-Chloro-3-methylphenol	68-130	44	41-128	22-147	73
2-Chlorophenol	55-130	37	36-120	23-134	61
2,4-Dichlorophenol	64-130	30	53-122	39-135	50
2,4-Dimethylphenol	58-130	35	42-120	32-120	58
2,4-Dinitrophenol	39-175	79	D-173	D-191	132
2-Methyl-4,6-dinitrophenol	56-130	122	53-150	D-181	203
2-Nitrophenol	61-165	33	45-167	29-182	55
4-Nitrophenol	35-130	79	13-129	D-132	131
Pentachlorophenol	42-152	52	38-152	14-176	86
Phenol	48-130	39	17-120	5-120	61
2,4,6-Trichlorophenol	69-130	35	52-129	37-144	58

[1] Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 1625. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.
[2] Test concentration = 100 µg/mL.
[3] Test concentration = 100 µg/L.
Q – Calibration verification (Sections 7.3.1 and 15.4).
s – Standard deviation for four recovery measurements in the DOC test (Section 8.2.4).
$\bar{X}$ – Average recovery for four recovery measurements in the DOC test (Section 8.2.4).
P_1, P_2 = MS/MSD recovery (Section 8.3.2, Section 8.4.2).
RPD = MS/MSD relative percent difference (RPD; Section 8.3.3).
D – Detected; result must be greater than zero.

Appendix 20.8
1,4-Dioxane sim analysis

Internal Standard Associated Analyte[1]	CAS Number	Primary Ion	Secondary Ion	Min RRF	Max %RSD	Max %D
1,4-Dichlorobenzene-d4 (IS)[1]	106-46-7	152	150	--	--	--
1,4-Dioxane	123-91-1	88	58	NA	15	20
d8-1,4-Dioxane (SS)	17647-74-4	96	64	NA	15	20

20.8.1. A seven-point calibration from 0.1-20µg/ml is performed for the initial calibration.

20.8.2. The initial and continuing calibration verification is prepared at 5.0µg/ml.

20.8.3. The method MRL for waters is 0.2µg/L.

20.8.4. The instrument acquisition is done in SIM(Selected ion monitoring) mode.

20.8.5. All method and quality control requirements as described in this SOP apply to SIM 1,4-Dioxane analysis.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Polychlorinated Biphenyls (Aroclor) Analysis

SOP 403S
Revision 26

Revision Date: 2/11/2020
Effective Date: 2/11/2020

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 21.1 outlines ARI's routine procedure. Please refer directly to DOD-QSM 5.3 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 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 stock solutions are attached as a pdf file to the standard registry 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 screwcaps. 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 six months 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 21.1.

9.1.1. Criteria for ARI's routine analyses are listed in Appendix 21.1

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 are 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]	-	-	-

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)					
1242	1242	-	-	250[1]	-	-	-
1248	1248	-	-	250[1]	-	-	-
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).

$$\textbf{RSD = SD / (Ave RRF) = } ((\Sigma (RRF_i - \text{Ave RRF})^2) / (n-1))^{1/2}$$

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 reviewer checklist.

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.

11.6. Rinses before CCVs are not allowed unless rinses are placed before all injections in the analytical sequence. Rinses are permitted before the ICV analyses.

11.7. Screen extracts as necessary

11.7.1. 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.

11.8. Remove sample extracts from refrigerator 15 and change the location to refrigerator 17 in Element under batch or sequence.

11.9. GC analysis

11.9.1. 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.

11.9.2. Load autosampler with the aliquots prepared in Section 11.8.1.

11.9.3. Enter the analytical sequence into the chromatography data system.

11.9.4. Begin the analytical sequence.

11.9.5. The injection volume must be the same volume used for the calibration standards. Recommended GC operating conditions are specified in Section 11.3.

11.9.6. The computer system will collect and process the chromatography data and export it to "Target" software.

11.9.7. The "Target" software assigns the chromatographic baseline and integrates the electronic signal producing a chromatogram.

11.9.8. Examine the chromatogram for the presence of elemental sulfur.

11.9.8.1. 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.

11.9.9. Verify that the computer has correctly identified the chromatographic baseline and integrated all peaks correctly.

11.9.9.1. If corrections are required, manually re-integrate the data file following guidelines in SOP 1021S "Manual Integration of Chromatographic Peaks".

11.9.9.2. Manual integrations must be identified and explained in the reviewer checklist associated with each analytical sequence loaded into Element.

11.9.9.3. 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.

11.9.10. Perform all qualitative and quantitative measurements as described in Section 12.

11.9.11. Replace the punctured septum on the auto-sampler vial with a new one.

11.9.12. Store the extracts at >0 to 6°C, protected from light in Refrigerator 17.

11.9.13. Following the data analysis, upload the data into Element using data tool.

11.9.14. 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.

11.9.15. Attach a .pdf of the virtual logbook to the sequence associated with the data.

11.9.15.1. Make sure the Reviewer Checklist(s) include all deviations from standard procedure and any other noteworthy information concerning the project analyzes.

11.9.16. The analyst initials as loaded into Element should reflect the analyst who reduced and uploaded the data if different from the analyst who initiated the analytical sequence.

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 reviewer checklist. 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 reviewer checklist 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 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. 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 storeroom 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 21.1 of this document.

15.2. Requirements for Method Blanks are tabulated in Appendix 21.1.

15.3. Internal Standards- All samples' internal standard peak areas must meet the technical acceptance criteria listed in Appendix 21.1 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 are 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 are 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 reviewer checklist 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 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. 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 608.3—Organochlorine Pesticides and PCBs by GC/HSD December 2016

19.3. USEPA Contract Laboratory Program, Statement of Work for Organics Superfund methods SOM02.4, October 2016.

19.4. “Determinative Chromatographic Separations”: Method 8000D, (SW-846), Revision 5, March 2018.

19.5. Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 5.3, June 2019

20. Appendices

20.1. Appendix 21.0: In-house PCB Quality Control Requirements

20.2. Appendix 21.1: Sulfur cleanup procedure

20.3. Appendix 21.2: Congener analysis by ECD

20.4. Appendix 21.3: Method 608 modifications

21. Appendix 21.0: In-House 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.

21.1. Sulfur Clean-up

21.1.1. Elemental Sulfur is precipitated from the sample extract using elemental Mercury which forms the insoluble salt HgS.

21.1.2. 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”.

21.1.3. 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.

21.1.4. Shake the vials for approximately 30 seconds each using a “Vortex” type shaker.

21.1.5. Let the vial stand for 15 to 20 minutes to allow the precipitate to settle.

21.1.6. Repeat steps 20.2.3 through 20.2.5 until no additional dark precipitate is produced.

21.1.7. When the precipitate has settled, the vial may be placed in the autosampler tray for re-analysis.

21.1.8. Following analysis, dispose of the Mercury contaminated vial in the designated container in Fume Hood 34.

21.2. Appendix 20.3 - PCB Congeners by GC/ECD - ARI Method based on 8082A

21.2.1. 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)

Congener*	BZ#
2,4'-Dichlorobiphenyl	8
2,2',5-Trichlorobiphenyl	18
2,4,4'-Trichlorobiphenyl	28
	31
	33
2,2',3,5'-Tetrachlorobiphenyl	44
	49
2,2',5,5'-Tetrachlorobiphenyl	52
	60
2,3',4,4'-Tetrachlorobiphenyl	66
	70
	74
3,3',4,4'-Tetrachlorobiphenyl	77[t]
	87
	95
	97
	99
	56
2,2',4,5,5'-Pentachlorobiphenyl	101
	105
2,3,3',4,4'-Pentachlorobiphenyl	110
2,3',4,4',5-Pentachlorobiphenyl	118
3,3',4,4',5-Pentachlorobiphenyl	126[t]
2,2',3,3',4,4'-Hexachlorobiphenyl	128
	132
2,2',3,4,4',5'-Hexachlorobiphenyl	138
	141
	149
	151
2,2',4,4',5,5'-Hexachlorobiphenyl	153

	156
	158
2,2',3,3',4,4',5-Heptachlorobiphenyl	170
	174
	177
2,2',3,4,4',5,5'-Heptachlorobiphenyl	180
	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	187
	194
2,2',3,3',4,4',5,6-Octachlorobiphenyl	195
	201
	203
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	206
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	209/

[t] These compounds not currently analyzed for.
* This is ARI's standard list of PCB congeners. Other congeners are available upon client request.

21.2.2. Congener analysis is recommended for samples containing multiple Aroclors that are indistinguishable from the patterns used in method 8082A

21.2.3. Detection limits-will depend on the amount of sample extracted and the final effective volume.

SAMPLE MATRIX	SAMPLE BASIS	FINAL VOLUME	MRL
Solid	12.5grams	2.5mL	1µg/kg

21.2.4. The congeners are quantitated from a 6-point curve ranging from 5ηg/mL to 100ηg/mL on column.

21.2.5. The curve points are 5, 10, 25, 50,75, and 100ppb

21.2.6. Compound identification is based on a dual column analysis.

21.2.7. 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.

21.3. Modifications Required for EPA Method 608

21.3.1. Modification Required for EPA Method 608

21.3.2. (**These modifications are only implemented when specifically requested by a client, otherwise Method 608 is analyzed as described in previously in this SOP**)

21.3.3. The Initial Calibration for Method 608 is a minimum of 3 points instead of 5 points required in Method 8082A.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Ammonia, Auto-phenate

SOP 615S
Version 006

Revision Date: 3/29/17
Effective Date: 3/29/17

Prepared by:

Mike Perkins

Approvals:

Casey English, Laboratory Supervisor

Eric Larson, Inorganics Division Manager

Annual Review

SOP Number: 615S

Title: Ammonia, Auto-phenate

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

Name	Reviewer's Signature	Date

Standard Operating Procedures: Ammonia, Auto-phenate

1. Scope and Application

1. This method is for the determination of ammonia nitrogen (NH_3-N) in drinking, surface, domestic and industrial wastes and saline (2M KCl) soil extracts using automated phenate, flow injection analysis (FIA). The procedure is based upon the requirements of Standard Methods 4500-NH_3 H-97.
2. The automated phenate method is applicable to the measurement of 0.04 mg/L to 1.00 mg/L NH_3-N/L in potable and surface waters and domestic and industrial wastes. The range may be extended by diluting samples for analysis.
3. While Standard Methods states that "sample distillation is unnecessary", the method is not applicable for NPDES reporting without a preliminary distillation (40 CFR 136.3, 2012 Method Update Rule, Table IB). The same is true for all NPDES ammonia methods. Footnote 6 to Table IB indicates that distillation is not required if comparability studies indicate that distillation is not required for the test effluent.
4. ARI does not normally distill samples for ammonia analysis by either ISE or the automated phenate procedure. Clients requesting ammonia analysis by either procedure should be aware of this potential limitation in the use of the data.

2. Summary of the Procedure

1. Ammonia (NH3) in natural waters derives largely from the microbial breakdown of organic materials (deamination of organic nitrogen (R-NH2), hydrolysis of urea (H2NCONH2), etc.) and, under anaerobic conditions, the reduction of nitrate (NO3). Ammonia exists either as a dissolved gas (NH3 aq) or as the ammonium ion (NH4+), primarily dependent upon pH (temperature and dissolved solids also affect the speciation). At pH <7, NH4+ predominates and as the medium becomes more basic (pH>7) gaseous NH3 predominates (approximately 50% at pH 9 and 100% at pH>11). The approximate speciation of ammonium and ammonia is shown in figure 1 below.

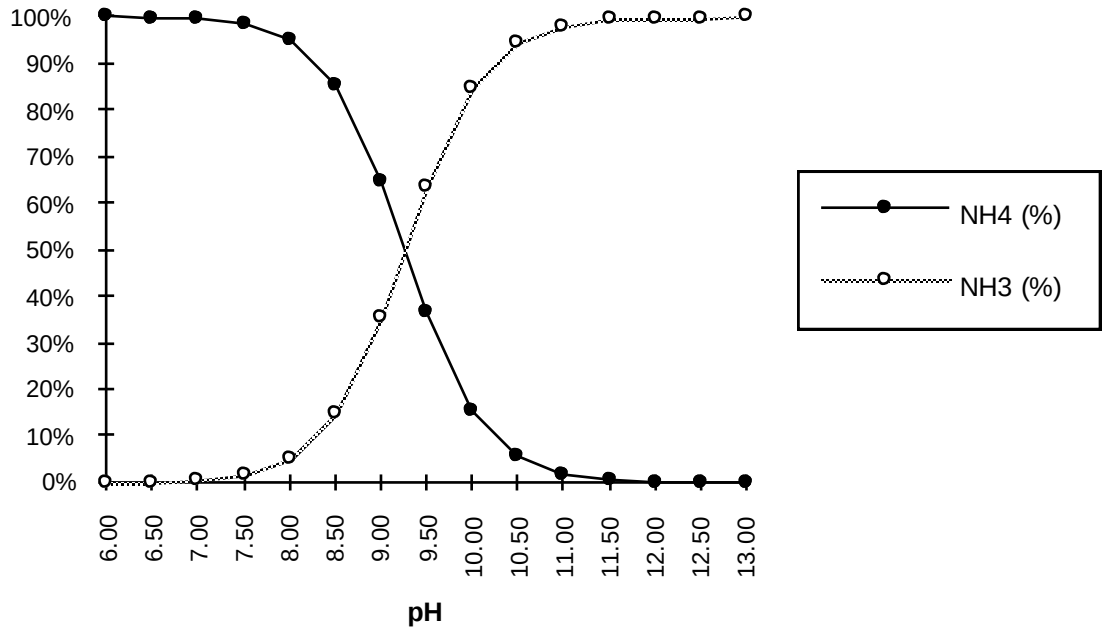


Figure 1. Approximate speciation of ammonium (NH_4) and ammonia (NH_3)

2. Two procedures are used for the analysis of ammonia in our laboratory, the automated phenate (this SOP) and ion-specific electrode (SOP ARI 616S). Both procedures measure ammonia as NH3-N under alkaline conditions. The phenate procedure allows for rapid analysis of large numbers of relatively clean low level samples (<10 mg/L) but is more subject to interference related to color, turbidity and dissolved solids. This is the procedure of choice for routine analysis. For samples which are highly turbid, colored, or have high TDS/Conductivity (>500 mg/L, >770µS) or have an ammonia concentration requiring a dilution greater than 1:100 (>100 mg/L) the ISE procedure should be used.
3. Soil/Sediment will be extracted following MSA 33.3.
   2.3.1. 1:10 Extraction with 2N KCl and a shake time of 1 hour.

3. Definitions

1. Method Detection Limit (MDL): Defined as the minimum concentration of an analyte that can be detected as being significantly greater than zero for a given instrument configuration. Defined in ARI SOP 1018S as synonymous with the Detection Limit (DL).

2. Analytical Batch: An analytical batch will consist of no more than 20 samples including one distillation blank, one Laboratory Control Standard, one Method Reporting Limit standard and matrix spikes and duplicates.
3. Method Blank (MB): The Method Blank is treated exactly the same as the samples during preparation. DI water is used for preparation of the method blank, all standards and for sample dilutions.
4. Method Reporting Limit standard (MRL): The MRL is a standard prepared at a concentration equal to the low point of the curve and treated exactly the same as the samples during preparation.
5. Laboratory Control Standard (LCS): The LCS is a standard prepared at a concentration mid-range of the curve from a secondary source and treated exactly the same as the samples during preparation.
6. Calibration Verification Standard (CVS): It is a standard prepared at a concentration mid-range of the standard curve and derived from a source other than that used for calibration. The CVS is used to verify the performance and stability of the standard curve throughout the batch run. Control limits are ±10% of the known concentration.
7. Matrix Spike (MS): A sample prepared by adding a known amount of ammonia to a specified amount of sample matrix. Matrix spikes are used to determine the effect of the sample matrix on a method's recovery efficiency.
8. Matrix Spike Duplicate (MSD): When requested will be analyzed following the MS. An MSD is required for work conducted under the Department of Defense (DoD) Quality Systems Manual. Such projects will be clearly identified by the Project Manager.
9. Matrix Duplicate: A second replicate matrix sample prepared in the laboratory and analyzed to obtain a measure of the precision of the determination with respect to the matrix.
10. Laboratory Information Management System (LIMS): Software program called Element used to track laboratory samples and produce data reports.

4. Interferences

1. Under basic conditions, NH3 is subject to loss by volatilization hence samples are preserved by acidification which also retards microbial activity.
2. Ammonia will react with residual chlorine to form chloramines (monochloramine, dichloramine and nitrogen trichloride) hence any residual chlorine should be removed immediately upon collection.

5. Safety

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.

2. Use extreme caution when handling phenol. This chemical causes severe burns and is rapidly absorbed into the body through the skin.
3. Consult the SDS for each chemical used in this procedure should questions arise. SDS are available as a hardcopy in the central office area, or online as linked on the ARI intranet.
4. Always wear appropriate PPE (personal protective equipment) when working in the Laboratory. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, etc. are provided for your protection
5. Environmental Samples may contain hazardous waste; treat them as potential health hazards.
6. Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan.
7. All acid and sample waste must be disposed following the ARI Waste Management Plan.
8. Dispose of all unwanted, broken glassware into a broken glassware container. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

6. Equipment and Supplies

1. Lachat Quikchem® 8000 series FIA
2. XYZ Autosampler
3. Reagent Pump and associated tubing
4. Omnion Software on equipped computer and printer.
5. Volumetric Flasks
6. Pipettes
7. Analytical Balance
8. Disposable Glass Tubes, Fisherbrand Cat. No. 14-961-29

7. Reagents and Standards

1. Reagents: Use fresh deionized water (DI) when making reagents and standards. Avoid using any DI which has been stored for appreciable period of time due to the potential for ammonia absorption from the atmosphere. All reagents including DI must be degassed (unless specifically noted) with Helium at 140 kPa (20 psi) with the use of a degassing tube or a fritted glass tube. Record preparation of reagents in Element and affix labels to containers.

   7.1.1. Sodium Phenolate: CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin. In a 1L volumetric flask, dissolve 83g crystalline phenol (C6H5OH), or 88mL of 88% liquefied phenol, in approximately 600mL DI water. While stirring, slowly add 32 g sodium hydroxide (NaOH). Cool, dilute to the mark, and invert to mix.

Do not degas this reagent. Prepare fresh every 3 to 5 days. Discard when reagent turns brown.

7.1.2. Sodium Hypochlorite: In a 500 mL volumetric flask, dilute 250 mL 5.25% sodium hypochlorite (NaOCl) to the mark with DI water. Invert to mix. Prepare fresh daily.

7.1.3. Sodium Nitroprusside: In a 1L volumetric flask dissolve 3.5g sodium nitroprusside (sodium nitroferricyanide [Na2Fe(CN)5NO.2H2O]). Dilute to the mark with DI water and invert to mix. Prepare fresh every 1 to 2 weeks.

7.1.4. 1M Sodium Hydroxide Solution: In a 1L volumetric flask dissolve 40.0 g sodium hydroxide (NaOH) in approximately 900mL DI water. Dilute to the mark and mix with a magnetic stirrer until dissolved.

7.1.5. Buffer: In a 1L volumetric flask, dissolve 50.0 g disodium ethylenediamine tetraacetic acid (Na2EDTA) and 225 mL 1 M sodium hydroxide in approximately 700 mL DI water. Dilute to the mark and mix with a magnetic stirrer until dissolved. Prepare fresh monthly.

7.1.6. 2N KCl: Partially fill a 1L volumetric flask with deionized water and dissolve 149.12g KCl. Let the reagent warm up to room temperature, then dilute to volumetric mark. Prepare fresh monthly.

2. Ammonia Standards. Ammonia standards are prepared from either ammonium chloride salt or from commercially prepared and certified reference standards. In general, the in-house prepared ammonium chloride standards will be used for preparation of standard curves and for matrix spiking. The commercially prepared standard will be used as the independent source for calibration verification. Preparation of any stock standard solution must be documented by entry of preparation data into the LIMS. You must verify that data entry is correct and that ammonia is expressed as elemental nitrogen (i.e. NH3-N). All standards must be made volumetrically using clean volumetric glassware and pipettes.

7.2.1. Ammonium chloride Stock standard (1,000 mg NH3-N/L). In a 1 liter volumetric flask dissolve 3.8189 g anhydrous ammonium chloride (NH4Cl, FW = 53.492, 26.18%N), pre-dried at 100 ºC, into approximately 500 mL fresh DI and dilute to 1000 mL. Enter data (exact weight and volume) into LIMS and print a label for the prepared bottle to show the name of the standard, the standard ID Number, the date of preparation and your initials. Use this standard for the preparation of the Intermediate ammonia standard and prepare fresh annually or as needed.

7.2.2. Intermediate NH3-N Standard (Concentration = 20 mg/L). Dilute 2 mL of the NH3-N Stock standard to 100 mL with DI. Use this solution for the preparation of the Standard Curve. Prepare this Intermediate Standard weekly.

3. Calibration Standards. Dilute the above Intermediate Standard to 100 mL as indicated in the table below: These standards must be made fresh weekly and should be labeled with the date of preparation and your initials.

Standard #	Final volume (mL)	Volume of Intermediate Std (20 ppm) (mL)	Concentration (mg/L NH_3-N)
S0	100	0.0	0.0
S1	100	0.20	0.04
S2	100	0.50	0.10
S3	100	1.00	0.20
S4	100	2.50	0.50
S5	100	4.00	0.80
S6	100	5.00	1.00

4. Method Blank. The Method Blank for preserved samples is prepared by adding 2 mL 9N H2SO4 to a 500 mL sample bottle containing DI. The method blank is used to prepare the MRL and LCS. For unpreserved samples the method blank is a DI filter blank. Prepare fresh with each batch.
5. Method Reporting Limit standard (MRL). The MRL is prepared at the low point of the curve by diluting 0.1 mL 20 ppm intermediate to 50 mL with the method blank. Prepare fresh with each batch.
6. Laboratory Control Standard (LCS). The LCS is prepared from a 1000 mg/L NIST traceable independent source stock solution. Dilute 0.05 mL of the 1000 mg/L stock to 100 mL using the method blank for a concentration of 0.50 mg/L. Prepare fresh with each batch.
7. Calibration Verification Standard (CVS). Calibration verification standard is prepared from a 1000 mg/L NIST traceable independent source stock solution. To prepare the working standard add 0.05 ml of the 1000 mg/L stock to a 100 mL volumetric flask containing about 50 mL of DI. Mix well and bring to a 100mL final volume, the concentration is 0.50 mg/L. This standard should be prepared weekly.

8. Sample Collection, Preservation, Shipment and Storage

1. Aqueous samples are collected in 500 ml HDPE containers, preserved with 9N H2SO4 to pH <2 and kept cool between 0 – 6 degrees C. Preserved samples can be held up to 28 days, but unpreserved samples must be analyzed within 48 hours from collection.
2. Solid samples are collected in 4 oz wide mouth glass jars and kept cool between 0 – 6 degrees C. The holding time for solid samples is 7 days.

9. Quality Control

1. Demonstration of Capability. Each analyst using this procedure must run an initial “Demonstration of Capability” by preparing and analyzing 4 replicates of the QC Check Solution. The recovery (Accuracy) must be within the range of ±10 % (90 to 110 %) with a relative standard deviation (Precision) less than 10 %. An on-going DOC will be provided by the analysis and recording of the QC Check Solution for each batch of ammonia analyses conducted.
2. Detection and quantitation limits are retained in LIMS. See SOP 1018S for additional information on how detection and quantitation limits are calculated.
3. Control charts for trend analysis. Control charts for the Ammonia Low Level Check Standard will be constructed and updated on a periodic basis. Results will be evaluated relative to Warning and Control limits set at 2 and 3 standard deviations of the mean, respectively.
4. The regression coefficient, r should be greater than 0.995.
5. Initial Calibration Verification (ICV) and Calibration Blank (ICB) must be run at the beginning of each batch. Continuing Calibration Verification standards and blanks (CCV, CCB) must be run after every ten samples in the batch and at the end of each run. The calibration verification standards must agree within ±10% of the "true" value and the concentration of the blanks should be less than the absolute value of the reporting limit.
6. Matrix spike and duplicate analyses are run with each batch or as requested by the client.
   9.6.1. Duplicate analysis. If both the original and duplicate sample concentrations are greater than 5X the detection limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the detection limit, then the absolute difference between the two should be less than or equal to the detection limit. If these criteria are not satisfied, corrective actions must be taken.
   9.6.2. Matrix Spikes. The acceptance limits for matrix spike recoveries are ±25% if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.
7. MRL Check Standard: A standard prepared at the low point of the curve and prepared exactly the same as the samples on the batch. Run immediately following the ICV/ICB.
8. Method Blank: A method blank should be analyzed with each batch after the MRL Standard. This blank should have a value less than the absolute value of the reporting limit.
9. Laboratory Control Standard: A positive control standard prepared with each batch. The LCS must agree within ±10% of the "true" value.

10. Calibration and Standardization

1. A six point calibration curve is prepared weekly, ranging from 0.04 to 1.0 mg/L NH_3-N, and analyzed with each sequence.

2. Initial Calibration Verification (ICV) and Calibration Blank (ICB) are run at the beginning of each sequence. Continuing Calibration Verification standards and blanks (CCV, CCB) are run after every ten samples in the sequence and at the end of each run.

11. Procedure

1. Preparations

11.1.1. If residual chlorine is suspected use Starch-Potassium Iodide paper to test the sample. If detected it can be removed by adding 1 mL of sodium thiosulfate solution (0.35 grams sodium thiosulfate dissolved in 100 mL DI) to 500 mL of sample. Retest for residual chlorine and add additional reagent as necessary. If present and sample treatment was required, document on the Analyst Notes “Green Sheet”.

11.1.2. Preserved samples should be neutralized before analysis. Adjust samples and batch standards to pH 5-9 with either 6.0 M NaOH or 1+1 H2SO4.

2. Operating Procedure (Lachat):

11.2.1. Basic Operation and Maintenance of the Lachat is more detailed in SOP 659S, Lachat Instrument Basic Operation and Data Management. Analysts should also consult the Lachat instrument user guides.

11.2.2. Note: NH3 is a heated chemistry. The manifold tubing is attached to the heater after the last ‘T’ and just prior to the flow cell/detector. To eliminate the possibility of reagents sitting in the tubing, while the heater in on in stand by mode, switch the pump to “MANUAL”.

11.2.3. Turn on the power to the autosampler, pump and system unit along with the associated computer and printer. Switch the pump to “MANUAL”. Note: Prior to running, perform any required maintenance as outlined in the instrument maintenance log. Document the maintenance performed.

11.2.4. Open OMNION 3.0 software displayed as an icon on the system computer desktop.

11.2.5. Method parameters and conditions including timing, designated pump tubing, sample loop size etc. are already defined within the system and should not be modified without consultation with Conventionals lab supervisor and adequate documentation. Refer to the appendices for the manifold diagram and system parameters.

11.2.6. Select ‘Run’, ‘Open’ in the toolbar.

11.2.7. Choose appropriate ammonia template from the available files (e.g. NH3.omn) Note: Ensure that proper calibration standard values appear for each corresponding standard ID. Verify ICV/CCV (Sample type = ‘Check Standard’) concentration is correct.

11.2.8. Enter batch QC and sample ID’s starting in the cell following the ICB. Sample Type = “Unknown”.

11.2.9. Enter CCV (Sample Type = "Check Standard")/CCB after every 10 injections including rinse blanks. Enter 0.5 ppm known concentration and ±10% acceptance criteria for the CCV and 0ppm known concentration and ±MRL acceptance criteria for the CCB. Schedule these as a Data Quality Management (DQM) set to be run after every 10 injections and at the close of the run.

11.2.10. Add lines in the sample tray template as needed for samples and QC. Note: CCV's and CCB's will be automatically entered into the tray at the required interval when defined as a DQM set. Adjust the cup numbers to correspond with sample tube placement in the autosampler rack.

11.2.11. Record the entries of the sample tray in the Lachat Run Log.

11.2.12. Filter all samples including the batch QC standards using a 20mL disposable syringe and 0.45µm syringe filters. One filter per sample and rinsing the syringe three times with DI water between samples.

11.2.13. Sample duplicates need to be analyzed for each batch of samples.

11.2.14. Matrix spikes are prepared at a 0.5 ppm concentration if QC limits stated in Section 9.6.2 are met. For samples requiring dilution the sample is first spiked with standard and then the dilution performed on the 10 mL final volume of spiked sample. "Spike first, then dilute". Add the appropriate spike as stated in the table below and take to a 10 mL final volume with filtered sample, then dilute. Spiking guidelines are as follows:

Required sample dilution	mL Intermediate Standard (20ppm)	mL of Stock Standard (1000ppm)	Final volume of spiked sample
Undiluted	0.250		10mL
1:5		0.025	10mL
1:10		0.05	10mL
1:20		0.10	10mL
1:50		0.25	10mL
1:100		0.50	10mL

11.2.15. Load the sample tubes in the exact sequence as indicated in the sample table. **Note**: Samples are loaded and run starting in the lower left-hand corner of the rack and continuing up then starting again at the bottom of the next column. Calibration standards are loaded highest to lowest concentration ending with the blank.

11.2.16. Observe pump tubing and manifold lines for jerky motion that indicates a flow problem and/or backpressure. Also check for any leaks at all tees and junctions. Refer to the troubleshooting section of the User's manual if problems are noted.

11.2.17. If no flow problems are apparent transfer reagent pump tubing from the DI water to the appropriate reagent containers. Continue pumping (pump speed at 35) until air bubbles are removed and baseline is void of air spikes and appears steady with no drift upward or downward. (Press 'Preview' on the toolbar to monitor current baseline.)

11.2.18. Press 'Start' on the toolbar to begin the run. Note: Calibration is run first and upon passing the samples will be analyzed. The methods have been set to halt the tray if the r<0.995.

11.2.19. Review the calibration while samples are running and note the peak area of the 1.0 ppm standard. Peak area should be approximately 35-40 V-s (volt-seconds). If this value falls outside this range, the run should be stopped and the cause of the peak area change should be determined. Refer to the User's manual for troubleshooting guidelines.

11.2.20. Save the run as MMDDYYXXXS.omn where M is a 2 digit code for the month, D is the 2 digits for the day, YY is the 2 digits for the year, X is the 3 letter code for the parameter, S is the sequence letter for the day's runs and 'omn' is the required filename extension needed for the Omnion software to recognize the file. Press 'Enter'. For example, if this is the second Lachat run conducted on February 5, 2004 the file name would be: 020504NH3B.omn.

11.2.21. To generate the final report for the run go to 'Tools' in the toolbar, 'Custom Report'. Click the Format icon.

11.2.21.1. Under the Table tab de-select 'Rep #', select 'Detection Time', 'Cup #', 'Peak Area' and 'Manual Dilution Factor' if the manual dilution factor was entered in the sample table prior to the sample running.

11.2.21.2. Under the Layout tab enter your initials in the 'Author' portion of the Header box and the filename and instrument name in the Right portion of the Footer box.

11.2.21.3. Under the Charts tab in the Options section select 'Calibration' and select Channel Data Display. Then select 'Show 10 Peaks per Chart for All Peaks'.

11.2.22. Click 'Apply' to incorporate all chosen options to the report then 'Close'.

11.2.23. Evaluate all results for the run including: Regression coefficient (r), calibration standard regressed values, initial calibration blank (ICB), initial calibration verification (ICV), batch QC standards, continuing calibration blanks and checks (CCB, CCV), RPD, matrix spike recovery and any off scale samples. If some of these parameters are out of the range, re-run the affected samples. IT IS THE RESPONSIBILITY OF THE ANALYST TO VERIFY ALL DATA.

11.2.24. Print out the final report.

11.2.25. At the end of the day's analysis. Turn off the heating coil. Place the transmission lines in cleaning buffer (65 g NaOH and 6 g tetrasodiumethylenediamine tetraacetic acid (EDTA) dissolved in 1 L DI water) and pump through the manifold for 10 minutes. After 10 minutes

place the transmission lines in DI water and pump water through for 10 minutes. After the water rinse remove the transmission lines from the water and pump the manifold dry.

11.2.26. Stop pump and remove lines from the pump cartridges. Turn off the power to the autosampler, pump, and system. Turn off computer.

11.2.27. Wipe down all instrument surfaces and wash pump cartridges. Record maintenance in the instrument maintenance log.

3. Operation Notes:

11.3.1. Staining of the pump tubing

11.3.1.1. Ensure the mixed stream between the last tee and the heater is between pH 11 and 12. Higher than 12.3 (usually caused by too much NaOH in the buffer) will contribute to staining.

11.3.1.2. Crystalline phenol is preferred over liquid or solid. The reagent needs to be prepared at least every 3-5 days, sooner if the color turns darker than pale orange.

11.3.1.3. Do not allow the pump to go to STANDBY mode.

11.3.2. Negative peaks

11.3.2.1. This can occur if the carrier and sample matrices are different. For best results neutralize the samples to a pH of 6-9 prior to running and use the non-acidified reagents.

11.3.2.2. Ammonia contamination of the carrier can produce negative peaks. Use fresh DI water and keep covered to prevent ambient ammonia contamination.

11.3.2.3. High metals concentrations within samples will precipitate and create negative peaks. Samples with this characteristic should be diluted to reduce the metals effect.

11.3.3. For high concentration samples, samples requiring >100X dilution, ion specific electrode (ISE) is the preferred method. See the NH3-ISE SOP for details.

11.3.4. Use the KCl extraction procedure for the analysis of soil and sediment samples. See the NH3-ISE SOP for details on the procedures for soils extraction.

12. Review

1. Refer to ARI's Laboratory Quality Assurance Plan for data review procedures.
2. Specifically for Ammonia, the analyst should check instrument output for accuracy and examine chromatograms to ensure all reported peaks are correctly integrated. Any anomalies such as abnormal peak shapes should be recorded in the analyst comments.

13. Data Analysis and Calculations

1. Calibration is done by injecting standards. The data system prepares a calibration curve by plotting response versus standard concentrations. Sample concentration is calculated from the regression equation.

2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

14. Method Performance

1. The reporting limit is set to the lowest calibration curve standard at 0.04 mg/ L NH_3-N.

15. Pollution Prevention

1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
2. The quantity of chemicals purchased should be based on expected usage during their shelf life to reduce disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

16. Data Assessment and Acceptance Criteria for QC Measure

1. The regression coefficient, r should be greater than 0.995.
2. The calibration verification standards must agree within ±10% of the "true" value and the concentration of the blanks should be less than the absolute value of the reporting limit.
3. If both the original and duplicate sample concentrations are greater than 5X the reporting limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the reporting limit, then the absolute difference between the two should be less than the reporting limit. If these criteria are not satisfied, corrective actions must be taken.
4. Matrix Spikes. The acceptance limits for matrix spike recoveries are ±25% if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.
5. The LCS must agree within ±10% of the "true" value.
6. The method blank should have a value less than the absolute value of the reporting limit.

17. Corrective Actions for Out of Control Events

1. If r is less than 0.995, new calibration standards must be prepared and the calibration repeated. All samples associated with the out of control standard curve must be re-run.
2. If Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB) are out of QC limits, new calibration standards or new ICV solution should be made. All samples associated with the out of control condition must be re-run. If the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are out of QC limits, they should be reread to verify. All samples between the last in control condition and the out of control condition must be re-run. All samples in any run must be bracketed by in control verification standards.

3. After the above two corrective actions, if the results are still outside the limits, the supervisor will review the entire procedure with the analyst to verify that correct procedures are being followed or check the instrument to make sure it is working properly.
4. If the method blank or LCS is out of control, it should be reread to verify. If the results are still out of control, stop the run and evaluate the filters and procedure. All samples on the batch will need to be re-filtered and reanalyzed. If results are persistent it may be required that each filter first be rinsed with DI water then with sample before filtering the portion used for analysis.
5. If RPD or matrix spike recoveries are outside the prescribed limits, the analysis will be repeated to confirm the outlying condition.
6. If any of the following situations arises, the supervisor will be immediately notified and the project manager will be informed for resolution with the client:
   17.6.1. Samples have exceeded holding times.
   17.6.2. Samples have been improperly preserved.
   17.6.3. There is insufficient sample to run the analysis.
7. Analyst's notes are recorded on the Analyst's Notes ("green sheet") in the job folder. Sample anomalies such as unusual sample characteristics or sample problems that were not covered on a Corrective Action form are recorded here.
8. As a general rule, all corrective actions taken during the course of an analysis must be described on the analysts comment sheet (i.e. the green sheet) and a Corrective Action Sheet must be submitted to the PM. It must be clearly evident to the data reviewer and PM exactly how a sample was handled during analysis.

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

1. Any out-of-control events (i.e. failed spike, high RPD, failed CCV) will be noted on a Corrective Action form including the recommended corrective action and corrective action taken. The form is generated and completed by the analyst. It is turned in for review with the affected data and signed by the supervisor.
2. Analyst's notes are recorded on the Analyst's Notes ("green sheet") in the job folder. Sample anomalies such as unusual sample characteristics or sample problems that were not covered on a Corrective Action form are recorded here.

19. Waste Management

1. The phenol hypochlorite waste generated as a result of this analysis is considered a hazardous waste mixture for the characteristic of toxicity (phenol in excess of 1%). These wastes must be collected during the run and transferred to the phenol/ammonia waste accumulation container located in the laboratory.

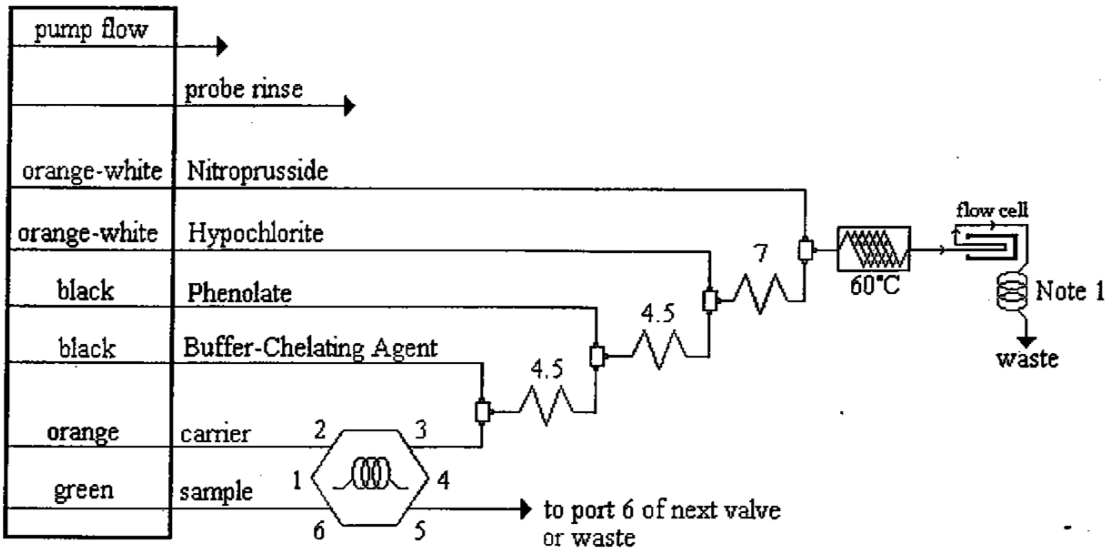
2. Analysis waste is collected under the rules of Satellite Accumulation at the site of generation and under the control of the operator of the process generating the waste. When the waste container is full it is transferred to the Central Accumulation Area.

20. Method References

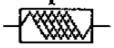
1. Standard Method for the Examination of Water and Wastewater. 1997. 20th ED. Method 4500–NH3 H.
2. Methods for Chemical Analysis of water and wastes. EPA-60014-79-020 (Rev 2, August 1993). Method 350.1.
3. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Table II, Required Containers, Preservation Techniques, and Holding Times.
4. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix B. Definition and Procedures for Determining the Method Detection Limit
5. Keeney and Nelson. 1987. Nitrogen, Inorganic Forms. 33-3. Extraction of Exchangeable Ammonium, Nitrate, and Nitrite. Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties - Agronomy Monograph no. 9 (2nd edition)

21. Appendices

1. Ammonia Manifold Diagram



Carrier: **DI water**
Manifold Tubing: **0.5 mm (0.022 in) i.d.** This is **2.5 µL/cm**.
AE Sample Loop: 125 cm x 0.022 in. i.d.
QC8000 Sample Loop: 125 cm x 0.022 in. i.d.
Interference Filter: 630 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows 650 cm of tubing wrapped around the heater block at the specified temperature.

4.5: **70** cm of tubing on a 4.5 cm coil support
7: **135** cm of tubing on a 7 cm coil support
8: **168** cm of tubing on a 8 cm coil support
12: **255** cm of tubing on a 12 cm coil support
22: **550** cm of tubing on a 22 cm coil support

Note 1: 200 cm backpressure loop (0.022 in. i.d.)
Note 2: PVC PUMP TUBES MUST BE USED FOR THIS METHOD

2. Data System Parameters

21.2.1. Analyte Data:

21.2.1.1. Pump Speed:	35
21.2.1.2. Cycle Period:	65
21.2.1.3. Concentration units:	mg NH3-N/L
21.2.1.4. Sample Period:	30 s
21.2.1.5. Inject to Peak Start:	80 s
21.2.1.6. Chemistry:	Direct

21.2.2. Calibration Data:

21.2.2.1. Calibration Rep Handling:	N/A
21.2.2.2. Calibration Fit Type:	1st Order Polynomial
21.2.2.3. Weighting Method:	None
21.2.2.4. Force through zero:	No

21.2.3. Sampler Timing:

21.2.3.1. Min. Probe in Wash Period:	12 s
21.2.3.2. Probe in Sample Period:	32 s

21.2.4. Valve Timing:

21.2.4.1. Time to Valve:	24 s
21.2.4.2. Load Period:	28 s
21.2.4.3. Inject Period:	37 s

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Dioxin/Furan Organic Analysis
H.R. Gas Chromatography/H.R. Mass Spectrometry
EPA Method 1613B
EPA Method 8290
HRSM01.2

SOP 806S
Version 008

Revision Date: 10/22/18
Effective Date: 10/22/18

Prepared by:

Peter Kepler

Approvals:

Brian N. Bebee, Laboratory Section Manager

Bob Congleton, Quality Assurance, Manager

Annual Review

SOP Number: 806S

Title: Dioxin/Furan Organic Analysis –HR Gas Chromatography/HR Mass Spectrometry – EPA Method 1613B

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. Method 1613B describes the detection and quantitation of tetra through octa Chlorinated Dibenzo-p-Dioxins (PCDDs) and Dibenzofurans (PCDFs) from various environmental sample matrices including sediments, soils, solid waste, ash, tissues, and waters.

1.2. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including EPA SW-846 Method 1613B, EPA CLP, NELAP and the Department of Defense Quality Systems Manual 5.0 (DoD-QSM). Appendix 20.1 outlines ARI's routine analytical procedure and additional requirements of in 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.**

1.3. Specific quality control requirements shown use the control limits listed in Method 1613B since that has been the analysis of choice (instead of 8290A) for our clients. State of California work will be reported with Method 8290.

1.4. Some text has been taken directly from the four methods referenced in Section 19.

1.5. The analytes and routine reporting limits for this procedure are listed below:

ANALYTE	CAS NUMBER	WATER RL	SOIL RL.
2,3,7,8-TCDD	1746-01-6	10 pg/L	1 pg/g
2,3,7,8-TCDF	51207-31-9	10	1
1,2,3,7,8-PeCDD	40321-76-4	10	1
1,2,3,7,8-PeCDF	57117-41-6	10	1
2,3,4,7,8-PeCDF	57117-31-4	10	1
1,2,3,4,7,8-HxCDD	39227-28-6	10	1
1,2,3,6,7,8-HxCDD	57653-85-7	10	1
1,2,3,7,8,9-HxCDD	19408-74-3	10	1
1,2,3,4,7,8-HxCDF	70648-26-9	10	1
1,2,3,6,7,8-HxCDF	57117-44-9	10	1
1,2,3,7,8,9-HxCDF	72918-21-9	10	1
2,3,4,6,7,8-HxCDF	60851-34-5	10	1
1,2,3,4,6,7,8-HpCDD	35822-46-9	10	1
1,2,3,4,6,7,8-HpCDF	67562-39-4	10	1
1,2,3,4,7,8,9-HpCDF	55673-89-7	10	1
OCDD	3268-87-9	20	2
OCDF	39001-02-2	20	2
Total TCDD	41903-57-5	NA	NA
Total TCDF	55722-27-5	NA	NA
Total PeCDD	36088-22-9	NA	NA
Total PeCDF	30402-15-4	NA	NA
Total HxCDD	34465-46-8	NA	NA
Total HxCDF	55684-94-1	NA	NA
Total HpCDD	37871-00-4	NA	NA

Total HpCDF	38998-75-3	NA	NA

1.6. Identification and quantitation of the non 2378-substituted (unnamed) PCDDs and PCDFs as totals are also described in this procedure to provide for total isomer quantitations.

1.7. This method is restricted to use by or under the supervision of analysts experienced in the use of high resolution gas chromatograph/high resolution mass spectrometry and skilled in the interpretation of high resolution spectrometry. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.8. ARI routinely performs quantitation limit studies (QLS) for each extraction and analytical method performed using this SOP. The results of these studies are used to generate LOD and LOQ values to verify that the reporting limits are being met. The results are kept by the QA department, and are distributed to the bench chemists and the LIMS administrator. For current LOD and LOQ limits refer to Element LIMS.

2. Summary of Procedure

2.1. An aliquot of sample is extracted by a matrix appropriate technique. Typically, this will be a separatory funnel extraction for aqueous samples and a Soxhlet extraction for solid samples. Soxhlet extraction is used for tissue samples. Extraction standards are added at the time of initial extraction providing for isotope dilution quantification.

2.2. After extraction and prior to extract cleanup with multi-bed silica gel a cleanup standard (^{37}CL-2378-TCDD) is added to every extract to measure the efficiency of the cleanup process.

2.3. Next the extracts are subjected to the appropriate cleanups and concentrated to 10µL. The extract is now delivered to the instrument lab for analysis. 10µL of Injection standard is added just prior to the analysis of the sample extract achieving a final effective volume of 20µL.

2.4. Next, 1µL of the 20µL sample extract is injected into the column of a properly calibrated HRGC/HRMS system for chromatographic determination. Analyte identification of 2378-substituted (named) Dioxins and Furans is performed using the relative time of elution (RRT, relative to the appropriate internal standard) and comparison of mass spectra ion ratios. Quantitation is performed by comparing the detector responses of each analytes' two characteristic mass ions and internal standard two characteristic mass ions to the responses of these ions in a calibration curve containing those analytes at known concentrations.

2.5. Identification and quantitation of the non 2378-substituted (unnamed) isomers is also performed by comparing the relative retention times and ion ratios against predefined acceptance limits discussed in section 10.

3. Definitions

3.1. PCDDs-Polychlorinated tetra through octa dibenzo-p-dioxin homologues

3.2. PCDFs-Polychlorinated tetra through octa dibenzofuran homologues

3.3. Named-Named Furan and Dioxins are native 2378-substituted isomers

3.4. Unnamed-Unnamed Furan and Dioxins are native non 2378-substituted isomers.

3.5. HRMS-A High resolution mass spectrometer capable of performing selected ion monitoring at resolving power of at least 10,000 (at 10 percent valley definition).

3.6. HRGC-A high resolution gas chromatography system

3.7. Continuing Calibration Verification (CCV): A process used to verify that the current instrument calibration is acceptable every 12 hours and at the end of each analytical sequence.

3.8. Continuing Calibration Verification and Window defining Standard (CCVS): a standard prepared near the mid-point concentration of the initial calibration, and prepared from the same source as the initial calibration. This standard also contains the WDM isomers used to define the homologue windows and additional TCDDs to verify the 2378-TCDD peak resolution.

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

3.10. Initial Calibration- A process used to generate a correlation between analyte response and analyte concentration by analyzing standards containing the analytes at known concentrations.

3.11. Initial Calibration Verification (ICV): A process used to verify that the current instrument calibration is accurate at the beginning of an analytical sequence.

3.12. 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 accuracy of the initial calibration. The second source standard must be purchased from a different manufacturer than the calibration standard whenever possible.

3.13. Window defining mixture (WDM) Additional furans are used as retention time markers to define the beginning retention times for the dioxin and furan isomers and evaluate descriptor switching times.

3.14. Isomer specificity check standard (ICS): A check standard containing 2378 TCDF peak resolution testing isomers and 2378-TCDD peak resolution testing isomers.

3.15. Extraction standards (ES): Extraction standards are added to every sample and its associated qc at the time of initial extraction.

3.16. Cleanup standard (CS): The cleanup standard is added to every sample and its associated QC samples just prior to silica gel cleaning

3.17. Injection Standard (IS): Injection standards are added to every sample and its associated QC samples 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 which are all at the same concentration in all the calibration standards.

3.18. Laboratory Control Sample (LCS) – A sample matrix, free from the analytes of interest, is 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. Same as Blank Spike (BS) as used in Element

3.19. Laboratory Control Sample Duplicate (LCSD) – A sample matrix, free from the analytes of interest, is 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. Same as Blank Spike Duplicate (BSD) as used in Element

3.20. 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. (DOD only)

3.21. Matrix Spike Duplicate (MSD): 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.

3.22. Initial precision standard (IPR) – Same as the LCS, except used for an initial demonstration of precision and recovery to assess the analytical method. The IPR is to assure that the results produced by the laboratory remain within the method specified limits for precision and recovery.

3.23. Limit of detection (LOD) – An estimate of the minimum amount of a substance that an analytical process can reliable detect.

3.24. Limit of quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target analyte that can be reported with a specified degree of confidence.

3.25. Quantitation limit standard (QLS) – A sample matrix, free from analytes of interest, is spiked at the reporting limit with all the target analytes to generate LOD and LOQ statistics. The QLS spike assures that the reporting limits are being met for each matrix.

3.26. Estimated detection limit (EDL) –The concentration of an analyte required to produce a signal with peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8-substituted isomer for which the response is less than 2.5 times the background level.

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

3.28. 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.

3.29. Static Resolution Checks-Resolution checks to demonstrate the minimum HRMS resolving power of 10,000 at 10% valley for selected PFK peaks.

3.30. RRT-Relative Retention Time- The elution time of an analyte relative to the elution time of its associated extraction or injection standard.

3.31. Instrument Blank – Clean solvent analyzed using the same conditions as a regular sample. An Instrument blank may be used to monitor and/or remove sample carryover from one injection to another.

3.32. Toxicity Factors-Used to determine an overall toxicity of a sample by assigning a toxicity equivalency factor to all the 2378 substituted PCDDs and PCDFs and used to calculate a total toxicity equivalent.

3.33. EMPC-An Estimated maximum possible concentration is calculated for the 2378-substituted isomers that meet retention time and signal/noise criteria, but fail ion ratio limits shown in Appendix 20.4.

3.34. PFK-Perfluorokerosene-Technical mixture used to calibrate the exact m/z scale in the HRMS.

4. Interferences

4.1. Extraction Interferences: Raw HRGC/HRMS data from all instrument blanks, method 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.

4.2. Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, DI water, methanol, or ethanol followed by air drying only.

4.3. High purity reagents must be used to minimize interference problems. The use of nitrile gloves is recommended for all procedures.

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 sample extract injections should be scrutinized for cross contamination.

4.5. Matrix interferants co-extracted with the sample include Polychlorinated Biphenyls, Polychlorinated Diphenyl ethers, Polychlorinated Naphthalenes and Polychlorinated Alkyldibenzofurans. Matrix interferences may be present at concentrations several orders of

magnitude greater than the analytes of interest and special cleanup steps may be necessary to assure the sensitivity and selectivity required by this method.

5. Safety

5.1. This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of safety data sheets (SDSs) should be available to all personnel involved in the chemical analysis of samples suspected to contain PCDDs/PCDFs. Additional information is also available at msdshazcom.com.

5.2. Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed.

5.2.1. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.2.2. Each laboratory must develop a strict safety program for the handling of PCDDs and PCDFs. The laboratory practices listed below are recommended.

5.2.3. Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood, or in a separate containment facility away from the main laboratory.

5.2.4. The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high boiling alcohols. Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength less than 290 nm for several days (use F 40 BL lamps, or equivalent). Using this analytical method, analyze the irradiated liquid wastes and dispose of the solutions when 2378-TCDD and 2378-TCDF congeners can no longer be detected.

5.2.5. The following precautions for safe handling of 2378-TCDD in the laboratory were issued by Dow Chemical U.S.A. (revised 11/78) and were amended for use in conjunction with this method. The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting

laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2378-TCDD isomer is extremely toxic to certain kinds of laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Many techniques used in handling radioactive and infectious materials are applicable to 2378-TCDD.

5.2.6. Protective equipment – Analysts must use disposable nitrile gloves, apron or lab coat, safety glasses and laboratory hood adequate for radioactive work.

5.2.7. Training -- Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.2.8. Personal hygiene -- Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

5.2.9. Confinement -- Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on bench tops.

5.2.10. Waste -- Good technique includes minimizing contaminated waste. Plastic bag liners will be used in waste cans.

5.2.11. Disposal of hazardous wastes -- Refer to the November 7, 1986 issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin containing materials.

5.2.12. Storage – All sample extracts and calibration standards will remain separate from the rest of the GC laboratory and be only stored in freezer# 6

6. Equipment 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 splitless injection and all required accessories, including syringes, analytical columns, autosampler, and gases. The capillary column is directly coupled to the source of the mass spectrometer.

6.1.2. Fused-silica capillary column – Restek RTX-Dioxin2 -60 m x 0.25 mm ID 0.25 µm film thickness treated with a Restek proprietary cross-bonded phase.

6.1.3. High Resolution Mass spectrometer –An instrument capable of achieving a static resolving power of 10,000 (10 percent valley).

6.1.4. GC/MS interface – The GC interface must be able to withstand 350 degrees. The GC column is directly fitted into the ion source without being exposed to the ionizing electron beam.

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 data system must be capable of acquiring data at a minimum of 10 ions in a single scan.

6.2.2. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic intervals. It should also be able to provide hard copies of peak profiles to demonstrate the required resolving power.

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

6.3. Ancillary supplies specific to the analytical laboratory.

6.3.1. Syringes 10, 25, and 100 µl

6.3.2. Fume hood with work bench

6.3.3. 2 ml amber solution vials with Teflon faced screw cap

6.3.4. Threaded Teflon faced screw caps and amber .3 ml autosampler vials

6.3.5. Nonane in Teflon squirt bottle

7. Reagents and Standards

7.1. Stock solutions- Stock solution standards are used to prepare working solutions. Neats are not used for any standard preparations.

7.1.1. Stock solutions expire either on the manufacturer's certified expiration date, or one year after they have been opened whichever occurs sooner. They must be replaced at this time.

7.1.2. Ampulized Stock solutions must be stored at ambient temperature and protected from light.

7.1.3. De-ampulized Stock solutions must be stored at <0-6 °C and protected from light.

7.1.4. Stock solutions should be checked frequently for signs of concentration or degradation.

7.2. LCS stock solution-A solution containing all the native PCDDs and PCDFs diluted into the working LCS solution used to prepare IPR, LCS and QLS extracts. This solution is purchased in Nonane with concentrations ranging from 400-4000 ng/ml.

7.3. Extraction standard stock solution-This solution is diluted 50x to produce the working extraction standard solution. This solution contains the carbon ^{13}C-2378-substituted PCDDs and PCDFs used for isotope dilution quantitation and to measure extraction efficiency. This solution is purchased in Nonane with concentrations ranging from 100-200ng/ml.

7.4. Cleanup standard stock solution-This stock solution is diluted 50x to produce the cleanup standard working solution added prior to extract cleanup. This solution contains ^{37}CL-2378-TCDD used to monitor the cleanup process. This solution is purchased in Nonane at 40ng/ml

7.5. Working solutions- working solutions are prepared from stock solutions or purchased as commercially certified working solutions.

7.5.1. Working standards expire either on the date of expiration of the stock solutions they are made from, or on the manufacturer's certified expiration date, or one year after opening whichever occurs first. They must be replaced at this time.

7.5.2. Working standards in un-opened ampoules should be stored at ambient temperature

7.5.3. When working standard ampoules are opened, the standard must be transferred to a screw-top vial and stored at <0-6 °C and protected from light. The volume level of the standard should be marked on the vial.

7.5.4. Working standards should be checked frequently for signs of concentration or degradation.

7.5.5. Working solutions are made in Ethanol, Acetone or Nonane.

7.6. Injection standard working solution- A solution purchased at working solution level and added to the final extract prior to analysis. The IS contains ^{13}C-1234-TCDD and ^{13}C-123789-HCDD at 200ng/ml in Nonane. It is purchased as a certified solution. 10ul is added to the 10ul extract, resulting in a final volume of 20 ul.

7.7. Calibration working solutions- All calibration standards used to generate initial and continuing calibrations are purchased as certified solutions. None are diluted from a stock standard. Calibration working solutions are purchased in Nonane and range in concentration from 0.1ng/ml to 2000ng/ml. These mixes are commonly referred to as CSL, CS1, CS2, CS3, CS4, and CS5. All certified solutions should have an associated Certificate of Analysis and have a chemical purity > 98%.

7.7.1. Window Defining Working Solution- The CS3 verification mix also includes the window defining compounds for determining homologue RT ranges. It is called the CS3WT, and is also purchased as a certified solution.

7.7.2. Isomer Specificity Working solution- The ISC contains 2378-TCDD, 2378-TCDF, and the closest eluting isomers on the RTX-Dioxin2 column. The isomers are 1278-TCDD, 2348-TCDF, and 3467-TCDF. The ISC is prepared in Nonane at 10 ng/mL from individual isomer solutions.

7.7.3. LCS/IPR working solution-A solution containing all the native PCDDs and PCDFs diluted from the LCS/IPR stock solution used to prepare IPR and LCS extracts. This solution is made in Acetone.

7.8. QLS working solution-A solution containing all the native PCDDs and PCDFs diluted from the LCS stock solution used to prepare QLS extracts. This solution is made in Acetone.

7.9. Extraction standard working solution-This solution is diluted from the extraction standard stock solution. The solution contains the ^{13}C-2378-substituted PCDDs and PCDFs used for isotope dilution

quantitation and to measure extraction efficiency. This solution is made in Ethanol for extraction purposes.

7.10. Cleanup Standard Working Solution-This working solution is diluted from the cleanup standard stock solution and added prior to extract cleanup. This solution contains ^{37}CL-2378-TCDD used to measure cleanup efficiency. This solution is made in Hexane at .8ng/ml.

7.11. ICVS solution-A Calibration solution at or near the curve mid-point used to verify the calibration curve. It should be purchased from a different supplier than the curve mixes, or from the same supplier with a different lot number.

7.12. Isomer Specificity Check Standard-Contains 2378-TCDD, 1278-TCDD, 2348-TCDF, 2378-TCDF, and 3467-TCDF. This solution is used to monitor the 2378-TCDD and 2378-TCDF peak resolution.

8. Sample and Extract Storage

8.1. Aqueous samples are to be maintained at 0-6 º C in the dark from time of collection to receipt at the laboratory. Aqueous samples are stored at the same conditions in the lab.

8.2. Solid, mixed phase, and tissue samples are to be maintained at < 4 ºC from time of collection to receipt at the laboratory. Store these matrices in the dark at < -10 ºC at the lab.

8.3. There are no maximum holding times for CDDs/CDFs in any matrices if stored as above. Samples may be stored up to one year prior to extraction. Following extraction, extracts may be stored as above up to one year prior to analysis.

8.4. Extracts are delivered to freezer #6 in the instrument laboratory and recorded into the Dioxin extract freezer Log (7005f).

8.5. Analysts in the instrument lab assume custody of the sample extracts by signing the freezer log prior to analysis

8.5.1. Extracts analyzed on the same day of completed extraction may be stored at ambient temperature.

8.5.2. Extracts not analyzed on the same day of completed extraction must be stored at -10 to -20 °C in the dark until analysis.

8.6. All Extracts must be analyzed within one year from the initial date of extraction.

9. Quality Control

9.1. Quality control requirements are tabulated in Appendix 20.1.

9.1.1. Acceptance criteria for ARI's routine 1613B analyses are listed in this table in Appendix 20.1.

9.2. Method defined (1613B) default quality control limits for Extraction standards recovery, cleanup standard recovery, LCS and IPR recoveries and relative percent difference for sample duplicates will be used.

9.3. Statistical Control- Internal quality control limits for Extraction standards, cleanup standard, LCS and IPR recoveries and relative percent difference for sample duplicates are not statistically generated at this time.

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 may be found on the ARI website

9.3.3. 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.

9.3.4. Client specific or quality systems specific control limits (DoD-QSM) are used when specified by the client.

10. Calibration and Standardization

10.1.1. Calibration standards – Calibration curves will consist of 6 standards, CSL – CS5. The exception is for the CLP/HRSM01.2 contract, which specifies 5 levels, CS1 – CS5.

10.1.2. One of the calibration standards will be at (or below) 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 HRGC/HRMS system. The lowest (or second lowest) calibration point of each individual target analyte becomes the reporting limit for that analyte. The actual detection limit for target analytes will be determined by the EDL calculation for each undetected target.

10.1.3. All target analytes quantitated below the reporting limit must be qualified with a “J” flag to show the quantitation is below the associated reporting limit. The reporting limit for each project is determined by the specific level requested (i.e. PSDDA, normal water, etc.)

10.1.4. All Calibration standards are purchased as working solutions at concentrations of 0.1-2000ng/ml (CSL-CS5). See Section 7.7. The working solutions contain all standards and target analytes necessary for the calibration.

10.1.5. Each standard must contain all analytes requested for a specific project, and no target analyte may be quantitated without first being calibrated.

10.1.6. All standards should be stored at 0-6 °C after opening and should be discarded after one year, or sooner if check standards indicate a problem. The volume level of the solution should

be marked on the vial after opening. If volume loss becomes evident, or degradation is suspected, the standard should be replaced.

10.1.7. The CSL point is included in the initial calibration in order to meet PSDDA reporting limit requirements, and provide the lowest reporting limits for all projects and clients, except CLP/HRSM. The CSL is 5 times lower than the CS1 mix.

10.1.8. The six calibration standards CSL-CS5 are analyzed and used to calibrate all analytes except TCDD and TCDF. CS1 is the low curve point for these analytes, which meets all requested reporting limits.

Concentrations of calibration points used for initial concentration in ng/ml

Analyte	CSL	CS1	CS2	CS3	CS4	CS5
2378-TCDD	0.1	0.5	2	10	40	200
2378-TCDF	0.1	0.5	2	10	40	200
12378-PeCDD	0.5	2.5	10	50	200	1000
12378-PeCDF	0.5	2.5	10	50	200	1000
23478-PeCDF	0.5	2.5	10	50	200	1000
123478-HxCDD	0.5	2.5	10	50	200	1000
123678-HxCDD	0.5	2.5	10	50	200	1000
123789-HxCDD	0.5	2.5	10	50	200	1000
123478-HxCDF	0.5	2.5	10	50	200	1000
123678-HxCDF	0.5	2.5	10	50	200	1000
123789-HxCDF	0.5	2.5	10	50	200	1000
234678-HxCDF	0.5	2.5	10	50	200	1000
1234678-HpCDD	0.5	2.5	10	50	200	1000
1234678-HpCDF	0.5	2.5	10	50	200	1000
1234789-HpCDF	0.5	2.5	10	50	200	1000
OCDD	1.0	5	20	100	400	2000
OCDF	1.0	5	20	100	400	2000
^{13}C-2378-TCDD (ES)	100	100	100	100	100	100
^{13}C-2378-TCDF (ES)	100	100	100	100	100	100
^{13}C-12378-PeCDD (ES)	100	100	100	100	100	100
^{13}C-12378-PeCDF (ES)	100	100	100	100	100	100
^{13}C-23478-PeCDF (ES)	100	100	100	100	100	100
^{13}C-123478-HxCDD (ES)	100	100	100	100	100	100
^{13}C-123678-HxCDD (ES)	100	100	100	100	100	100
^{13}C-123478-HxCDF (ES)	100	100	100	100	100	100
^{13}C-123678-HxCDF (ES)	100	100	100	100	100	100
^{13}C-123789-HxCDF (ES)	100	100	100	100	100	100
^{13}C-234678-HxCDF (ES)	100	100	100	100	100	100
^{13}C-1234678-HpCDD (ES)	100	100	100	100	100	100
^{13}C-1234678-HpCDF (ES)	100	100	100	100	100	100
^{13}C-1234789-HpCDF (ES)	100	100	100	100	100	100
^{13}C-OCDD (ES)	200	200	200	200	200	200
^{37}CL-2378-TCDD (CS)	0.1	0.5	2	10	40	200
^{13}C-1234-TCDD (IS)	100	100	100	100	100	100
^{13}C-123789-HxCDD (IS)	100	100	100	100	100	100
ES = Extraction Standard, CS = Clean-up Standard, IS = Injection Standard						

10.2. MS tuning- prior to initial calibration, the HRGC/HRMS system must be hardware-tuned to meet the minimum resolving power of 10,000 for a minimum of three PFK masses in each scan function. Tuning is done using the 331 PFK mass or similar, although each function may have its own tune file based on an appropriate PFK mass in that function. Analysis cannot begin until 10,000 resolving power has been demonstrated throughout all functions.

10.2.1. Static resolution must be verified at the beginning and ending of each 12 hour analytical sequence bracket.

10.2.2. The total cycle scan time for each of the individual ion functions must be less than one second.

10.2.3. All analyses performed in the twelve-hour QC period following the static resolution check must use the same instrument parameters (GC program, MS parameters, etc.)

10.2.4. Column Performance must also be verified with the isomer specificity check standard (ISC) containing 2378-TCDF resolution testing isomers and 2378-TCDD resolution testing isomers before proceeding with the calibration.

10.2.5. Separation between 2378-TCDD and 1278-TCDD must show a maximum valley of 25%. Separation between 2378-TCDF, 2348-TCDF, and 3467-TCDF must show a maximum valley of 25% between all peaks. If these criteria are met, all analytes may reported from a single column run.

10.2.6. Verify the identification of all first and last eluters for each PCDF homologue group and assure retention times are greater than 10 seconds between ion function changes and any target analytes.

10.3. Signal to noise ratio-The signal to noise ratio must be verified to be greater than 10 for all calibration points used.

10.4. Ion Abundance ratios-All Analytes in all calibration points should meet the limits shown in table 3 (Appendix 20.3) for their respective ion abundance ratios.

10.5. Calculate Relative Response Factors (RRFs)

10.5.1. Evaluation of the initial calibration begins by calculating relative response factors (RRFs) for each analyte in each calibration standard. Areas from both the primary and secondary quantitation ions are added together to give the total ion area for all standards and targets. The formula for calculating each response factor involves the combined areas of both quantitation ions for 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*Cs)
Where

As = The combined ion area of both ions from the analyte or surrogate
Cis = The concentration of the internal standard in ug/L
Ais = The combined ion area of both ions from the internal standard
Cs = The concentration of the analyte or surrogate in ug/L

10.5.2. The RRF for each analyte should consistent for each of the calibration levels. Special care should be taken to monitoring the RRF in the lowest calibration standard (CSL) to ensure adequate sensitivity at the reporting limit.

10.6. Analyte Linearity

10.6.1. After measuring the relative response factors for each analyte in each of the calibration standards, the linearity of the analyte must be measured.

10.6.2. The average RRF should be calculated for each compound using the formula

$RRFav = \frac{\sum RRFi}{n}$
Where
RRFi = the RRF of the analyte in each calibration level
n = the number of calibration levels (usually six or five)

10.6.3. The percent relative standard deviation (% RSD) should also be calculated for each compound using the formula

$RSD = (100 * SD)/n = 100 * ((\sum(RRFi - RRFav)^{2)}/(n-1))^{1/2}/RRFav$
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)

10.6.4. The % RSD should be less than 20% 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 20% RSD will attempt to utilize an alternative calibration option. **CLP HRSM01.2: Target analytes require 20% RSD. Labels require 35% RSD.**

10.6.4.1. 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. In reality, if the system is operating well, all targets and labels should have % RSDs well within limits. If any compound fails to meet the RSD limits, maintenance is likely required.

10.6.5. Although alternative calibration methods are optional, ARI does not use alternative calibration methods for PCDF analysis. If % RSD values are > 20% for any analytes, corrective action should be taken and the calibration rerun.

Evaluation of retention times - The relative retention time (RRT) of each target analyte in the calibration standard should agree within 0.05 RRT units for each calibration point. 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. All relative retention times should be within the ranges previously established for the RTX-Dioxin2 column used by ARI.

10.6.6. All named isomers with labeled extraction standards must show an absolute retention time -1 to +3 seconds of that for the corresponding labeled standard.

10.7. Initial Calibration verification - Prior to use for sample processing, the acceptability of a calibration curve should be verified through analysis of a second source calibration verification solution (SCV). The SCV ideally should be purchased from a different supplier than the working standards used in the calibration curve. The SCV may be from the same supplier as the calibration standards, but the SCV must be from a different lot number than the calibration solutions. Target analytes should have % D < 20% when compared to the curve, and labels should have % D < 30%. Any targets or labels exceeding these limits should be noted.

10.8. Calibration Acceptance.

10.8.1. An initial calibration for an analyte is deemed valid when it meets all criteria discussed in sections 10.1 through 10.9

Quantitated values for any analyte which fail calibration acceptance criteria must be at a minimum approved by the organics manager, project manager, and client and will be discussed in the case narrative.

10.8.2. Daily GC/MS calibration verification - Performed at the beginning and ending of each 12-hour analytical sequence. NOTE: The ending continuing calibration verification is technically not a 1613B method requirement (as it is for 8290 and CLP), but it will always be analyzed and included in the data package.

10.8.3. MS tuning- prior to calibration verification, each GC/MS system must be hardware-tuned to meet the minimum resolving power of 10,000 for a minimum of three PFK masses in each scan function. Sample analyses may not begin until all these criteria are met. Static resolution must be verified at the beginning and ending of all analytical sequences.

10.8.4. .All analyses performed in the twelve-hour QC period following the static resolution check must use the same instrument parameters (GC program, MS parameters, etc.)

10.8.5. Column Performance (ISC check) must also be verified before proceeding with sample analysis. CLP HRSM01.2 requires a passing ISC check at the end of each 12-hour sequence as well. Resolution measurement on the RTX-Dioxin2 column includes the following isomers in the ISC Mix: Separation between 2378-TCDF, 2348-TCDF, and 3467-TCDF must show a maximum valley of 25% between all peaks. Separation between the 2378-TCDD and the 1278-TCDD isomers must show a maximum valley of 25% between peaks.

10.8.6. Ion Abundance ratios-All analytes must meet the limits shown in table 3 (Appendix 20.3) for their respective ion abundance ratios.

10.8.7. The relative response factors calculated in Section **10.6** 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.)

10.8.7.1.1. 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 standard.

10.8.7.1.2. Percent difference for each native analyte must meet the limits shown in Table 20.9. **CLP HRSM01.2 has standardized CCV limits: Target analytes require %D within 25%. Labeled surrogates require %D within 35%. Also, DOD has limits of 20% for targets and 30% for labels.** Problems similar to those listed under the minimum response factors could affect this criterion. See Section 16.3 for procedures for dealing with linearity failure.

10.8.7.1.3. Reporting data for analytes failing any acceptance criteria must be discussed in the analysts notes and be approved by the Organics manager, project manager, client and discussed in the case narrative.

10.8.7.1.4. Evaluation of retention times - The relative retention time (RRT) of each target analyte in the calibration standard should agree within 0.005 RRT units for each calibration point. 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. The relative retention times must meet those limits established by ARI.

10.8.8. All 2378-substituted isomers with labeled extraction standards must show an absolute retention time -1 to +3 seconds (-.02 to +.05 minutes) of that for the corresponding labeled standard

10.8.9. The results from the continuing calibration verification analysis must meet the acceptance criteria detailed above in Sections 10.11 and 10.12.

11. Procedure

11.1. Prior to the determinative analysis, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods.

11.2. Sample Preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	Separatory funnel, SPE
Soil/sediment	Soxhlet, Microwave
Tissue	Soxhlet

11.3. Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Matrix	Methods
Waters	Multibed Silica/ florisil/ acid washing
Soil/Sediment	Multibed Silica/ florisil/ acid washing
Tissues	Multibed Silica/ florisil/ acid washing

11.4. The recommended HRGC/HRMS operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration).

Mass range:	Discrete 5 function descriptor
Scan time:	<1 sec/scan
Initial temperature:	160°C, hold for 1 minute
1st Temperature program:	160-200°C at 40C°/min
2nd Temperature program:	200-300°C at 3C°/min
3rd Temperature program:	300-320 at 15C°/min
Final temperature:	320°C, hold for 9.3 minutes
Injector temperature:	280°C
Transfer line temperature:	280°C
Source temperature:	290°C
Injector:	Grob-type, splitless/split
Sample volume:	1 µL
Carrier gas:	Helium at 40 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 Sections 10.3 and 10.9.

11.6. Prior to sample analysis the continuing calibration verification is analyzed (CS3) and this ICV must meet the criteria found in Sections 10.11 -10.12. 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 ICV provided it meets the requirements.

11.7. HRGC/HRMS analysis

11.7.1. Difficult sample matrices may require that the sample extract be screened on a GC/ECD or GC/MS using a similar type of capillary column. This will minimize contamination of the HRGC/HRMS system from unexpectedly high concentrations of organic compounds. Samples showing a high background or lipid content may require a modified extraction using less sample material.

11.7.2. Inject 1µL of the 20µL sample extract (10 µL extract plus 10 µL Injection Standard) into the HRGC/HRMS system. The volume injected (1µL) should contain 100 pg/µL of the injection standards. 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.

11.7.3. When the response for any target analyte except OCDD/OCDF exceeds the high point of the initial calibration curve) corrective action will be required. Dilution may be performed on the extract as described in section 16.10 or Sample re-extraction may take place using less sample material. See section 16.10 for guidance on over range values. Dilution for OCDD/OCDF is required only if the peak is saturated.

11.8. Perform all qualitative and quantitative measurements as described in Section 11. Store the remaining extract at -10 to -20°C protected from light in screw-cap vials equipped with un-pierced Teflon lined septa.

12. Data Analysis and Calculations

12.1. Qualitative identification-

12.2. An analyte is identified by comparison of the sample EICP characteristic ion ratios to the reference EICP ion ratios generated in the initial calibration. The referenced method ion ratios must be met by the laboratory using the conditions of this SOP. Method specific reference ion ratios are shown in table 3 (appendix 20.3). Alternatively, ion ratios within ±10% of the last CS3 calibration point or continuing verification whichever is most recent may be used. The following retention time criteria must be also satisfied to verify identification for any target Analyte.

12.2.1. 2378-substituted isomers with corresponding labeled standards will require an absolute retention time at maximum height within -.02 to +.05 minutes of that for corresponding labeled standards. In addition, the two quantitation ion RTs must be within ± .03 minutes of each other. The RRT must be within .005 RRT units of that in calibration verification standard.

12.2.2. 2378-substituted isomers without corresponding labeled standards must show the RRT must to be within .005 RRT units of that in calibration verification standard.

12.2.3. Non 2378-substituted isomers require that the retention time window be established by the window defining mixture included in the CS3 standard for each homologue group. In addition, RTs for both quantitation ions must be within ± .03 minutes of each other in the peak profile.

12.3. Ion abundance ratios must meet for any PCDD or PCDF to be reported as a non-EMPC. See the ion abundance ratios shown in table 3. Alternatively, ion ratios within ±10% of the last CS3 calibration point or continuing verification whichever is most recent may be used. PCDDs and PCDFs with failing ion ratios are reported as EMCP's on the final data reports. Ion abundance ratios apply to all analytes reported by this method, except for the cleanup standard which only uses one quantitation ion. EMPC values are not to be corrected for ion ratio.

12.4. Signal to noise ratio of all calibration standards compounds must be > 10.

12.5. Signal to noise ratio for all reported sample/QC peaks must be > 3.

12.6. Polychlorinated diphenyl ether (PCDE) interferences must be evaluated for all 2378-substituted PCDF isomers. PCDE interferences will not be evaluated for the non 2378-substituted isomers. PCDE's at the same retention time (± .03 minutes) as any detected 2378-sustituted furan isomer, that also have a height > 1% of either furan isomer, will require the furan value to be flagged as potentially false positive due to an interference. Corrective action may also be warranted. See section 16.12 for further guidance. See Appendix 20.10 for the theory of PCDE interference.

12.7. Quantitative analysis

12.7.1. When a compound has been identified, the quantitation of that compound will be based on the summated integrated abundance from the EICP of the primary and secondary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used are shown in Table 3 (Appendix 20.3)

12.7.2. Calculate the concentration of each identified analyte in the sample as follows:

12.7.3. Water

Concentration (pg/L) =	$\frac{(Ax)(Is)(Vt)}{(Ais)(RRF)(Vo)(Vi)}$
Where:	

A_X = Area of characteristic ions for compound being measured
Is = Amount of internal standard injected (pg)
Vt = Total volume of the extract (µL)
A_{IS} = Area of characteristic ions for the internal standard
RRF = Relative response factor for compound being measured
Vo = Volume of water extracted (L)
Vi = Volume of extract injected (µL)

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

$$\textbf{Concentration (pg/g)} = \frac{(Ax)(Is)(Vt)}{(Ais)(RRF)(Vi)(Ws)}$$

where:

A_X = Area of characteristic ions for compound being measured

Is = Amount of internal standard injected (pg).

Vt = Total volume of the extract (µL)

A_{IS} = Area of characteristic ions for the internal standard

RRF = Relative response factor for compound being measured

Vi = Volume of extract injected (µL)

Ws = Dry weight of the sample extracted (g)

12.7.5. Concentrations for unnamed PCDDs and PCDFs isomers in the sample are also quantitated using an average of the response factors from the named 2378-substituted isomers at the same level of chlorination.

12.7.6. An EDL is calculated for all non-detects in the method blank and samples. The EDL becomes the limit of detection reported for that individual analyte.

12.7.6.1. The EDL calculation for a water sample is calculated as follows:

$$\textbf{Aqueous EDL (pg/L)} = \frac{(3)(Hx)(Is)(D)}{(His)(RRF)(Vo)}$$

Where:

H_X = Combined height of ions for compound being measured

Is = Total pg of internal standard added (e.g. 2000pg)

D=Dilution factor

H_{IS} = Combined height of ions for the internal standard

RRF = Relative response factor for compound being measured

Vo = Volume of water extracted (L)

12.7.6.2. The EDL calculation for a solid sample is calculated as follows:

Solid EDL (pg/g) =	**$\frac{(3)(Hx)(Is)(D)}{(His)(RRF)(W)}$**
Where:	
H_X = Combined height of ions for compound being measured	
Is =Total pg of internal standard added (e.g. 2000pg)	
D=Dilution factor	
H_{IS} = Combined height of ions for the internal standard	
RRF = Relative response factor for compound being measured	
W = Weight of solid extracted (g)	

12.8. Data Processing and LIMS entry

12.8.1. All the calculations above are done by the TargetLynx data processing software and/or the Element LIMS system. A working knowledge of Targetlynx and Element is required.

12.8.2. When evaluating data for a sequence, first determine if all calibrations, mass resolution checks, and ISC checks met their respective QC criteria. **Note that 8290 and CLP/HRSM01.2 require a closing CCV, and CLP requires a closing ISC as well**. Closing res checks are required by all methods. If any required standards fail to meet QC criteria, take corrective action and rerun any affected samples.

12.8.3. For sample data, check IS response for each run. Although there are no method limits for IS recovery, recoveries should generally be within a range of –50% to +100% from the ICV. Anomalies (especially on the low side) should be investigated and possibly require rerun.

12.8.4. Evaluate labeled surrogate recoveries. Surrogate recovery limits vary by compound, but are in the range of 25-150%. Any recoveries that are near the edge of that range should be checked against the relevant limit. Once the data is imported into Element, recoveries outside of acceptable range will be listed in red.

12.8.5. Evaluate the peaks for all detected Dioxins/Furans (DFs). All reported peaks must have S/N >3 for both quant ions, and the quant ions must have RT's within .03 min of each other. Additionally, the RT for each quant ion must be within -.02 to +.05 min of the associated surrogate. Peaks that do not satisfy these criteria should be deleted.

12.8.6. Evaluate the RRT's for all 2378-DFs. All 2378-DFs should have RRT's with the ranges established for the RTX-Dioxin2 column. All non-2378-DF RT's must fall within the associated homologue range established by the marker peaks in the CS3WT. All peaks outside of the range markers should be deleted.

12.8.7. Evaluate the integrations for all DFs. Baselines that are unreasonable in the opinion of the analyst should be manually adjusted, unless the adjustment would have insignificant impact on the peak concentration. Manual integrations are shown on the chromatograms and listed on both the raw data report and the audit report produced by TargetLynx. This audit report must be included in the final data package, and for HRSM01.2 and DOD the report must be signed by the analyst. For CLP and DOD, the data reviewer must also indicate this report was reviewed.

12.8.8. Once the analyst is satisfied with the data for the sequence, the processed data set is saved to the instrument folder on the target server, so that it may be accessed by others. The list of manual integrations (Audit Report) should be printed to PDF and included in the data package with the sequence. See 12.8.24.

12.8.9. All calibration runs, ISC checks, and resolution checks for the sequence should be printed to PDF in the ServerFolders\Data_PDF\Autospec folder. Using PDFCreator, merge each CS3 and its associated res check and ISC into a single pdf with the CS3 filename.

12.8.10. All sample and QC files are also printed directly to PDF in the ServerFolders\Data_PDF\Autospec folder. The file name must be edited to match the run file name, with the pdf file extension. e.g. 18061002.pdf. Element will automatically associate the pdf with the data file of the same name.

12.8.11. The data set is exported to Element from TargetLynx through the File menu, Export, XML. Name the export file the same as the data batch.

12.8.12. In Element, create a sequence that matches the run log, if not already done. Choose the extraction batch and add samples and QC. Also add ICV, CCVs, and ISCs (Res). Enter the IS ID and standards ID's. Check that Analysis method, instrument, calibration, and sequence date are correct. Fill in the requested info under User Fields. Also, in the Benchsheet for the batch, edit the status to "Processing." Then under Extracts, edit the location of the extracts to "Dioxin lab." This should be done when the extracts are put on the instrument for analysis, to update the chain of custody.

12.8.13. Import the data through the DET table and Data Tool, using the "Waters Masslynx Dioxin .xml" file type. Choose the target\share drive folder in which the Targetlynx xml file was saved, then select the files to be imported. Check that the cross table file listed on the bottom of the Data Tool window is the correct Dioxin cross table, before merging the files.

12.8.14. After merge, check that all files are listed in the Merged Upload tab. For those that are not listed, replace the instrument name with the correct Element name under the Instrument Data tab, then Refresh. All files should now appear under the Merged Upload tab. Save the xls (Excel) file in the appropriate folder on the data server.

12.8.15. In the DET table, first Save, then Query the data. The data fields should be populated for all files that were imported. Lock the data, then update the status to "Processing" if not done previously.

12.8.16. If any files are dilutions, enter the appropriate dilution factor in the Diln column **for the surrogates only.** Recoveries will be corrected and should no longer be red. Target compound values are already corrected for dilution, based on the diluted surrogate recoveries. For special cases where a split was taken from the extract during extraction, the split factor is entered in the DILN column for target analytes and totals, but not surrogates (because surrogates are added post-split and should be at normal levels).

12.8.17. After dilution factors have been entered and saved, run the "rev_DioxinEMPC.exe" program using the Print button. This program will add EMPC flags and adjust MDLs/MRLs based on the surrogate dilution factor. "Z" flags will be added to indicate adjusted reporting limits. This program should always be run to get EMPC flags, even if there are no dilutions in the sequence.

12.8.18. Because the quantitation of 123789-HxCDD is based on the average of two HxCDD surrogates, the average response of the 2 surrogates must be manually calculated and entered in Element. 13C12-123478/123678-HxCDD is listed as a virtual, non-reported surrogate in Element, and is used only for Form 7 percent D calculation. A spread sheet is used to average the areas of the 4 quant ions. This value is entered in the Response field for the virtual surrogate for all calibration files (Cal, ICV, CCV). This field is left blank (and will be red) for all non-calibration files.

12.8.19. The percent valley between ISC isomers must also be manually entered. Print to PDF a close up view of the TCDD/TCDF peaks in the ISC chromatogram. With a ruler, measure the valley height and the height of the smaller adjacent peak for both TCDD and TCDF. Calculate the percent of valley height to adjacent peak height and label the chro with this calculation. The percent valley for both compounds must be < 25% to be in control. Enter the calculated percentage in the RES column for TCDD and TCDF in all ISC files. All other compounds in the ISC files are irrelevant and may be deleted.

12.8.20. "E" flags are indicated in the DET table in the FResult column, but must be manually entered in the Qualifier column. Add the "E" qualifier to all target compounds where indicated. A dilution is required for "E" values on any target compounds other than OCDD/OCDF. Per EPA, only saturated OCDD/OCDF peaks require dilution. **Special note:** For diluted files, target compound values are already corrected for dilution based on the diluted surrogates. Actual on column values must be back calculated by dividing the IResult by the dilution factor. e.g. For a 10x dilution of a sample where OCDD has an IResult of 5000 and a FResult of 10000 E, the

true on column value for OCDD is 500 (5000/10). This is below the upper calibration limit of 2000, and therefore no "E" qualifier is warranted. All potential "E" flags for diluted files must be similarly evaluated. "E" flags indicated for surrogates in Element can be disregarded.

12.8.21. Homologue peak counts are required for CLP/HRSM01.2. The values are automatically imported into the DET AnalyteInfo 7 field through the "rev_DioxinEMPC.exe" program. Because PeCDF's occur in 2 functions, however, the two PeCDF values must be summed and manually entered for the PeCDF total. Peak counts should be included in the DET table for all HRSM01.2 samples and blanks.

12.8.22. Sample chromatograms should be evaluated for potential chlorinated diphenyl ether (CDPE) interference, which may inflate the response of the target Furans. CDPE's are very similar compounds to Furans and can fragment into the same quant ions. The data reports include a chromatogram for potential CDPE masses with each Furan homologue group. If there is an integrated CDPE peak within .03 min of a target Furan peak, and the CDPE peak has a height > 1% of the Furan height, the Furan value should get an "X" flag, indicating potential CDPE interference. The "X" qualifier text must be filled in each time, but can be copied/pasted from a saved text file to avoid typing. See Appendix 20.10 for detailed CDPE theory.

12.8.23. The HRMS Reviewer Checklist should be filled in once all the data has been imported and evaluated. Items in red should either be fixed or addressed with comments in the lower box. General comments should be listed in the Additional Notes at the bottom.

12.8.24. A PDF of the Sequence should be created once the raw data has been evaluated and all manual integrations have been applied. This can be done before or after the data is imported to Element. The Sequence PDF should include the Element Sequence, including relevant user data, a run log showing data acquisition times, and the Targetlynx Audit report. The latter two reports are printed to PDF from TargetLynx, and can then be edited with sequence comments and analyst initials as needed. Merge the 3 files into a single PDF in PDFCreator, name as the Sequence number, and place in the Data_PDF\Sequence folder.

12.8.25. Once the Sequence data is ready for review and all associated PDFs have been attached, the status should be changed to Analyzed.

13. Method Performance

13.1. The QA department measures method performance using a combination of initial performance and recovery (IPR) studies, ongoing performance and recovery (LCS) studies, quantitation limit studies (QLS) and the monitoring of extraction and cleanup standard recoveries.

13.1.1. Limits of Detection (LOD)- detection limits for all analytes quantitated using this SOP are determined by an estimated detection limit (EDL) calculation for each individual sample and named congener reported.

13.1.2. IPR studies are performed each year for each analyte by each preparatory and analytical method (for example, analytes quantitated for in sediment samples will have IPR studies performed for both the microwave and soxhlet extraction).

13.1.3. LCS spikes are prepared with every extraction batch and result values may be found for each analyte on the ARI website.

13.1.4. QLS spikes are used to statistically derive LOD and LOQ results which are used to verify the LOQ.

13.1.5. Laboratory precision and bias measurements are performed by monitoring extraction and cleanup standard recoveries in samples and quality control samples.

13.1.6. Control limits may be calculated by monitoring these recoveries. These control limits are disseminated to the bench chemists and LIMS administrator for use in monitoring method performance in real time. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found on the ARI website.

13.1.7. Method default control limits from method 1613B for extraction and cleanup standard recoveries will be used until a sufficient number of data points have been collected to generate meaningful statistics. ARI may use these in-house limits to monitor method performance, but they will not supersede those limits listed in the method1613B.

14. Pollution Prevention

14.1. All syringe rinsing must be performed over charcoal to minimize the exposure of the environment to solvent or extract. The charcoal container must remain covered when not in use to prevent fugitive emissions.

14.2. All GC split vents will be connected to a charcoal filter and an exhaust vent.

14.3. All MS vacuum pumps will be connected to an exhaust vent.

14.4. All spent vials and pipettes are placed into the blue waste vial receptacle in the Dioxin extraction lab for proper disposal.

14.5. 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 above.

15.2. Method Blanks- For non CLP contract work, the method blank should contain less than the reporting limit of all analytes except OCDD/OCDF, which can be up to 5 times the RL. Corrective

action should be performed for any detected target analyte in a sample that is also found in the method blank at a concentration greater than the RL. **For CLP HRSM01.2, all target analytes other than OCDD/OCDF should be less than 1/2 the CRQL in the method blank. OCDD/OCDF should be less than 3 times the CRQL to be in compliance.**

15.3. Extraction and cleanup standard Recoveries

15.3.1.1. All method blanks, IPR, LCS, duplicates, SRMs and samples must have acceptable extraction and cleanup standard recoveries. Standard recoveries are listed in table 5 (Appendix 20.5) and are not to exceed the method default limits as shown.

15.3.2. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet project specific standard acceptance criteria that supersede those limits listed in Table 5.

15.3.3. Extraction and cleanup standard 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. ARI will use 1613B method default limits until appropriate in-house limits are generated.

15.3.4. Extraction and cleanup standard 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.

15.4. Performance and recovery Control Samples (IPR and LCS)

15.4.1. The IPR/LCS/LCSD recovery values should fall within the method specified recovery acceptance limits shown in table 6 (Appendix 21.6). IPR/LCS/LCSD 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. Matrix Spike/Matrix Spike Duplicates (MS/MSD)- <u>DOD ONLY-</u> (NOTE: Must be reported with Element)

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

15.5.2. 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. MS/MSD recoveries are advisory and should not be used to reject batch data.

15.6. Holding Times

15.6.1. Samples should be extracted within holding times (one year for all samples).

15.6.1.1. Extracts must be analyzed within the extract holding time (one year from the initial date of extraction).

15.6.1.2. In the event that re-extraction due to an out of control event requires that samples be re-extracted after their one year holding time has elapsed, 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 the sample was compromised in the interval between extractions.

15.6.1.3. If any extracts are analyzed after the one-year extract holding time has elapsed, the analyst must document this in the analytical notes accompanying the data so that it may be included in the case narrative.

16. Corrective Actions for Out of Control Events

16.1. Mass Spectrometer Tuning

16.1.1. MS tuning- prior to initial calibration, each GC/MS system must be hardware-tuned to meet the minimum resolving power of 10,000 (at 10% valley) for 3-5 PFK masses representing each scan function utilized. Analyses must not begin until all these criteria are met with no exceptions. Evaluate the static resolution check not only for resolution but to insure that the level of PFK ion bleed is less than one volt for each mass.

16.1.2. If the re-tuned mass spectrometer still fails to meet the criteria found in 16.1.1 the MS may require maintenance. Maintenance may include, but is not limited to: replacing the filaments, exchanging the MS inner source, exchanging the MS outer source, cleaning the MS inner or outer source lenses, and adjusting the slit settings.

16.2. Ion ratio factors- If the ion ratio factors exceed the limits found in table 3 (Appendix 20.3), the mass spectrometer or chromatographic system may need maintenance. Inspect the MS system for leaks or other tuning issues. Should none be found, perform maintenance on the chromatographic system. This maintenance includes, but is not limited to: replacing the inlet liner, 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. Any maintenance is to be documented in the maintenance logbook for that instrument.

16.3. Signal/Noise Failure-Initial calibration is not acceptable until all calibration points have S/N > 10. Corrective action is required if this limit is not met.

16.4. Initial calibration linearity failure- should any of the analytes in the initial calibration show RSDs greater than 20% corrective action is required and sample analysis should not begin until the problem is corrected.

16.5. Continuing verification linearity failure- should any of the named analytes, extraction standards, or cleanup standard in the continuing calibration verification show % D greater than the limits shown in Appendix 20.9 corrective action is required and sample analysis should not begin until the problem is corrected. The closing continuing calibration verification will also be evaluated to these same tolerances and any failures clearly documented in the analysts notes for inclusion in the case narrative.

16.5.1. 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 16.5

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

16.5.1.2. 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.

16.6. Extraction and cleanup standards

16.6.1. When the extraction standards or cleanup standard fail to meet their recovery acceptance criteria, reanalyze the extract.

16.6.2. If the extraction and cleanup standard recoveries do not meet their recovery acceptance criteria after reanalysis, check calculations, sample preparation logs, the extraction and cleanup standard spiking and calibration solutions and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the extraction or cleanup standards meet their acceptance criteria. If the sample preparation logs indicate that the incorrect amount of extraction or cleanup spiking solution was added either recalculate standard recoveries based on the actual amount of standard spiking solution added, or re-extract/reanalyze the sample, adding the correct amount of standard spiking solution. If the standard compound spiking solution and/or instrument calibration solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze samples.

16.6.3. If the analytical instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. This correction will mostly involve maintenance similar to the maintenance discussed in Section 16.2. Verify that the standard recoveries meet their acceptance criteria. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.6.4. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps.

16.6.4.1. Re-extract and reanalyze the sample. The laboratory may decide to extract a smaller sample volume or amount in order to reduce the interfering aspect of the sample matrix.

16.6.4.2. If the extraction and (or) cleanup standard recoveries meet acceptance criteria in the re-extracted/reanalyzed sample, then the problem with the initial analysis is deemed to be within the laboratory's control. Therefore, submit data only from the re-extraction/reanalysis if the re-extraction was performed within holding time, otherwise report both sets of data.

16.6.4.3. If the extraction and (or) cleanup standard recoveries fail to meet the acceptance criteria in the re-extracted/reanalyzed sample, then submit data from both analyses, distinguishing between the initial analysis and the re-extraction/reanalysis on all deliverables.

16.7. Method Blanks- Corrective action for a method blank may involve re-extraction and reanalysis of all associated samples in the case where blank concentrations are greater than ½ of the reporting limit, except for OCDD/OCDF, which can be up to 5 times the RL. Sample hits less than 10 times the MB concentration will be “B” flagged.

16.8. LCS/IPR control Samples

16.8.1. If the LCS compounds fail to meet recovery acceptance criteria, reanalyze the extract.

16.8.2. If the LCS recoveries do not meet their recovery acceptance criteria after reanalysis, check calculations, sample preparation logs, the LCS compound spiking and calibration solutions and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the LCS compound recoveries meet their acceptance criteria. If the sample preparation logs indicate that the incorrect amount of LCS compound spiking solution was added either recalculate LCS recoveries based on the actual amount of LCS compound spiking solution added or re-extract/reanalyze the samples, adding the correct amount of LCS spiking solution. If the LCS compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze samples.

16.8.3. If the analytical instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the LCS recoveries meet their acceptance criteria. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.8.4. If the LCS compounds still fail to meet their acceptance criteria, re-extract and reanalyze the LCS and all associated samples and QC samples if deemed appropriate (i.e. after consideration of all batch QC data) or mandated by contract-specific requirements. Any

decision to forgo re-extraction/reanalysis based on failure to meet LCS acceptance criteria will require approval of the Project Manager and the Lab Manager, at a minimum.

16.9. Matrix Spike/Matrix Spike Duplicates-DoD only-(reportable in Element only)

16.9.1. All MS/MSD control limits are advisory and should not be used to reject batch data.

16.10. Over range values- Should the quantitated value of any analyte except OCDD/OCDF exceed the working range of the curve, a dilution of the original extract may be performed. Over range values will be qualified with an “E” flag. Sample extracts may be diluted a maximum of 50x, so that the labeled surrogates are not diluted below approximately 1 pg on column. The concentration of the injection standard must remain at 100pg/ul in all dilutions, as in undiluted extracts. An aliquot of the diluted extract is analyzed and only the over range analytes are reported for the dilution run. Samples requiring greater than a 50x dilution to bring all analytes within curve range will require a re-extraction with a smaller sample volume (weight). OCDD/OCDF may be reported as "E" values. See 16.10.1. See Appendix 20.11 for dilution procedure.

16.10.1. When ions from a target compound in the sample saturate the detector or when the chromatographic system is overloaded the analyst must;

16.10.1.1. Analyze a Solvent Blank consisting of clean solvent until the system has been decontaminated.

16.10.1.2. Evaluate subsequent samples and QC for any possible carryover or contamination.

16.10.1.3. The chromatographic system should be decontaminated before the analytical sequence may be resumed.

16.11. EMPC - When named target analytes do not meet ion abundance ratio criteria they must be calculated as an EMPC and flagged as an EMPC on the final report. See Appendix 20.2 for EMPC area correction calculations.

16.12. PCDE interference - Named target analytes showing PCDE interference will be evaluated as follows. In cases where the area of the interference is less than 1% area of either Furan quantitation ion, no corrective action is required. In cases where the area of interference is greater than 1% of either Furan quantitation ion, the furan value will be “X” flagged. In cases where the interference exceeds 10%, ARI may perform additional cleanups on the original extract and/or may re-extract the sample at a smaller volume. Such corrective actions are discretionary and must be approved by the Organics supervisor and project manager. See appendix 20.10 for further discussion of PCDE interferences.

16.13. PFK traces must not exceed 20% variation for the lock mass in each function. Negative peaks in the PFK trace caused by interferences are acceptable, as long as the general trend of the trace is still within the 20% limit, and the chromatography of IS, labeled surrogates, and target

analytes are unaffected, and the labeled surrogate values are within method recovery limits (See Appendix 20.5). Corrective action is required if all of the above conditions are not met.

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

17.1. See Section 16.1 for guidance on dealing with out-of-control tuning events.

17.2. See section 16.2 for guidance on ion ratio limit failures for initial and continuing calibrations.

17.3. See Section 16.3 for guidance on dealing with signal/noise limit failures.

17.4. See Section 16.6 for guidance on dealing with initial calibration linearity failures (%RSD).

17.5. See Section 16.7 for guidance on dealing with continuing verification linearity failures (%D).

17.6. See Section 16.8 for guidance on dealing with extraction and cleanup standard control limit failures.

17.7. See Section 16.9 for guidance on dealing with method blank related out-of-control events.

17.8. See Section 16.8 for guidance on dealing with IPR/LCS recovery limit failures.

17.9. See Section 16.9 for guidance on dealing with MS/MSD control limit failures. -DoD only

17.10. See Section 16.10 for guidance on over range value events.

17.11. See Section 16.11 for guidance on reporting values as an EMPC.

17.12. See Section 16.12 for guidance on reporting values with PCDE interference.

17.13. See Section 16.13 for guidance on reporting data with PFK interference

18. Routine Instrument Maintenance

18.1 GC Maintenance. If chromatography shows excess tailing, or TCDD/TCDF resolution is poor, change the injector liner and clip one or two loops from the front of the column. Remember to adjust the RT windows for the five functions in the acquisition method. One loop corresponds to approximately 0.3 min of RT shift.

18.2 Source Maintenance. If tuning is abnormal and/or sensitivity declines significantly, check the inner source. If it looks dirty or has been in use more than a couple months, replace the inner source with a clean one. Also look at the outer source. If it looks particularly dirty, or if the clean inner source does not improve performance sufficiently, replace the outer source as well. Always have a clean inner source (including new filament) and outer source available to use if needed.

18.3 Preventative Maintenance. ARI will always have a service contract, which includes a yearly preventative maintenance visit. This visit normally includes changing pump oil, cleaning all lenses in the source, and possibly in the analyzer, as well as checking the source and collector slits. For other non-routine performance issues, especially electronic or computer related, call Waters for service.

19. Waste Management

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

19.2. 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. The charcoal waste container must be covered when not in use.

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

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

20. Method References

20.1. Method 1613B - "Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS", Revision B, October 1994.

20.2. Method 8290A - Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), Revision 1, February 2007.

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

20.4. "Department of Defense Quality Systems Manual for Environmental Laboratories", Version 5.0, July 2013.

20.5. Method 8290 - Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), Revision 0, September, 1994.

20.6. Multi-Media, Multi-Concentration Dioxin and Furan Analysis (DLM 02.2) SOW. EPA CLP. December 2009.

21. Appendices

21.1. Appendix 20.1: Quality Control Requirements

21.2. Appendix 20.2: Example EMPC calculations

21.3. Appendix 20.3: Method 1613B Retention Time References

21.4. Appendix 20.4: Method 1613B Ion Abundance Ratios and QC Criteria

21.5. Appendix 20.5: Method 1613B Labeled Compound Recovery When All CDDs/CDFs Are Tested

21.6. Appendix 20.6: Method 1613B IPR/LCS Recovery Acceptance Criteria

21.7. Appendix 20.7: Retention Time Window Defining Isomers

21.8. Appendix 20.8: ARI five Function Scan Descriptor

21.9. Appendix 20.9: Method 1613B Initial and continuing calibration verification %RSD and %D requirements.

21.10. Appendix 20.10: Theory of CDPE interference.

21.11. Appendix 20.11: Extract dilution procedure

21.12. Appendix 20.12: Example of ISC peak resolution calculation

Appendix 20.1. Quality Control Requirements for Dioxin/Furan Analysis by HRGC/HRMS (Method 1613B)					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Demonstrate acceptable analytical capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, test method, or sample matrix.	QC acceptance criteria published by ARI, if available; otherwise, method-specified criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA.	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure.No analysis shall be allowed by analyst until successful demonstration of capability is complete.
LOD determination and verification (See Box D-13)					
establishment and verification (See Box D-14)					
Tuning	At the beginning and the end of each 12-hour period of analysis.	Static resolving power ≥ 10,000 (10% valley) for identified masses per method, and lock-mass ion between lowest and highest masses for each descriptor and level of reference compound ≤ 10% full-scale deflection, per method.	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.
GC column performance check	Prior to ICAL or calibration verification. Use GC performance check solution per method.	Peak separation between 2378-TCDD and other TCDD isomers result in a valley of ≤ 25%, per method; and Identification of all first and last eluters of the eight homologue retention time windows; and Absolute retention times for switching from one homologous series to the next ≥ 10 sec. for all components of the mixture.	Correct problem then repeat column performance check.	Flagging criteria are not appropriate.	

Appendix 20.1. Quality Control Requirements for Dioxin/Furan Analysis by HRGC/HRMS (Method 1613B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial calibration (ICAL) for all analytes identified in method	ICAL prior to sample analysis, as needed by the failure of calibration verification standard, and when a new lot is used as standard source for HRCC-3, sample fortification (IS), or recovery solutions.	Ion abundance ratios in accordance with criteria in Table 8 of the method; and S/N ratio ≥ 10 for all target analyte ions; and RSD ≤ 20% for the response factors (RF) for all 17 unlabeled standards and RSD ≤ 20% for the RFs for the 9 labeled IS.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed. Calibration may not be forced through origin.
Calibration verification	At the beginning of each 12-hour period.	Ion abundance ratios in accordance with criteria in Table 8 of the method; and meets method 1613B %D requirements listed in Appendix 20.9	Correct problem, repeat calibration verification standard. If that fails, repeat ICAL and reanalyze all samples analyzed since the last successful CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last successful calibration verification.	Problem must be corrected. Results may not be reported without a valid calibration verification. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Method blank	One per preparatory batch, run after calibration standards and before samples.	No analytes detected ≥ ½ LOQ. or ≥ 5% of the associated regulatory limit for the analyte or ≥ 10% of the sample result for the analyte, whichever is greater, per method.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS	One per preparatory batch.	QC acceptance criteria specified by method, 1613B. Appendix 20.6	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Sample duplicate	(OPTIONAL)	RPD ≤ 25% (between sample and sample duplicate), per method.	Contact the client as to additional measures to be taken.		
Extraction and cleanup standards	Every field sample, standard, and QC sample.	% recovery for each IS in the original sample (prior to dilutions) must be within 1613B method requirements.	Correct problem, then reprep and reanalyze the samples with failed recoveries.	Apply Q-flag to results of all affected samples.	

Appendix 20.3: Retention Time References, Quantitation References, Relative Retention Times, and Minimum Levels for CDDS & CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum Level		
			Water pg/L;ppq	Solid ng/kg;ppt	Extract pg/µL; ppb
COMPOUNDS USING $^{13}C_{12}$-1,2,3,4-TCDD AS THE INJECTION STANDARD					
2,3,7,8-TCDF	$^{13}C_{12}$-1,3,7,8-TCDF	0.999-1.003	10	1	0.5
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002	10	1	0.5
1,2,3,7,8-PeCDF[3]	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002	50	5	2.5
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002	50	5	2.5
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002	50	5	2.5
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103			
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043			
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052			
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425			
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526			
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567			
COMPOUNDS USING $^{13}C_{12}$-1,2,3,7,8,9-HxCDD AS THE INJECTION INTERNAL STANDARD					
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001	50	5	2.5
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005	50	5	2.5
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001	50	5	2.5
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001	50	5	2.5
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001	50	5	2.5
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004	50	5	2.5
1,2,3,7,8,9-HxCDD	_[2]	1.000-1.019	50	5	2.5
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001	50	5	2.5
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001	50	5	2.5
OCDF	$^{13}C_{12}$-OCDD	0.999-1.008	100	10	5
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001	100	10	5
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975			
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047			
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021			
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085			
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110			
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311			

[2] The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

[3] The last eluting TCDF (1289) elutes after the first PeCDF (13468) congener on the RTX-DIOXIN2 column. The window is set from the last eluting TCDF (1289) marker. Additional PeCDFs (12468 and 13678) are also used to ensure the windows have been set correctly.

Appendix 20.4: Theoretical Ion Abundance Ratios and QC Limits

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	QC Limits [1]	
			Lower	Upper
4[2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
6[3]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.04	0.88	1.20
7[4]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

[1] QC limits represent ±15% windows around the theoretical ion abundance ratios.

[2] Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).

[3] Used for $^{13}C_{12}$-HxCDF only.

[4] Used for $^{13}C_{12}$-HpCDF only.

Appendix 20.5: Labeled Compound Recovery When All CDDs/CDFs Are Tested

Compound	Test Conc. (ng/mL)	Labeled Compound Recovery	
		(ng/mL) [1]	(%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25 – 164	25 – 164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24 – 169	24 – 169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25 – 181	25 – 181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24 – 185	24 – 185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21 – 178	21 – 178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32 – 141	32 – 141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28 – 130	28 – 130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26 – 152	26 – 152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26 – 123	26 – 123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29 – 147	29 – 147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28 – 136	28 – 136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23 – 140	23 – 140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28 – 143	28 – 143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26 – 138	26 – 138
$^{13}C_{12}$-OCDD	200	34 – 313	17 – 157
$^{13}C_4$-2,3,7,8-TCDD	10	3.5 – 19.7	35 – 197

[1] Specifications given as concentrations in the final extract, assuming a 20 µL volume.

Appendix 20.6: Acceptance Criteria for IPR/LCS Results When All CDDs/CDFs Are Tested[1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3]		LCS (ng/mL)	VER (ng/mL)
		S (ng/mL)	X (ng/mL)		
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	2	8.7-13.7	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71	39-65
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67	41-60
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80	41-61
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82	39-64
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67	39-64
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81	41-61
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67	45-56
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65	44-57
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65	45-56
2,3,4,6,7,8-HxCDF	50	7.4	37-74	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69	43-58
OCDD	100	19	89-127	78-144	79-126
OCDF	100	27	74-146	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	26-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	21-158	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	20-186	77-129
$^{13}C_{12}$-OCDD	200	95	41-276	26-397	96-415
$^{13}C_{4}$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.1-19.1	7.9-12.7
2,3,7,8-TCDD	10	2.7	8.7-12.4	7.3-14.6	8.2-12.3
2,3,7,8-TCDF	10	2	9.1-13.1	8.0-14.7	8.6-11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32-115	25-141	85-117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35-99	26-126	76-131
$^{13}C_{4}$-2,3,7,8-TCDD	10	3.4	4.5-13.4	3.7-15.8	8.3-12.1

[1] All specifications are given as concentrations in the final extract, assuming a 20 µL volume.

[2] s = standard deviation of the concentration.

[3] X = average concentration.

Appendix 20.7: Retention Time Window Defining Isomers		
PCDD / PCDF	**First Eluted**	**Last Eluted**
TCDF	1368	1289
TCDD	1368	1289
PeCDF	13468	12389
PeCDD	12479	12389
HxCDF	123468	123789
HxCDD	124679	123789
HpCDF	1234678	1234789
HpCDD	1234679	1234678

RTX-DIOXIN2 TCDD SPECIFICITY TEST STANDARD

2378-TCDD
1278-TCDD

RTX-DIOXIN2 TCDF SPECIFICITY TEST STANDARD
2348-TCDF
2378-TCDF
3467-TCDF

Appendix 20.8: Five Function Scan Descriptor			
DESCRIPTOR	**EXACT MASS**	**MASS TYPE**	**SUBSTANCE**
1	303.9016	M	TCDF
	305.8987	M+2	TCDF
	315.9419	M	^{13}C-TCDF
	317.9389	M+2	^{13}C-TCDF
	319.8965	M	TCDD
	321.8936	M+2	TCDD
	327.8847	M	^{37}CL-TCDD
	330.9792	LOCK	PFK
	331.9368	M	^{13}C-TCDD
	333.9339	M+2	^{13}C-TCDD
	339.8597	M	PeCDF
	341.8567	M+2	PeCDF
	375.8364	M+2	HxCDPE
	409.7974	M+2	HpCDPE
2	339.8597	M	PeCDF
	341.8567	M+2	PeCDF
	342.9792	LOCK	PFK
	351.9000	M	^{13}C-PeCDF
	353.8970	M+2	^{13}C-PeCDF
	355.8546	M+2	PeCDD
	357.8516	M+4	PeCDD
	367.8949	M+2	^{13}C-PeCDD
	369.8919	M+4	^{13}C-PeCDD
	409.7974	M+2	HpCDPE
3	373.8208	M+2	HxCDF
	375.8178	M+4	HxCDF
	380.9760	LOCK	PFK
	383.8639	M	^{13}C-HxCDF
	385.8610	M+2	^{13}C-HxCDF
	389.8157	M+2	HxCDD
	391.8127	M+4	HxCDD
	401.8559	M+2	^{13}C-HxCDD
	403.8529	M+4	^{13}C-HxCDD
	445.7555	M+4	OCDPE
4	407.7818	M+2	HpCDF
	409.7788	M+4	HpCDF
	417.8253	M	^{13}C-HpCDF
	419.8220	M+2	^{13}C-HpCDF
	423.7766	M+2	HpCDD
	425.7737	M+4	HpCDD
	430.9728	LOCK	PFK
	435.8169	M+2	^{13}C-HpCDD
	437.8140	M+4	^{13}C-HpCDD
	479.7165	M+4	NCDPE
5	441.7428	M+2	OCDF
	443.7399	M+4	OCDF
	457.7377	M+2	OCDD
	459.7348	M+4	OCDD
	469.7779	M+2	^{13}C-OCDD
	471.7750	M+4	^{13}C-OCDD
	480.9696	LOCK	PFK
	513.6775	M+4	DCDPE

Appendix 20.9: Calibration requirements for initial and continuing verifications

Compound	Soln. Conc. (ng/mL)	Labeled Compounds	
		ICAL	CCAL (%D)
$^{13}C_{12}$-2,3,7,8-TCDD	100	20% RSD	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	20% RSD	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	20% RSD	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	20% RSD	24 – 185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	20% RSD	21 – 178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	20% RSD	32 – 141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	20% RSD	28 – 130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	20% RSD	26 – 152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	20% RSD	26 – 123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	20% RSD	29 – 147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	20% RSD	28 – 136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	20% RSD	23 – 140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	20% RSD	28 – 143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	20% RSD	26 – 138
$^{13}C_{12}$-OCDD	200	20% RSD	17 – 157
$^{13}C_{4}$-2,3,7,8-TCDD	10	20% RSD	35 – 197

Appendix 20.9: Calibration requirements for initial and continuing verifications

Compound	Soln. Conc. (ng/mL)	Native Compounds	
		ICAL	CCAL (%D)
2,3,7,8-TCDD	10	20% RSD	78-129
2,3,7,8-TCDF	10	20% RSD	84-120
1,2,3,7,8-PeCDD	50	20% RSD	78-130
1,2,3,7,8-PeCDF	50	20% RSD	82-120
2,3,4,7,8-PeCDF	50	20% RSD	82-122
1,2,3,4,7,8-HxCDD	50	20% RSD	78-128
1,2,3,6,7,8-HxCDD	50	20% RSD	78-128
1,2,3,7,8,9-HxCDD	50	20% RSD	82-122
1,2,3,4,7,8-HxCDF	50	20% RSD	90-112
1,2,3,6,7,8-HxCDF	50	20% RSD	88-114
1,2,3,7,8,9-HxCDF	50	20% RSD	90-112
2,3,4,6,7,8-HxCDF	50	20% RSD	88-114
1,2,3,4,6,7,8-HpCDD	50	20% RSD	86-116
1,2,3,4,6,7,8-HpCDF	50	20% RSD	90-110
1,2,3,4,7,8,9-HpCDF	50	20% RSD	86-116
OCDD	100	20% RSD	79-126
OCDF	100	20% RSD	63-159

Appendix 20.10: Theory of CDPE Interferences

20.10 The theory of Chlorinated Diphenyl Ether (CDPE) interference is that because they are such similar compounds to Chlorinated Furans (CDFs), during ionization they will fragment into the exact CDF quant masses. This creates a potential for false positive CDF values.

For example, for potential PCDF interference, the HPCDPE mass 409.7974 is monitored. As evidenced by the spectra of HPCDPE, it can be shown that it will fragment into the PCDF quant masses 339.8597 and 341.8567, and it is impossible to measure exactly how much of the peak areas at those masses came from the CDPE fragment. The TCDF value must therefore be flagged as a false positive because there was a CDPE detected at the same retention time which will add to the PCDF quant mass peaks.

From the spectra of CDPEs it can also be determined that the area of the masses contributing to the CDF quant ions are generally 2-4 times the area of the respective CDPE molecular mass being monitored. The potential interference amount can then be estimated by multiplying the CDPE area by the factor of 2-4. Therefore, if the CDPE area is 2% of the CDF area, approximately 4-8% of the CDF area is likely from the CDPE contribution.

Appendix 20.11: Extract Dilution Procedure

20.11. Because of the unique nature of dioxin extracts, and the need to add injection standard at a specific ratio to the extract volume, they should be diluted as follows:

5X Dilution: 10 µL nonane, 10 µL IS, 5 µL sample
10X Dilution: 9 µL nonane, 9 µL IS, 2 µL sample

This procedure assumes the original extract had a final volume of 20µL, including 10 µL of internal standard. Multiple dilutions can be made to get higher dilution factors such as 25X or 50X. Also note that on- column values for target analytes in dilutions already have the dilution factor included, since they are calculated from the labels which have been diluted. Dilution values are normally very close to the values in the original extract, unless the original value was from a saturated peak.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Sulfide by Iodometric Titration

SOP 650S
Version 001

Revision Date: 11/30/16
Effective Date: 11/30/16

Prepared by:

Mike Perkins

Approvals:

Casey English, Laboratory Supervisor

Eric Larson, Inorganics Division Manager

Annual Review

SOP Number: _____

Title: _____

Revision: _____

Revision Date: _____

Effective date: _____

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

Name	Reviewer's Signature	Date

Standard Operating Procedure

Sulfide by IodometricTitration

1. Scope and Application

1.1. Sulfide in a water or soil sample exists in a variety of states dependent upon pH and redox potential of the sample matrix. Primary forms include H_2S, HS^-, $S^=$, and various metal sulfide complexes which vary widely in their degree of solubility. Preserved aqueous samples or distillates will have sulfide present in the form of a metal complex (zinc sulfide).

1.2. Sulfide can be analyzed by either direct iodometric titration or by the spectrophotometric methylene-blue procedure. The difference is one of sensitivity and detection limit. Titration can be used for higher levels of sulfide (>1.0 mg/L) while the spectrophotometric procedure must be used for concentrations <1mg/L. If samples are known to contain high levels of sulfide, it is more efficient and accurate to analyze them using the titrimetric procedure.

1.3. The iodometric titration procedure is applicable to the determination of total and dissolved acid soluble sulfide at concentrations in excess of 1 mg/L in drinking, surface, saline waters, domestic and industrial wastes, and in sample distillates. This procedure (along with potentiometric determination) is specified for distillates from the SW-846 9030 distillation for acid soluble and acid insoluble sulfides. The procedure is also specified for the standardization of stock sulfide solutions when used for the preparation of standards in the colorimetric analysis.

1.4. This SOP follows protocol as given in EPA 376.1, SW-846 9034 and Standard Methods 4500-S^{2-} F.

2. Summary of the Procedure

2.1. The iodometric method for the determination of sulfide is based upon the stoichiometric oxidation-reduction reactions that occur between sulfide and iodine in acid solution. Sulfide becomes oxidized to sulfur while iodine (I_2) becomes reduced to colorless iodide (I^-). A known amount of iodine is added to the test solution and allowed to react with sulfide under acidic conditions. Excess iodine remaining in solution is then titrated with sodium thiosulfate

reducing agent using starch or Thyodine indicator for the end point detection. Relevant reactions are:

$$H_2S + I_2 \text{ ----------> } S + 2I^- + 2H^+$$

$$I_2 + \text{thio}_{red} \text{ ----------> } 2I^- + \text{thio}_{ox}$$

Knowing the equivalents of iodine originally added to the solution (mL iodine X normality of iodine) and the equivalents of reducing agent (mL thio X normality thio) required to reduce the remaining iodine after reaction with sulfide allows for the calculation of sulfide by difference according to the following equation.

$$\text{mg } S^{=}/L = [(\text{mL } I_2 \text{ X N } I_2) - (\text{mL thio X N thio})] \text{ X } 16{,}000 \text{ / mL sample}$$

3. Detection Limit

3.1. The detection limit for the method is specified at 1 mg/L using the designated normality of the iodine and thiosulfate reagents. A concentration of 1 mg/L is coded into LIM's for the titrimetic procedure.

3.2. The actual detection limit is based upon the volume and concentration of reagents used and upon the resolution of the burette employed for the titration. The Class A burettes used are graduated in units of 0.05 mL with a resolution of 0.02 mL. Coupled with a 50 mL sample volume, 0.025 N iodine and 0.025 N sodium thiosulfate, the titration would yield a theoretical detection limit of 0.4 mg/L.

4. Definitions

4.1. Sulfide in a water or soil sample exists in a variety of states dependent upon pH and redox potential of the sample matrix. Primary forms include hydrogen sulfide (H2S), bisulfide (HS-), and various metal sulfide complexes which vary widely in their degree of solubility. Sulfide itself (S2-) is generally negligible due to the high dissociation constant of hydrogen sulfide. Preserved aqueous samples or distillates will have sulfide present in the form of a metal complex (zinc sulfide).

4.2. Total Sulfide includes soluble hydrogen sulfide (H_2S), dissociated HS^- and sulfides present as complexes within the suspended phase of the sample (generally metal complexes).

4.3. Dissolved sulfide is that sulfide remaining in solution after suspended solids have been removed. Dissolved sulfide can only be determined on samples that have not been preserved with zinc acetate.

4.4. Unionized hydrogen H_2S may be calculated from the concentration of dissolved sulfide, the sample pH and the ionization constant for H_2S.

4.5. Stoichiometry is the study and calculation of the quantitative relationships of the reactants and products in a chemical reaction. In general chemical reactions will combine in definite ratios of chemical elements. Stoichiometric relationships are those in which the reactants and products exist in direct proportion thus allowing calculation of one component from knowledge of the other.

4.6. Redox potential. The term redox comes from oxidation reduction potential (ORP) and is a measure of the electronegativity (Eh) of a system expressed in units of volts or millivolts. Redox potential is a measure of the tendency for a system to either gain or lose electrons when it is subject to change by introduction of a new species. A system with a higher redox potential (positive mv, oxidizing conditions) will have a tendency to gain electrons from new species (i.e. oxidize them and becoming reduced) and a system with a lower redox potential (negative mv, reducing conditions) will have a tendency to lose electrons to new species (i.e. reduce them and become oxidized).

4.7. 4.5. Preparation and Analytical batches. Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** (i.e. a sulfide distillation is involved) is composed of one to 20 environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. The twenty environmental samples do not include method blanks, LCS, matrix spikes or matrix duplicates. At a minimum, each batch must include a Method Blank, a Laboratory Control Standard mid-range on the standard curve, and a Detection and Quantitation Limit DQL) standard prepared at a concentration equal to the low curve point (0.05 mg/L). An analytical batch (i.e. just the colorimetric analysis) is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An **analytical batch** can include prepared samples originating from various quality system matrices and can exceed 20 samples (NELAC 2007. Quality Systems: General Requirements. The NELAC Institute, V1M2 CLN_IS_122807, December, 2007).

5. Interferences

5.1. Sulfides are highly volatile and subject to rapid oxidation to elemental sulfur and sulfate. Exercise care in the handling of samples to minimize atmospheric contact

5.2. Reduced compounds that react with iodine (e.g. sulfite, thiosulfate) will yield false positive results.

5.3. Turbid and/or intensely colored samples can interfere with the detection of the end-point for the titration.

5.4. Interferences can be removed by precipitation of sulfide using zinc acetate and then re-suspending the zinc acetate precipitate in clean de-oxygenated water.

6. Safety

6.1. Hydrogen sulfide gas is toxic. The gas can inhibit olfactory senses such that exposure to toxic levels may not be apparent to the exposed person(s). The gas can form sulfuric acid in solution leading to corrosive properties. The gas is toxic to fish and other aquatic organisms. There is a local (King County Metro) 10 mg/L sink disposal limit on solutions containing hydrogen sulfide.

6.2. Stock and Intermediate sulfide standards and samples with sulfide in excess of 10 mg/L should be oxidized prior to sink disposal. For oxidation, carry out the following operations:

6.2.1. Place spend standards and samples into a suitable I liter plastic beaker. Stir and test with lead acetate paper to confirm the presence of sulfide.

6.2.2. Treat with small additions of calcium hypochlorite (bleach) to oxidize the sulfide. Test with lead acetate paper to confirm absence of sulfide.

6.2.3. Dispose of the treated solution to the sink and flush with cold water.

6.3. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

6.4. Eye protection, gloves and lab coats should be worn when handling all samples, spike solutions, acids, caustics and other reagents. Safety glasses must be worn all the time in the Laboratory.

6.5. Use CAUTION with strong irritants such as acids, bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals.

6.6. Review the Laboratory Safety Manual and the Contingency Plans and Emergency Procedures for a Hazardous Waste Generator.

6.7. Use CAUTION with strong irritants such as acids, bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals.

6.8. There is a local (King County) 10 mg/L sink disposal limit on solutions containing hydrogen sulfide. Stock and intermediate sulfide standards should be oxidized prior to sink disposal.

6.8.1. Carry out the following operations in fume hood.

6.8.2. Place spent standards into a suitable 1 liter plastic beaker. Stir and test with lead acetate paper to confirm presence of sulfide (blacking of the paper).

6.8.3. Treat with small additions of calcium hypochlorite to oxidize sulfide. Test with lead acetate paper to confirm absence of sulfide (a negative test).

6.8.4. Dispose of the treated standards to the sink and flush with cold tap water.

6.9. All the non-hazardous wastewater can be dumped into sink if its pH range is 10 to 5. If it is not, the wastewater has to be neutralized before dumping. Review the Laboratory Safety Manual and the Contingency Plans and Emergency Procedures for a Hazardous Waste Generator.

6.10. Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

6.11. A reference file of material data handling sheets is kept in the office area, across from the entrance to the tech room (room A316J). Refer to this file for any material you handle. Update this file upon receiving new chemicals or reagents. The MSDS for many chemicals can also be viewed online, at http://hazard.com/MSDS/.

7. Equipment and Supplies

7.1. Routine laboratory glassware for titration.

7.2. Magnetic stirrer with Teflon stir bars

7.3. Volumetric flasks

7.4. Digital Buret (calibrated)

7.5. Glass Buret (Kimax, Class A, 10 / 0.05 mL)

7.6. Automatic Pipettors (calibrated)

8. Reagents and Standards

8.1. Oxygen-free deionized water. Prepare approximately 2 liters de-oxygenated deionized water (DDIW) by purging with an inert gas (nitrogen or helium) for 15 to 20 minutes. Use this de-oxygenated water to prepare stock, intermediate, and curve sulfide standards. Store in a tightly covered container (i.e. a 2 liter flask with Parafilm seal). The DDIW should be prepared daily. Some reagents and all sample dilutions should be made with DDIW. Open only when needed.

8.2. Hydrochloric Acid (6N). Carefully, and with mixing, add 500 mL conc. HCl to 400 mL deionized water. Allow to cool and bring to final volume of 1000 mL.

8.3. Sodium Thiosulfate (0.025N). Dissolve 6.205 grams $Na_2S_2O_3$ $5H_2O$ in 500 mL deionized water. Add 1.5 mL 6N sodium hydroxide and dilute to 1000 mL. Standardize daily against standard potassium bi-iodate solution

8.4. Potassium bi-iodate primary standard (0.025 N). Dissolve 0.8124 g $KH(IO_3)_2$ in deionized water and dilute to 1000 mL. Record the exact weight of salt used and the prepared volume (mL). Equivalents of bi-iodate = grams $KH(IO_3)_2$ / 32.495.

8.5. Potassium iodide (KI)**:** Iodine standard (0.025 N). Dissolve 20-25 grams potassium iodide (KI) in 500 mL DI and then add 3.2 g iodine (FW I = 126.9045), when the iodine has dissolved, dilute to 1000 mL. Store in amber glass bottle at room temperature, avoid direct sunlight. Standardize against the standardized sodium thiosulfate solution.

8.6. Thyodene Indicator (Fisher T138-100).

8.7. Sulfide Standard. Dissolve approximate 0.5 grams crystalline $Na_2S{\cdot}9H_2O$ (FW = 240.18, 13.35% S) in 100 mL DDIW. Standardize daily against standardized iodine/thiosulfate solutions. Record the exact weight of crystals used as a check on standardization. *NOTE: due to the deliquescent nature of sodium sulfide and the possibility of oxidized coatings on the surfaces of the crystals, you cannot accurately weigh the salt to obtain a value for the sulfide content of the standard solution. The sulfide stock solution must be titrated to determine its actual concentration. The value derived from the weight of salt used is an approximation only and should be around 0.6 mg/mL when prepared as directed.*

8.8. DQL Standard. This standard will be used to evaluate detection and quantitation limits according to protocol described in "DQFAC Single Laboratory DL-QL Procedure (Version 2.4). The initial QL standard will be set at a concentration of 1 mg/L. The benchsheet will calculate the volume of standardized sulfide to be added to 50 mL of de-oxygenated water for the preparation of the standard.

9. Sample Collection, Preservation, Shipment and Storage

9.1. See the Sulfide Distillation / Preservation SOP 640S.

9.2. Samples for "Total Sulfide" must be preserved at the time of collection. Unless the requested analysis is for soluble or dissolved sulfide, preservation of aqueous samples is accomplished in the field by the addition of zinc acetate resulting in the formation of slightly soluble zinc sulfide (a white colored precipitate). The pH of the sample must also be adjusted to greater than 9 with sodium hydroxide.

9.3. Sample bottles sent out to clients will contain the required volume of 2N zinc acetate (0.5 mL or 0.2 mL 2N /100 mL sample volume). To avoid the transport and usage of caustic chemicals by field personnel, sodium hydroxide is added once the samples are returned to the laboratory.

9.4. Upon receipt in the laboratory, the samples are adjusted to pH >9 using 6N sodium hydroxide. The lab must verify that the sample bottle is labeled "zinc acetate" and that the pH is >9. Laboratory personnel will add zinc acetate and sodium hydroxide as necessary.

10. Quality Control

10.1. Demonstration of Capability. Each analyst using this procedure must perform an initial "Demonstration of Capability" by preparing and analyzing 4 replicates of a QC Check Solution. The recovery (Accuracy) must be within ±10% with a relative standard deviation (Precision) less than 1%.

10.2. Method Detection Limit (MDL): MDL are determined as described in ARI SOP 1018S

10.3. Reagent Blank (Method Blank). The Method Blank for the Titration is provided by the analysis of DI water blanks during the course of sample analysis. If a distillation procedure is used for a given batch analysis, the method blank will also include a DI water blank run through all steps of the distillation. One method blank will be extracted for each batch of 20 or fewer samples.

10.4. Laboratory Fortified Blank (Blank Spike or laboratory Control Sample). The Blank Spike for the Titration is provided by the analysis of DI water spiked with known amounts of sulfide (approximately 15 mg/L). This standard is un-distilled and provides both Initial and continuing verification during the course of the analysis. If a distillation procedure is used for a given batch analysis, a 15 mg/L distillation standard will also be included. This standard is used to verify recovery through all steps of the batch analysis. An additional blank spike for DQL analysis will be prepared at a level of 1 mg/L for on-going analysis of Detection and Quantitation Limits. One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.

10.5. Matrix Spike (MS) and Matrix Spike Duplicate (MSD). Matrix spikes will be run for each of 1 in 20 client samples (5% spiking) or as requested by the client. These spikes will be used

to evaluate the accuracy (% Recovery) of the analysis relative to the sample matrix. Spiking will be at a level in the range of 1 to 10 times the sample background or at a minimum of 10 mg/L (10 times the detection limit at 1 mg/L). MSD's for the evaluation of the precision of the analysis (Relative Standard Deviation, RSD) will be run upon request of the client. Otherwise, precision of the analysis will be evaluated by the duplicate analysis of at least one client sample in twenty (5% duplication). Upon client's request one MS/MSD will be extracted for each batch of 20 or fewer samples, providing sufficient sample is available for the analysis.

10.6. Standards, Surrogate Standards. Not Applicable to Iodometric sulfide analysis..

10.7. For every set of samples (not to exceed twenty samples), a reagent blank, two lab fortified blanks and duplicate matrix spikes must be prepared. If there is insufficient sample available to prepare duplicate sample matrix spikes, prepare one reagent blank, two laboratory fortified blanks, and one matrix spike. If there is insufficient sample available to prepare a single sample matrix spike, prepare one reagent blank, two laboratory fortified blanks, and no matrix spike.

11. Calibration and Standardization

11.1. All determinations are documented on the Excel spreadsheet used for daily analysis.

11.2. Standardization of sodium thiosulfate against potassium bi-iodate. This titration would not be necessary if using commercially prepared, certified, 0.025N thiosulfate solution. However, if the normality of the thiosulfate solution came into question, it could be verified using this procedure.

11.2.1. Dissolve approximately 1 g potassium iodide (KI) in 50-100 mL DI contained in a 100 mL beaker.

11.2.2. Add 1 mL 6N HCl and 2 mL 0.025 N bi-iodate solution.

11.2.3. Dilute to 200 mL and titrate with the sodium thiosulfate solution. Calculate Normality of the thiosulfate as

11.2.4. mL bi-iodate X Normality bi-iodate / mL thiosulfate

11.2.5. Calculations are done on the bench sheet automatically. The value should fall within 10% of the prepared normality. If it does not, the bench sheet will flag the occurrence "Chk for Error" and the analyst should evaluate their procedure and/or prepare a fresh thiosulfate solution.

11.2.6. Conduct three replicate titrations and record data on bench sheet.

11.3. Standardization of iodine solution

11.3.1. Add 3 mL of the iodine solution and 0.5 mL of 6N HCl to a 125 mL Erlenmeyer flask

11.3.2. Titrate with standardized thio to light straw yellow color.

11.3.3. Add 1 scoop of thyodene indicator and continue titration to just remove the blue color. Record the mL of thiosulfate used and then repeat the titration 2 more times.

11.3.4. Normality is calculated from the mean of the three replicate determinations as:

Normality iodine = (mL thio X Normality thio) / mL iodine

11.4. Standardization of sulfide stock solution.

11.4.1. The standardization of the stock is based upon iodometric titration in which hydrogen sulfide (H2S) becomes oxidized to sulfur (S) while iodine (I2) becomes reduced to iodide (I-) according to the following reaction:

H2S + I2 ----> S + 2I- + 2H+

11.4.2. When the solution is titrated with standardized thiosulfate reducing agent, any iodine remaining in solution will be reduced to iodide while thiosulfate is oxidized to tetrathionate as follows:

Reduction of iodine: I2 + 2 S2O32- ----------> 2I- + S4O62

11.4.3. Knowing the equivalents of iodine originally added to the solution (mL iodine X normality iodine) and the equivalents of reducing agent (mL thiosulfate X normality thiosulfate) required to reduce any iodine remaining after reaction with sulfide allows for the calculation of sulfide (16 mg/meq) by difference, as follows:

mg S=/mL = {[(mL I2 X N I2) - (mL S2O32- X N S2O32-)] X 16} / mL sample

11.4.4. Proceed as follows:

11.4.4.1. Add 3 mL of standardized iodine solution and 0.5 mL of 6N HCl to a 125 mL Erlenmeyer titration flask. Add 50 mL deoxygenated DI water and mix.

11.4.4.2. Add 1 mL of the sulfide stock solution, mix gently and titrate with standardized thiosulfate to a light straw yellow color.

11.4.4.3. Add one scoop of thyodene indicator and continue titration to just remove the blue color. Record the volume of iodine and the mL of thiosulfate in the appropriate cells of the benchsheet.

11.4.4.4. Repeat the titration 2 more times. Sulfide concentration in the stock solution (mg S/mL) is calculated as the average of the three replicate determinations. This solution will be used for the preparation of the verification standard and for conducting matrix spikes.

12. Procedure

12.1. Obtain a copy of the Sulfide Titration Benchsheet. Manually record all data as you proceed through the analysis.

12.2. Fill the burette with sodium thiosulfate solution. Conduct the standardization routines as described above.

12.3. Prepare Calibration Verification and Distillation Check standards, as necessary, by entering the mL of stock standard added to a specified mL of DDIW water. Use the appropriate cells of the benchsheet to enter these data. Calculations are done automatically.

12.4. Analyze an initial undistilled, calibration verification standard and blank as prepared above. If distillation is used, run the distillation blank and standard as prepared above. Titrate as follows:

12.4.1. Add 3 mL of iodine and 0.5 mL of HCl to the titration flask.

12.4.2. Next add 50 mL of the blank or standard solution.

12.4.3. If the iodine color disappears, you must add additional iodine and record the total volume of iodine added.

12.4.4. Proceed with the titration by rapidly adding sodium thiosulfate to a light yellow color.

12.4.5. Add 1 or 2 scoops of thyodene and note the dark blue/Black color.

12.4.6. Gradually add thiosulfate to a light blue color. Continue dropwise addition to just discharge the blue.

12.4.7. Record all data and notes on the benchsheet. The sulfide concentration will be calculated upon entry of the data into the computer.

12.4.8. Confirm recovery of the verification standard within 10 percent of its prepared concentration.

12.5. Proceed with sample analysis only after successful analysis of the verification standard.

12.5.1. Add 3 mL of iodine and 0.5 mL of HCl to a clean titration flask.

12.5.2. Gently mix the sample to achieve a uniform distribution of any precipitate and add 50 mL to the flask. If a sample aliquot is diluted to 50 mL, you will enter the actual mL of sample used.

12.5.3. If the iodine color disappears, you must add additional iodine and record the total volume of iodine added.

12.5.4. Proceed with the titration as previously run.

12.5.5. Record all data and notes on the benchsheet: The sulfide concentration will be calculated upon entry of the data into the computer. If a sample returns a value < 1mg/L, the colorimetric procedure should be used and the benchsheet will flag it as "Use colorimetric analysis".

12.6. If distillation has been used to remove interference and/or concentrate the sulfide, enter the sample and distillation volumes (mL) in the appropriate boxes on the benchsheet, Sample concentration will appear in the column headed "Concentration if distilled" and is calculated as:

(mg/L distillate X mL distillate) / mL sample distilled

12.7. Matrix QC samples (duplicates and spikes) should have been prepared at the time the sample was distilled.

12.8. If distillation is not used, enter a zero in the "Distill Volume" column or leave it blank.

12.9. For each batch of samples or job number, process at least 1 duplicate and 1 spiked sample. The format sections of the benchsheet may be copied and pasted into the desired location on the benchsheet. Proceed as follows:

12.9.1. enter the sample ID, the "dup" and "ms" will be added automatically.

12.9.2. enter the mL of sample titrated and, if distillation was used, the mL of sample distilled.

12.9.3. Spiking will be conducted using the Stock Sulfide standard. Enter the mL of stock standard added, sample volume will be automatically assigned based

upon your entries above. Suggested spike levels are 0.2 mL of stock to 50 mL sample. In any event, the spike concentration should be in the range of 1 to 10 times the ambient background concentration.

12.9.4. RPD and % Recovery values will be calculated automatically. If any value is less than 1 mg/L, an "na" flag will appear.

12.10. After every 10 samples, process a blank and check standard. Finish every run with a final blank and check standard.

12.11. Enter data into computer. Place a copy of the computed data reduction into every Job File run. The original is placed in chronological sequence in the Methods file.

13. Review

13.1. The analyst verifies Service Request, reviews the SOP, obtains the appropriate benchsheets and proceeds with the analysis. A handwritten benchsheet is generated and the data are then entered into the computer for data reduction.

13.2. The final computer generated benchsheet, the handwritten copy and the distillation log (if run), are all placed into the job folder. A copy of the handwritten benchsheet and a copy of the final benchsheet are placed into the method folder in chronological sequence.

13.3. The analyst enters the data into LIMs to create the initial analyte worklist.

13.4. The supervisor reviews the job folder for completeness of analysis (all requested parameters have been run) and sufficiency of Quality Control.

13.5. The analysis package and LIMs worklist files are then reviewed by the Conventionals QA reviewer. Worklists are distributed and final LIMs report printed.

13.6. The final report is reviewed for accuracy and completeness and then signed by the Conventionals QA reviewer. The report is then delivered to the Project Manager

14. Data Analysis and Calculations

14.1. See “Calibration and Standardization”.

15. Method Performance

15.1. A detection and quantitation study will be conducted with undistilled Method Blanks and the DQL standard at 1 mg/L. These will be used to calculate the detection and quantitation limits for the analysis of sulfide using the tiitrimetic procedure. Calculated limits will be evaluated relative to the method specified limit of 1 mg/L.

16. Pollution Prevention

16.1. These procedures may result in the generation and identification of aqueous wastes having sulfide concentrations in excess of 10 mg/L. These will be collected and treated to oxidize contained sulfide prior to sink discharge.

17. Data Assessment and Acceptance Criteria for QC Measure

17.1. If the initial verification standard (ICV) and blank (ICB) are not within control limits (± 10% for the standard and <1.0 mg/L for the blank), the analysis will stop. The analyst will immediately re-analyze the out-of-control sample to confirm the original observation. If re-analysis returns an acceptable result, analysis will proceed. If re-analysis confirms the out-of-control condition the analyst must evaluate the source of the problem. New solutions (verification standard and/or blank) will be prepared and the verification repeated. Do not proceed with sample analysis until the titration has been verified.

17.2. If either the distilled standard or blank returns a value outside the respective control limits an error message will appear. Otherwise, the % recovery will appear. If the distilled standards are not within control limits, the analyst will first re-analyze the LCS sample distillate to confirm the out lying value. If confirmed, the error is most likely due to recovery from the distillation process (you should have just confirmed that the titration was OK!). In this case, all samples associated with that distillation batch are suspect. The analyst should notify the supervisor of the recovery error and allow the supervisor to determine whether the entire batch should be re-distilled. If insufficient sample remains, all samples associated with that distillation should be flagged with a warning regarding possible recovery error.

17.3. If any of the continuing verification standards or blanks returns an out-of-control value the analysis will be immediately stopped and the problem identified. The analyst should first re-analyze the standard or blank to confirm its outlying value. If confirmed, the analyst must re-standardize the reagents, verify the titration and re-analyze all samples preceding the out-of-control condition and after the last in-control condition. Samples must be bracketed by in-control verification standards and blanks.

17.4. For replicate analysis, if the RPD for duplicate determinations is greater than 20%, the analyst should re-analyze both samples to confirm the initial values. If either

concentration is less than 5X the detection limit, then the absolute difference between the two should be less than or equal to the detection limit.

17.4.1. If the out-of-control values are confirmed, consult the supervisor and process one additional replicate, as necessary. Report the results for triplicates along with the relative standard deviation (RSD) and note on the analyst's comment sheet triplicates were run due to the out-lying RPD.

17.5. If the matrix spike returns a value less than the titrated sample concentration, a new matrix spike should be prepared and distilled (as necessary) at a level of 1 to 10 times the sample concentration. If the matrix spike returns an out-of-control value, the analyst should first re-analyze the distillates to confirm the values. If the out-of-control values are confirmed, consult the supervisor and process an additional spike, as necessary. Report the results for both spikes along with the percent recovery and note on the analyst's comments sheet that additional spikes were run due to an initial outlying recovery.

18. Corrective Actions for Out of Control Events

18.1. As defined above

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

19.1. In the event of significant batch QC failure, analysis will stop and the analyst will perform corrective action as discussed above.

19.2. In general, sample data associated with out-of-control batch QC sample results (Method blanks, calibration verification and Laboratory Control Samples) will not be reported. Re-runs will be conducted based upon availability of sample volume. If insufficient sample remains or the remaining sample has been compromised by other withdrawals from the sample bottle or by holding time, the client will be notified to determine an appropriate course of action.

19.3. Batch analysis is not controlled by Matrix Specific QC and failing matrix QC does not reflect a failure in the analytical protocol. Failing matrix QC will be reported to the client along with supporting information as may be available to qualify the result.

19.4. All QC failures and associated corrective actions will be documented on the Yellow Corrective Action Sheets.

20. Waste Management

20.1. These procedures may result in the generation and identification of aqueous wastes having sulfide concentrations in excess of 10 mg/L. These will be collected and treated to oxidize contained sulfide prior to sink discharge.

21. Method References

21.1. EPA 376.1. Sulfide, Method 376.1 (Titrimetric, Iodine). Methods for the Chemical Analysis of Water and Wastes. EPA /600/4-79020

21.2. SW-846. Titrimetric Procedure for Acid Soluble and Acid Insoluble Sulfides, Method 9034, USEPA. Test Methods for Evaluating Solid Waste.

21.3. Standard Methods, 4500-S_2^- F-00. Iodometric Method. Standard Methods for the Examination of Water and Wastewater.

22. Appendices

22.1. Titrimetric Sulfide Excel Benchsheet

Appendix 22.1:

SULFIDE BENCHSHEET (TITRATION)						Date	Analyst		
SM 4500-S2- F-00 Iodometric Method					*Distillation*				
If distilled, specify Procedure:					*Finish*				
Buret used for titrations:									
CalibrationData					*ZnOAc:*				
1. Standardization of sodium thiosulfate titrant									
Thiosulfate ID:									
Bi-iodate ID:						*Titration of bi-iodate with thiosulfate*			
Stock bi-iodate =	**0.8116**	*grams to*	1000	*mL*	*mL bi-iodate =*	3.00	3.00	3.00	
Normality =	**0.025**				*mL thiosulfate =*	3.15	3.12	3.13	*nthio*
					*Normality thiosulfate = (mL bi-iodate*normbio) / mL thiosulfate =*	0.024	0.024	0.024	**0.024**
2. Normality of Iodine Soln						*Titration of Iodine with thiosulfate*			
Iodine ID:					*mL iodine =*	3.00	3.00	3.00	
					mL thiosulfate =	3.080	3.060	3.050	*ni*
					*Normality iodine = (mL thiosulfate*nthio) / mL iodine=*	0.025	0.024	0.024	**0.024**
3. Standardization (Sulfide Stock Solution)						*Titration of standard with thiosulfate*			
Stock ID =	**0066-9**				*mL Standard =*	1.00	1.00	1.00	
Approx conc in 100ml					*mL iodine =*	3.00	3.00	3.00	
g Na2S =	0.7626	*mg /mL =*	1.018		*mL thiosulfate =*	1.16	1.20	1.16	*stkconc (mg/mL)*
					*Sulfide (mg/mL) = {[(mL iodine*ni)-(mL thio *nthio)]*16} / mL standard =*	0.728	0.713	0.728	**0.723**
4. Verification Standard									
Add	1.0	*mL Stock to*	50	*mL DI water*	***CV =***	**14.5**	***mg/L sulfide***		
5. DQL Standard									
Add	0.1	*mL Stock to*	50	*mL DI water*	***DQL =***	**1.0**	***mg/L sulfide***	confirm	1.0
6. Distillation Standard									
Add	1.0	*mL Stock to*	50	*mL DI water*	***Dist Chk =***	**14.5**	***mg/L sulfide***		

SAMPLE DATA

Calculation: mg/L = [((mL I X N I) - (mL thio X N thio)) X 16,000] / mL sample

	DISTILL DATA		TITRATION DATA						
SAMPLE ID	Sample Volume (mL)	Trap Volume (mL)	Sample Volume (mL)	IODINE ADDED (mL)	Thiosulfate TITRANT (mL)	CONC (mg S/L)	Concentration If distilled (mg S/L)		
ICB	50.0	50	50.0	3.0	3.05	0.1	0.1		
ICV	50.0	50	50.0	3.0	1.10	15.0	15.0		*103.88%*
DQL	50.0	50	50.0	3.0	2.93	1.0	1.0		*102.03%*
Dist Blank	50.0	50	25.0	3.0	3.05	0.2	0.2		
Dist Check	50.0	50	25.0	3.0	2.10	14.7	14.7	102%	*101.94%*
CCB									
CCV									

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:

$\%\ Difference = \frac{RRF_i - RRF_c}{RRF_i} * (100)$
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

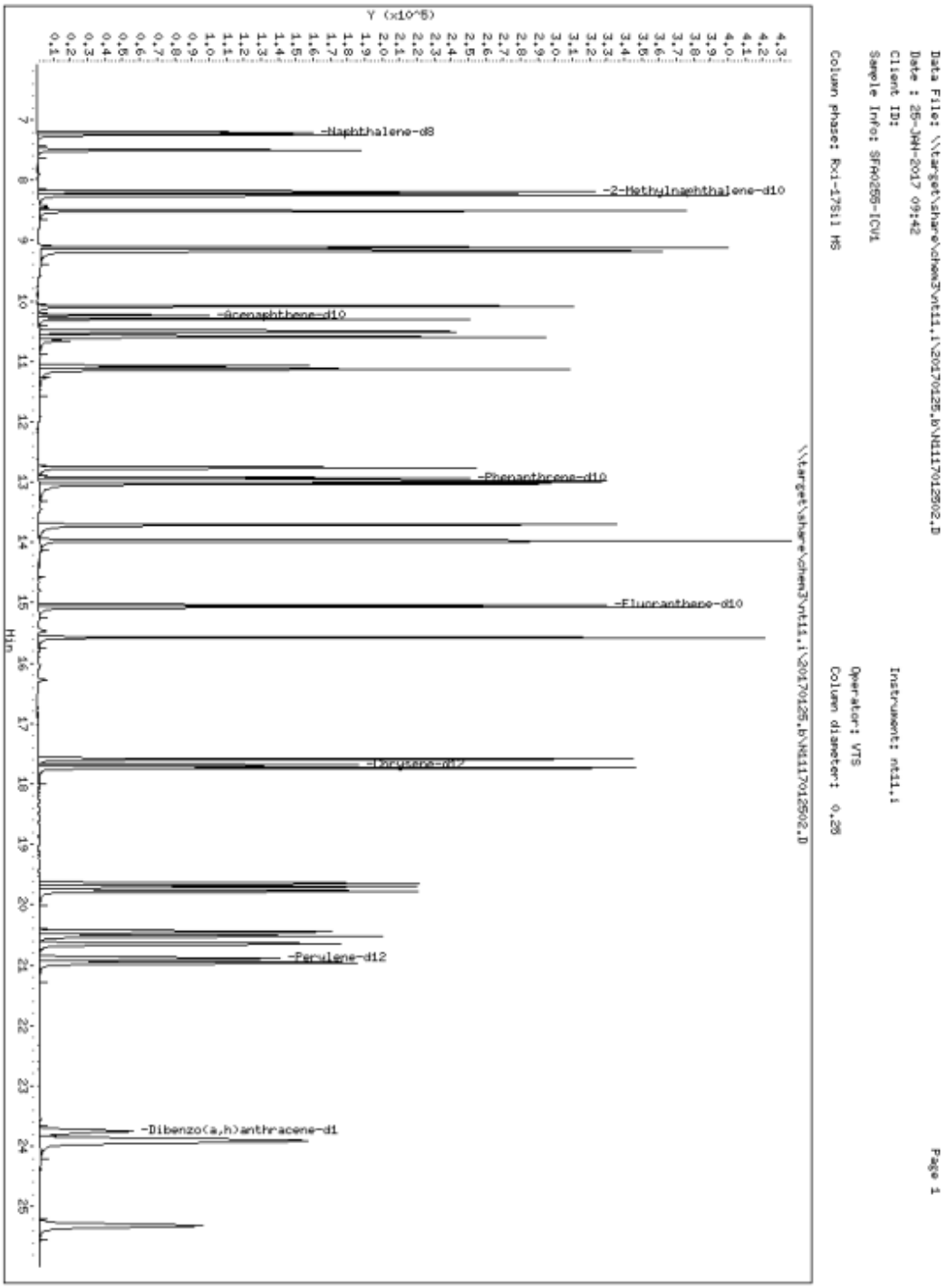
1 – A maximum of 2 compounds are allowed > 20%RSD .
2 – Compounds followed by (IS) are internal standards
3 – Compounds followed by (SS) are surrogate standards
4 – Optional Analyte
5 – This surrogate added only when Pentachlorophenol is a targeted analyte

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	17A0190-01		5	7.21	237737	10.23	144735	12.92	252088	17.69	245938	20.89	282243
7	1220	N1117012507.D	17A0190-02		1	7.21	220793	10.23	142050	12.92	276263	17.69	236409	20.89	259121
8	1252	N1117012508.D	17A0190-03		1	7.21	234838	10.23	150579	12.92	290487	17.68	261735	20.89	269272
9	1324	N1117012509.D	17A0190-04		1	7.22	211399	10.24	127812	12.92	218356	17.69	218439	20.90	260632
10	1356	N1117012510.D	17A0195-01		1	7.21	224142	10.23	148934	12.92	285573	17.69	239906	20.89	263386
11	1427	N1117012511.D	17A0195-02		1	7.21	230494	10.23	152661	12.92	293341	17.69	251162	20.89	271337
12	1458	N1117012512.D	17A0195-03		1	7.21	223053	10.23	147219	12.92	290845	17.69	248371	20.89	270876
13	1530	N1117012513.D	17A0195-04		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	17A0195-05		1	7.21	224053	10.23	130718	12.92	235703	17.69	229616	20.89	262068
17	1735	N1117012517.D	17A0195-06		1	7.21	220375	10.23	150175	12.92	297429	17.69	264403	20.89	292951
18	1806	N1117012518.D	17A0190-01		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

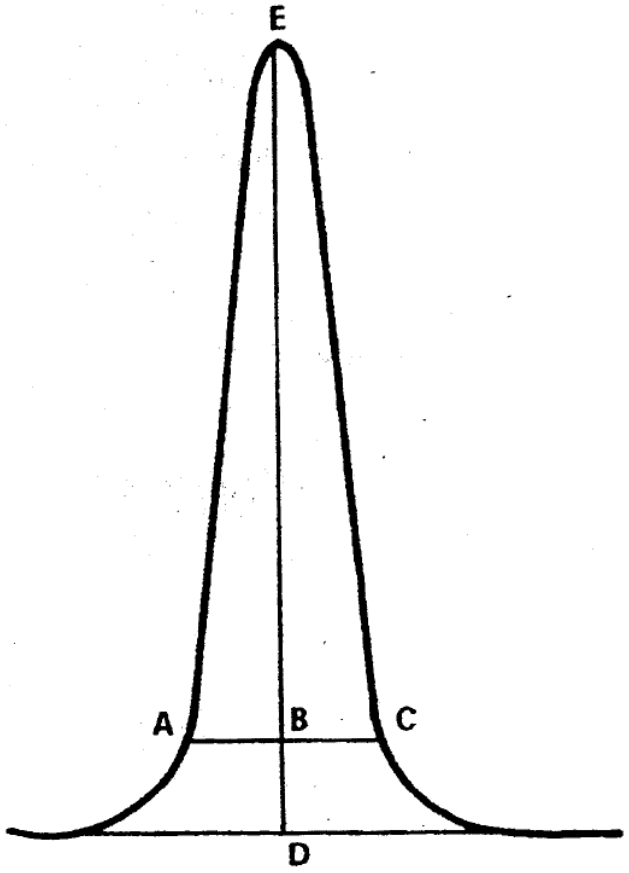
MANUAL INTEGRATION SUMMARY FOR DATABATCH - \\target\share\chem3\nt11.i\20170125.b

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.

Standard Operating Procedure

Carbon Analysis of Soil and Sediment

SOP 671S
Version 002

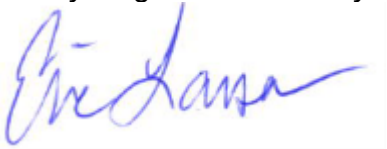
Revision Date: 5/24/2019
Effective Date: 5/24/2019

Prepared By:

Casey English

Approvals:

Casey English, Laboratory Supervisor



Eric Larson, Inorganics Division Manager

Annual Review

SOP Number: _____

Title: Carbon Analysis of Soil and Sediment

Revision: _____

Revision Date: _____

Effective date: _____

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 covers the determination of Total Carbon (TC), Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) in soils and sediments.

1.2. There are a number of procedures available for the analysis of Carbon in soils and sediments. Most of these have been reviewed by Schumacher (2002). The procedure used by ARI is Temperature-dependent and gas switching differentiation with IR detection of evolved carbon dioxide (CO2) using components of procedures specified by Plumb (1981), PSEP (1986, 1993),Pitt et al, (2003), EPA, LG601 (2005), DIN EN 15936, DIN 19539, DIN EN 13137, ISO 10694, (LECO, 1996, soot quantification method of Gustafsson et al. (1997), (Nelson and Sommers, (1996), Zimmerman et al, (1997) and Abstracts, (2003 Meeting of ASA, Denver, CO)

1.3. In Temperature-dependent and gas switching differentiation, the analysis is for TOC, TIC, TC and ROC (Elemental Carbon), separated by temperature and time coupled with gas switching techniques to separate TIC from ROC. Carbon will be converted to CO2 as a result of oxidative combustion. Complete combustion of inorganic carbonates requires temperatures in excess of 950 ºC while organic materials will generally combust at temperatures in excess of 500 ºC (Plumb, 1981).

1.4. The above reference methods for the analysis of carbon in soil or sediment samples are all similar. Each method addresses temperature dependent separation of TOC and TIC. Measurement of evolved organic carbon is dependent upon the capabilities of the analytical instrumentation and methods generally defer to the specific instrument manufacturer's instructions for detailed operating procedures and protocol. Methods vary with respect to the temperature used for organic and inorganic separation and the quantification procedures used. Our procedure follows the Elementar specified procedures. (Note: SW-846 Method 9060A is a procedure for the combustion analysis of TOC in aqueous solutions. It provides neither discussion of nor procedures for the analysis of organic carbon in soils or sediments).

1.5. We use an Elementar Soli TOC Cube Elemental analyzer with IR detection.

2. Summary of the Procedure

2.1. A soil or sediment sample received for Carbon analysis is evaluated, homogenized, and a representative aliquot (0.005 to 2.000 g) is taken and weighed into a clean crucible.

1.6. The sample is then dried at 70 ºC to remove excess moisture before analysis.

1.7. The sample is combusted with a temperature ramp of 90° K/min from ambient to 400°c in a nitrogen+oxygen gas flow producing a TOC peak. After a wait time of 240sec. The furnace then ramps up to 900°c and switches gas flow to pure nitrogen producing a TIC peak. After an additional wait time of 150sec, the gas is then switched back to Nitrogen+Oxygen to produce the

elemental carbon as ROC peak. At each of these hold points, the evolved gas from combustion is passed through a platinum catalyst to insure conversion of combustion products to CO2.

1.8. The gas then travels through a series of water traps and halide scrubbers to remove interfering components and into the CO2 sensitive infrared detector of the Soli TOC Cube where it is quantified as % carbon.

1.9. Samples which exceed the range of the standard curve are diluted with pre-combusted silica gel or Ottowa sand and then re-combusted for carbon determination.

1.10. Samples are processed independently for the determination of dry weight (percent solids at 104°C) then corrected for the standard dry weight at 104 ºC for reporting as percent carbon.

3. Definitions

3.1. The total carbon (TC) content of solids may be divided into inorganic and organic forms. Inorganic carbon (IC) consists primarily of carbonates or mineral complexes thereof, predominantly calcite ($CaCO_3$), aragonite (denser, more packed $CaCO_3$, the main component of mollusk shells), and dolomite ($CaMg(CO_3)_2$), among others. Total organic carbon (TOC) includes organics derived from the decomposition of plants and animals (naturally occurring organic matter or NOM) and organics derived from spills or releases of synthetic or natural contaminants to the environment. These may include both volatile and non-volatile species.

3.2. Preparation and Analytical Batches. NELAC (2011) defines Preparation and Analytical batches as follows: "*Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A* ***preparation batch*** *is composed of one (1) to twenty (20) environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An* ***analytical batch*** *is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.*" For TOC analysis, the preparation batch will be those samples which are processed together in an Element Batch. This will be limited to 20 samples which have gone through weighing and the drying steps of the preparation, as necessary. The analytical batch will be the actual combustion of the prepared samples for the determination of carbon which may include more than one preparation batch.

3.3. Analytical Blanks. Several types of blanks can be run during the analytical process.

3.3.1. Method Blanks (BLK). The Method Blanks consist of approximately 200mg of pre-combusted Ottawa sand which is processed along with each batch of samples. Method blanks

are used for verifying the absence of contamination through the preparation process and the calculation of Detection and Quantitation limits.

3.3.2. Crucible Blanks (Blank), Crucible blanks have no added solid material and can be processed as samples throughout the run to clean the crucibles or verify absence of contamination or carry-over. There is no need to document boat cleaning procedures.

3.4. Detection Limit (DL). The detection limit is that concentration of analyte that produces a response that can be considered significantly different from that of a "zero standard" or blank with a false positive rate (reporting the presence of analyte when it is absent) less than or equal to 1% (DQFAC, 2007). The DL must be based upon the Method Blank.

3.5. Method Detection Limit (MDL). The MDL is, "…the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero…", as defined in 40 CFR part 136 Appendix B. The MDL is conceptually equivalent to the DQFAC detection limit when determined using a low level standard.

3.6. Level of Quantitation (QL). That concentration of analyte that can be considered significantly different from the DL based upon statistical considerations and components of the calibration (DQFAC, 2007). The QL targets a false negative rate (reporting the absence of analyte when it is present) of 5%. The QL must be greater than the DL and at least equivalent to the lowest point on the standard curve. The QL serves as the reporting limit. Observed concentrations less than the QL will be reported as non-detects at the level of the QL. The QL must be based upon the complete analysis of a standard prepared at a concentration of at least 2 times the DL. The QL standard is prepared in pre-combusted, ground Ottawa Sand.

3.7. Calibration Verification Standard (CVS). A standard made from another source at a concentration within the calibration range. An independent source is defined as a source different than that used to make the calibration standards. This standard is run at the beginning of every sequence (Initial Calibration Verification) and then again after every ten samples processed (Continuing Calibration Verification). The CVS verifies the calibration, not the method.

3.8. Standard Reference Materials (SRM). These are sediment standards from the National Institute of Standards and Technology (NIST) that have "Reference Values", for the analyte being tested. Reference Values are non-certified values that NIST considers to be the best estimate of the true value of the analyte. These "Reference Materials" are used to verify recovery of a known concentration of carbon when run through the appropriate steps of the analysis.

3.8.1. NIST 8704 “Buffalo River Sediment” has an assigned reference value for Total Carbon (TC = 3.351 ±0.017 %C).

3.8.2. NIST 1941B, “Organics in Marine Sediments” has an assigned reference value for Total Organic Carbon (TOC = 2.99 ±0.24 %C).

4. Interferences

4.1. Sample homogeneity. Distribution of organic matter within a sample is critical for Carbon analysis (Schumacher 2002). This especially applies to solid phase samples. Samples must be thoroughly mixed and/or blended (homogenized) prior to withdrawing the sub-sample for analysis so that it accurately represents both the sample and the data needs of the client. Many sediment and some soil samples are fairly fine-grained and homogeneous such that sub-sampling is not a significant issue. However, many samples can be extremely heterogeneous, ranging from fine silts and sand to coarse rocks, shell fragments, and organic debris (roots, leaves, wood chips, etc.). Large inorganic particles (greater than 2mm) are generally inert and do not contribute significantly to the Carbon content (Schumacher, 2002). From a practical point of view, large organic debris, rocks, gravel, and shell fragments would be difficult to accurately sub-sample and process. Organics of significance are generally associated with the finer grained materials so that inclusion of coarse organic elements may bias the observed result and data objectives of the client (Schumacher, 2002). However, such particles may also be covered by significant organic surface films of detritus and periphyton which may or may not be of interest to the client. Removal of coarse elements from the sample may or may not be in line with the objectives of the client. The Project Manager should be consulted prior to commencing analysis on heterogeneous samples so that they may discuss acceptable protocol with the client and other labs that may be processing the same sample (e.g. if Carbon data is being used for carbon normalization then the sample base for all affected analytes should be equivalent). Exclusion or inclusion of coarse elements from any sample should only be conducted upon the direction of the project manager and, preferably, the 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.

4.2. Volatiles - Volatile organic carbon will be lost from the sample matrix as a result of oven drying. We are unaware of any readily available procedure for including the volatile content in the TOC analysis of soils or sediments without adding significant time and expense to the analysis. Additionally, Carbon is generally expressed on the basis of sample dry weight at 104 °C. To reduce the temperature related loss of volatile organics, solid samples are dried at 70 °C with the analysis conducted on the dried sample. A separate aliquot of sample is taken for the analysis of percent solids at 104 °C which is used for conversion to the 104 °C dry weight basis.

4.3. Oily Samples. Oily samples and/or those containing petroleum residues present significant problems for Carbon analysis in that they may not dry properly at 70 °C and may be subject to significant loss of volatiles. Additionally, they will likely require significant dilution to fit within the range of the standard curve. Such samples should be analyzed on an "as received" basis (i.e. no correction for dry weight) with a known weight of sample being diluted directly to pre-combusted silica gel or Ottowa sand. The PM should be contacted prior to beginning the analysis of these kinds of samples.

5. Safety

5.1. The procedure for Carbon involves high temperature combustion of sample aliquots. Use caution and common sense when working around or replacing components of Soli TOC Cube.

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.

Environmental Samples may contain hazardous materials; always treat them as potential health hazards.

Use CAUTION with strong irritants such as acids, bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals. Avoid contact of these irritants with skin and clothing by appropriate use of gloves, apron, face–mask, hood shield, etc. Safety glasses must be worn all the time in the Lab.

Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

1.11. All safety procedures outlined in the laboratory Chemical Hygiene Plan must be following.

1.12. 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 the SDS for all chemicals handled. SDS are also available online at www.msdshazcon.com, as linked on the ARI intranet.

6. Equipment and Supplies

1. General supplies and glassware

6.1. Carbon analyzer, Elementar Soli TOC Cube

6.2. Combustion catalyst. Platinum (Elementar S05 001 380)

6.3. Stainless Steel crucibles (Elementar S03 002 278)

6.4. Cotton wadding (Lohmann & Rauscher REF 10 111)

6.5. Brass Wool (Elementar S38.00-0124)

6.6. Quartz wool (Elementar S03 679 908)

6.7. Corundum balls (Elementar S50 008 467)

6.8. Sicapent (Elementar S03 960 352)

6.9. Drying oven. Maintained at 70 ±2 ºC.

6.10. Analytical balance (accurate to 0.0001g)

6.11. Nitrogen (99.995% pure)

6.12. Ultra pure oxygen (99.995% pure)

7. Reagents and Standards

7.1. All stock chemicals, reagents, standards, and standard solutions must be entered into the Element database at the time they are received and/or prepared. Element will assign a unique identifier to each chemical and prepared solution.

7.2. Organic Carbon Standard. Cellulose (44.44% Carbon by weight). (MP Biomedicals P/N:0219149980 or similar (Assay >95% pure))

7.3. Inorganic Carbon Standard. Calcium Carbonate (12.01% Carbon by Weight). (Elementar P/N: B35.00-0155 or similar (Assay >95% pure))

7.4. Elemental Carbon Standard. Carbon (99.95% pure Carbon by weight). (Aldrich P/N: 484164-10g or similar (Assay >95% pure))

7.5. Calibration Verification Standard (Elementar S05 005 345 TOC/TIC/TC standard or similar)

7.6. Standard Reference Material (SRM). Due to the high cost of these SRM's, they will be processed only upon client request.

7.7. The TOC SRM is, NIST 1941B, "Organics in Marine Sediment" with a reference TOC content of 2.99 ± 0.24 %C (range of 27,500 to 32,300 mg/kg).

7.8. The TC SRM is NIST 8704, "Buffalo River Sediment" with "Reference Value" for TC in the range of 3.351 ±0.017 %C. NIST 8704 is used only when Total Carbon is the requested analyte.

7.9. Ottawa Sand (or equivalent), washed, ground, and ignited (EMD SX0075-1, Fisher MSX0075-1).

7.10. While Ottawa Sand is stated to be "washed and ignited", it will be washed and pre-combusted at 950 °C for at least 2 hours before being used to prepare the method blank and for standard and sample dilution.

7.10.1. Place 400g of Attowa sand into the ball mill and grind to a fine powder over the course of a few days. The mill must be checked to be sure grinding is sufficient to continue to the combustion step.

7.10.2. Transfer the ground sand to a container (stainless steel or porcelain evaporating dish) suitable for combustion.

7.10.3. Combust in the muffle furnace at 950 °C for at least 2 hours to remove any residual carbon.

7.10.4. Allow the furnace to cool to a reasonable temperature to be safely removed from the furnace and then finish cooling to room temperature under desiccation.

7.10.5. After completely cooled to room temperature, transfer to a tightly closed glass container and store in a desiccator. The container should be labeled and dated.

7.11. DQL Standard. This is a low-level standard prepared by spiking pre-combusted and ground Ottawa Sand with the standard of the analyte to be analyzed to a concentration of approximately 200 ppm (0.02%C). Actual concentration will vary relative to gravimetric parameters at the time of preparation.

7.11.1. The sand and standard mixture must be thoroughly homogenized in order to achieve a uniform, homogeneous, mixture of the sand and standard. Very important! Grind the sand to a very fine powder and mix thoroughly before use. Then transfer to a tightly closed glass container and store in a desiccator. The container should be labeled and dated.

7.12. The DQL standard and the Ottawa Sand blank should be run with each analytical batch.

8. Sample Collection, Preservation, Shipment and Storage

8.1. The carbon concentration of collected samples can be altered due to microbial degradation, chemical oxidation and volatilization due to physical processing (drying and selective removal of materials) prior to analysis (Schumacher, 2002). All of these factors should be taken into consideration when handling samples for analysis and interpreting results from that analysis.

8.2. Samples can be collected in clean, either glass or plastic, jars with Teflon® lined caps

8.3. Analytical holding times vary relative to author and the treatment of the sample. In general, samples should be processed within 14 days (Lloyd Kahn, 1988; Fox, 1991) but some extend this to 28 days (Schumacher, 2002) or, if frozen, 6 months (PSEP, 1986). ARI uses a holding time of 14 days for prepping un-frozen samples, extending this to 6 months if samples are frozen.

8.4. Sub-sampling to achieve a representative aliquot can have a significant impact upon the resulting concentration (**Read Section 4.2 for a discussion of the influence of sample heterogeneity**). Sample processing should be discussed with the PM prior to commencing analysis for non-routine matrices. Ideally, the client will have removed, at the time of collection, coarse elements and artifacts they do want included in the analysis. Occasionally, ARI will receive multiphase heterogeneous samples. Do not process multiphase samples without specific, documented instructions from ARI's Project Manager and/or Client.

9. Quality Control *(Essential QC components following 40 CFR Part 136.7, May 18, 2012, EPA 2012 Method Update Rule.)*

9.1. Demonstration of Capability. *Each analyst using this procedure must run an initial "Demonstration of Capability" by preparing and analyzing 4 replicates of a NIST standard reference material (SRM). The recovery (Accuracy) must be within the expected range of the standard with a relative standard deviation (Precision) less than 20%. An on-going DOC will be provided by the analysis and recording of the SRM for each batch of carbon analyses conducted..*

9.2. Method Detection Limit. *The detection limit for this procedure has been determined by on-going analysis of Ottawa Sand Method Blanks following the protocol of the Federal Advisory Committee on Detection and Quantitation Procedures (FACDQ10-13, August 2007).*

9.3. Method Blank (BLK). *As documented in this SOP.*

9.4. Laboratory Blank Spike (BS). A matrix blank spiked with a known concentration of the analyte to be tested.

9.5. Matrix Spike (MS) and Matrix Spike Duplicate (MSD as required). *As documented in this SOP.*

9.6. Calibration. *As documented in this SOP.*

9.7. Control charts for trend analysis. *As documented within Element LIMS system.*

9.8. Corrective action (root cause analysis). *As documented in this SOP*

9.9. QC acceptance criteria. *As documented in this SOP.*

9.10. Definition of preparation and analytical batches. *See section 3.2.*

9.11. Frequency for conducting QC elements. *QC samples will be run with each batch of samples as defined above.*

9.12. Quality control is provided by the analysis of blanks and standards at the level of instrumental calibration and sample preparation. Standard Reference Materials will be inclusive of all preparation steps as appropriate to the analyte being measured.

9.13. Negative control, the absence of carbon background or contamination, is provided by the analysis of crucible blanks and the calibration verification blanks. Method Blanks, prepared with pre-combusted Ottawa Sand, will be run to verify absence of contamination through the procedure.

9.14. Positive control within the level of calibration is provided by the recovery of carbon from a second source carbon standard. The source of this carbon standard is different from that used for instrument calibration and hence it serves as a calibration verification standard.

9.15. Two Standard Reference Materials (SRMs) are available. One, NIST 8704, Buffalo River Sediment) has a reference value for Total Carbon and the other, NIST 1941B, Organics in Marine Sediment, has a reference value for Total Organic carbon. NIST 8704 is used only when Total Carbon is the requested analyte. NIST 1941B (Organics in Marine Sediments) is the routine SRM for TOC.

9.16. Quality control with respect to the sample matrix is provided by the analysis of replicate and matrix spike samples. Review the service request to identify any client specific QC requests *(e.g. specific samples to be used, number of replicates, number of spikes*). Normally, duplicate analysis (duplicate withdrawals from the original sample jar) on a single sample from within each client batch of 20 or less samples will be run. If more than 20 samples or if matrices differ significantly, additional sample replicates may be required.

9.17. Replicate aliquots are taken from the original sample jar (*after removal of any non-representative material*). The replicates are used to evaluate both the precision of the analysis and heterogeneity in the distribution of carbon in the original matrix. Batch analysis will not be controlled by measures of dispersion (*relative percent difference or relative standard deviation*) due to the potentially inherent variability of soil or sediment samples. Rather, measures of dispersion will be reported to the client so that they may evaluate how closely the reported values represent the actual concentration of carbon in the sample submitted for analysis.

9.18. Matrix spikes. One additional aliquot from the same sample (*after removal of any non-representative material*) used for replication will be taken for matrix spike analysis. Batch analysis will again not be controlled by the result of the matrix spike. The matrix spike will be used to

evaluate the accuracy of the analysis and the influence of the matrix and sample processing upon the observed carbon content. Spiking will be conducted by adding a known weight of standard to a known wet weight of sample (prior to drying). Clients may sometimes request Matrix Spike duplicates (MSD) in order to provide estimates for both accuracy and precision on a single sample matrix.

10. Calibration and Standardization

10.1. Carbon standards are prepared at known concentrations as indicated by the equipment manufacturers guidelines.

10.2. A standard curve is derived from least squares linear regression of the output peak area as a function of the known carbon injected.

10.3. The carbon for dry sample combustion is calculated from the regression slope and intercept statistics.

10.4. Calibration procedure. Calibration consists of two steps, defining the standards on the curve and then analyzing them. Calibration should be conducted if major maintenance is performed and/or upon confirmed failure of calibration verification standards.

10.5. Consult the Software User manual for Defining the Standards.

10.6. Cleaning the crucibles. Crucibles should be pre-combusted to remove all traces of organic residue that might be present after cleaning. Crucibles will be placed into a stainless steel pan and combusted at 900°C for at least 30 minutes to remove all carbon residuals. Store the crucibles in a covered container while they are not being actively used.

10.7. Running the Standards. Consult the Software User manual.

10.8. The Correlation Coefficient (r) for the curve (or for each curve if using the split curve function) should be greater than 0.995. The instrument returns the Coefficient of Determination (r) and this must be greater than 0.995 to satisfy the requirement for r (r^2 = 0.990 equals r =0.995). If it is not, evaluate the curve to determine if any of the injections depart significantly from the line of best fit. Uncheck the questionable standard and recalculate the curve. If the r value is greater than 0.995 the curve is acceptable.

11. Procedure

11.1. The Ottawa Sand BLK and the MRL Standard should be prepared along with each batch of samples being processed. The sand has been pre-combusted and stored in a desiccator (see Section 7.7). The DQL standard has been prepared and stored in a desiccator. Take

approximately 0.2 gram of the blank sand and the DQL standard and process them along with the samples.

11.2. The SRM (NIST 1941 B for TOC, and NIST 8704 for TC, see Section 7.6) only needs to be run when requested by the client.

11.3. Initial Sample processing: The analyst should carefully evaluate the sample prior to preparation and identify its color, predominant grain size (percent gravel, sand, silt, clay or combinations of these) and the presence of any artifacts or inclusions. These characteristics should be used to determine the likely appropriate amount of sub sample required for the analysis and should documented on the analysts Green Sheet, as appropriate for anomalies.

11.4. In general, coarse elements (large rocks or shell fragments) which are either too large to fit in the crucible, or are not representative of the bulk of the sample might be excluded. Contact the PM if there is any ambiguity as to what should or should not be included in the sample aliquot taken for analysis. Do not exclude or remove any coarse elements unless there is documented authorization from the PM and/or client.

11.5. Obtain clean crucibles for the sequence QC, Batch QC, and for each sample. Enter the sequence, batch, and sample ID's into the instrument sequence screen then place a clean crucible in the balance and tare the balance. Transfer 0.005 to 3.000 grams (*depending on expected concentration*) of the well homogenized sample (*after exclusion of any coarse elements*) to the crucible, and weigh (x.xxxx grams) by pressing the print button on the balance. This will record the result as the sample wt.(g) for analysis into the instrument sequence.

11.6. Take at least one sample, from each batch of client's samples, for batch QC analysis. Spike by adding a known weight of standard at the desired concentration for the sample (~0.0300 for unknown samples) to the wet weight of sample in the crucible. Record the weight of the standard used to "memo" column of the sequence.

11.6.1. (Spike weight(g) X %C of spiked standard)/(weight of sample(g)) = %C spiked.

11.7. Transfer the crucibles to a drying oven set at 70 ±2 ºC. Samples must be dry enough not to introduce a significant moisture content to the instrument. Residual moisture will be removed during analysis by the Sicapent dryer tube.

11.8. Remove crucibles from the oven and transfer to the autosampler. Store dried samples in a desiccator if they will not be analyzed immediately.

11.9. To set-Up, Elementar Soli TOC Cube. Follow the instructions in the Short manual for packing, installation and conditioning of the combustion tube, catalyst, filter, absorber, drying tubes, and for proper initialization of the instrument.

11.10. Sample Analysis. Refer to the User manual for operation instructions.

11.11. Begin each sequence with at least 1 crucible burn, and 2 daily factor samples for the analyte(s) to be analyzed.

11.12. Samples may not be entirely homogenous. If a particular burn looks out of line with other samples within the batch, it would be advisable to re-run the sample to confirm. Process a third replicate for any suspect sample.

12. Review

12.1. The supervisor reviews the Service Request, enters information into the Conventionals database and assigns samples to the analyst.

12.2. The analyst verifies Service Request, reviews the SOP, and any special workorder/project special requests, and proceeds with the analysis.

12.3. The Analyst enters data into the Element LIMS system and checks the entered data for errors and completeness before setting the status to Analyzed.

12.4. Peer review is then performed on the final data and it is again checked for errors and status will continue to Peer Reviewed.

12.5. The supervisor or lead analysts then review the final generated results. Upon satisfactory review Status is then changed to Reviewed and data is ready for release by the project manager.

13. Data Analysis and Calculations

13.1. The Soli TOC Cube results are exported as %C Wet. No further calculations are required before entry to the Element LIMS system. Final results will be calculated on a dry weight basis at 104°C within the Element LIMS system.

13.2. Calculations performed by the instrument:

Absolute element content
a = absolute element content in [mg]
w = sample weight in [mg]
c = element concentration in [%]

$$a = \frac{w * c}{100}$$

Calibration coefficient
y = absolute element content in [mg]
a...e = calibration coefficients
x = peak area

$$y = a + b*x + c*x^2 + d*x^3 + e*x^4$$

Daily factor
f = daily factor
c_{theo} = theoretical element concentration
c_{act} = element concentration computed actually

$$f = \frac{c_{theo}}{c_{act}}$$

Element concentration of analysis samples
c = element concentration in [%]
a = absolute element content in [mg]
f = daily factor
w = sample weight in [mg]

$$c = \frac{a * 100 * f}{w}$$

factor for polynomials of the 1st degree
r^2 = correlation coefficient
x_i = peak area of the corresponding sample
y_i = absolute content of the corresponding sample
n = number of samples
i = index from 1 to n

$$r^2 = \frac{\left[\sum(x_i y_i) - \frac{(\sum x_i \sum y_i)}{n} \right]}{\left[\sum x_i^2 - \frac{(\sum x_i)^2}{n} \right] \left[\sum y_i^2 - \frac{(\sum y_i)^2}{n} \right]}$$

Blank value determination
$\bar{b}$ = blank value
b_i = peak areas of the individual blank samples
n = number of blank samples
i = index from 1 to n

$$\bar{b} = \frac{\sum b_i}{n}$$

Blank value compensation
a_{comp} = compensated peak area
a = measured peak area of the sample
$\bar{b}$ = blank value

$$a_{comp} = a - \bar{b}$$

14. Method Performance

14.1. Detection and quantitation studies are conducted following protocol as outlined by the Federal Advisory Committee on Detection and Quantitation Procedures (DQFAC DQ10-13, 8/31/2007).

Analysis for Method Blanks and spikes at the Quantitation Limit are conducted with each analytical run. Data are evaluated after each run and summarized on an annual basis.

15. Pollution Prevention

15.1. Not Applicable.

16. Data Assessment and Acceptance Criteria

16.1. For each burn, the % carbon value will be compared to the high and low values for the standard curve. If the value is greater than the high curve the burn will be flagged by the software as C1=TOC400, C2=ROC900, C3=TIC900.

16.1.1. If the value is below the low curve the burn will be flagged “C#u” (# being the analyte defined by the instrument).

16.1.2. If the value is above the high curve, the burn will be flagged “C#o”. the analyst must either use a smaller sample weight for combustion or use a dilution. If the burn result is below the low curve point, the analyst should increase the burn weight.

16.1.3. The weight of the sample analyzed can bias sample results by decreasing precision of lower concentration samples if not analyzed at an appropriate volume. If the result for a sample is <5x the RL, and the weight burnt was <0.5g, the sample should be re-analyzed at a higher burn weight to produce a more accurate result.

16.2. Initial Calibration Verification (ICV) and Calibration Blank (ICB) must be run at the beginning of each sequence. Continuing Calibration Verification standards and blanks (CCV, CCB) must be run after every ten analytical samples in the sequence and at the end of each run. The calibration verification standards must agree within ±10% of the "true" value and the concentration of the blanks should be less than the Reporting limit (½ the RL for DoD).

16.3. Blank (BLK) must be run with each batch. Result should be less than the Reporting limit (½ the RL for DoD).

16.4. Blank Spike (BS) must be run with each batch. Controle limits for the BS are ±20%.

16.5. SRM samples are processed along an analytical batch when requested by the client. The TOC SRM is, NIST 1941B, “Organics in Marine Sediment” with a reference TOC content of 2.99%. The TC SRM is NIST 8704, “Buffalo River Sediment” with “Reference Value” for TC of 3.351%C. Control limits for either SRM are ±20%.

16.6. Triplicate analysis. One sample per batch of 20 samples or job is prepped and analyzed in triplicate. The RSD is calculated within LIMS. Ideally, the value for the RSD should be less than

20%. Due to the inherent variability of Carbon in solids, we do not control on the RSD and no corrective action will be taken other than to advise the PM and client of the variability.

16.7. Matrix Spikes. One sample per batch of 20 samples or job is prepped and analyzed as a matrix spike. The appropriate spike is added to the wet sample and is processed through all steps of the analysis. Ideally, the spike recovery should be 75 -125% of the added concentration. Again, due to the inherent variability of TOC in solids, we do not control on the matrix spike recovery and no corrective action will be taken other than to advise the PM and client of the recovery and probable causes for excessively low or high values.

17. Corrective Actions for Out of Control Events

17.1. If Initial Calibration Verification (ICV) or Initial Calibration Blank (ICB) are out of QC limits, new calibration standards or new ICV solution should be made and the instrument re calibrated. If the Continuing Calibration Verification (CCV) or Continuing Calibration Blank (CCB) are out of QC limits, all samples not bracketed between in control condition must be re-run.

17.2. If results are outside the limits, the supervisor will review the entire procedure with the analyst to verify that correct procedures are being followed or check the instrument to make sure it is working properly.

17.3. If the SRM is not within 75-125% of its “true” value, it will be re-run to confirm the outlying condition. If confirmed, the analyst should verify operating conditions with respect to cleanliness of the crucibles, accuracy of the weight of sample combusted and dry status of the SRM. Re-run the SRM after verifying proper operating conditions and note the condition on the Corrective Action form. The SRM is prepared with the batch and therefore the batch samples will be controlled based upon the recovery value and the batch will be re-prepped.

17.4. If any of the following situations arises, the supervisor will be immediately notified, and the project manager be informed for resolution with the client:

17.4.1. The original sample contains excessive large coarse elements.

17.4.2. Samples have exceeded holding times.

17.4.3. There is insufficient sample to run the analysis.

18. Contingencies for Handling Out of Control or Unacceptable Data

18.1. 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 entered into the LIMs system but set to non-reportable. Re-runs will be conducted based upon availability of sample volume. If insufficient sample remains or the remaining sample has been compromised

by modification of the remaining sample volume or by holding time, the client will be notified to determine an appropriate course of action.

19. Waste Management

19.1. There are no known hazardous chemicals associated with this procedure.

20. Method References

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20.4. Plumb, R.H., 1981. 'Procedures for Handling and Chemical Analysis of Sediment and Water Samples". USEPA, USACOE. Environmental Laboratory, USAE, Waterways Experiment Station.

20.5. PSEP 1986. Recommended Protocols for Measuring Conventional Sediment Variables inPuget Sound. March 1986. (Minor Corrections April 2003). Total Organic Carbon (TOC).

20.6. PSDDA Clarification Paper. K. Bragdon- Cook. 1993. Recommended Methods for Measuring TOC in Sediments

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20.8. WSDOE. 2009. Quality Assurance Project Plan. The Puget Sound Assessment and Monitoring Program: Sediment Monitoring Component. Washington State Department of Ecology. PublicationNo. 09-03-121.

20.9. NELAC (2011). TNI Standard. Volume 1. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute. Publication EL-V1-2011.

20.10. EPA LG601 2005. Standard Operating Procedure for Analysis of Total Organic Carbon in Sediments (Dry Combustion, IR Detection). EPA, Great Lakes National Program Office. Revision 04, March 2005.

20.11. Test Methods for Evaluating Solid Wastes. EPA, SW-846. Volume 1C. Method 9060A. Rev. Nov. 1990.

20.12. DQFAC, 2007. DQFAC Single Laboratory DL-QL Procedure (Version 2.4). Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs.

20.13. DIN EN 15936 - Sludge, treated biowaste, soil and waste – Determination of total organic carbon (TOC) by dry combustion.

20.14. DIN 19539 - Investigation of solids — Temperature-dependent differentiation of total carbon.

20.15. DIN EN 13137 - Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments.

20.16. ISO 10694 - Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis).

20.17. Pitt, J.L., T.L. Provin, F.M. Hons, F. Dou, and J.S. Waskom.

20.18. Abstracts, 2003 Meeting of ASA, Denver, CO.

20.19. Elementar 2018 Soli TOC Cube Operation Manual.

21. Appendices

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Chlorinated Pesticides
EPA Method 8081B

SOP 423S
Revision 019

Revision Date: 2/11/2020
Effective Date: 2/11/2020

Prepared by:
Van Spohn

Approvals:

Brian N. Bebee, Laboratory Section Manager

David R. Mitchell, Quality Assurance Manager

Annual Review

SOP Number: 423S

Title: Chlorinated Pesticides EPA Method 8081B

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 used by Analytical Resources Inc. (ARI) to implement EPA Method 8081B for qualitative and quantitative analysis of sample extracts for organo-chlorine pesticides. This SOP is written to meet the requirements of EPA Method 8081B Revision 2, November 2000 and EPA Method 608. Specific requirements for Method 608 are listed in Appendix 20.4 when required.

1.1.1. Routine analytes for this procedure are listed in Table 01:

Table 01

Compound / Analyte Name	CAS Number
Aldrin	309-00-2
alpha-BHC	319-84-6
beta-BHC	319-85-7
delta-BHC	319-86-8
gamma-BHC (Lindane)	58-89-9
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
cis-Chlordane	5103-71-9
trans-Chlordane	5103-74-2
Dieldrin	60-57-1
Endosulfan-I	959-98-8
Endosulfan-II	33213-65-9
Endosulfan Sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Methoxychlor	72-43-5
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3

1.1.2. Additional single component analytes may include those listed in Table 02:

Table 02

Compound / Analyte Name	CAS Number
2,4'-DDD	3424-82-6
2,4'-DDE	53-19-0
2,4'-DDT	789-02-6
Oxychlordane	27304-13-8
trans-Nonachlor	39765-80-5
cis-Nonachlor	5103-73-1
Mirex	2385-85-5

1.1.3. Additional multi-components analytes may include those listed in Table 03:

Table 03	
Compound / Analyte Name	**CAS Number**
Chlordane (N.O.S.)	57-74-9
Chlordane (Technical)	12789-03-6
Toxaphene	8001-35-2

1.2. Trans-Chlordane (CAS#5103-74-2) is named as such in EPA Method 8081B (Feb 2007). It has also been named *gamma*-Chlordane and beta-Chlordane previously. *Cis*-Chlordane (CAS#5103-71-9) is also named in EPA Method 8081B (Feb 2007). It has also been named *alpha*-Chlordane previously.

1.3. Total Chlordane's are calibrated and reported as not otherwise specified (N.O.S) chlordane (CAS#57-74-9). Technical Chlordane (CAS#12789-03-06) may also be requested on a project specific basis. N.O.S. chlordane is used for calibration and pattern matching when technical chlordane is requested.

1.4. This method is restricted to use by analysts experienced in the use of a gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5. The additional multi-component analytes are mixtures that may interfere with identification and quantification of other target analytes. These mixtures are also prone to environmental degradation (weathering) that may alter their composition compared to non-weathered standards. In samples containing these multi-component mixtures a higher level of analyst expertise is required to assure proper qualitative and quantitative analysis.

1.6. This method employs a single injection, dual column system. Injected sample extract flows from the GC injection port onto a guard column and then is split onto two analytical columns using a glass "Y" connector. Each column elutes into a separate ECD detector resulting in two chromatograms for each sample injection.

1.7. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including the EPA SW-846 methods, the NELAC Institute Program and the Department of Defense Quality Systems Manual (DoD-QSM). The table in Appendix 20.2 outlines ARI's routine procedure. The table in appendix 20.3 shows acceptance criteria for EPA method 608 when requested. 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.**

1.8. The reference methods for this procedure are listed in Section 20.

1.9. Detection Limits

1.9.1. Detection limits depend on the volume of sample extracted, the final extract volume and the lowest calibration point of the instrument calibration. The MRL values found in Table 4 are for those analytes curved to the lowest values. For those analytes shown in Table 5 to have higher values for the low point of the initial calibration the MRL will be raised proportionately.

Table 04

Sample Matrix	Extraction Solvent	Sample Volume or Weight	Final Volume (mL)	Reporting Limit (ppb)
Water	CH_2Cl_2	500 mL	5.0	.025-0.05
Water (low)	C_6H_{14}	1000 mL	0.5	.000625-.00125
TCLP Extract	CH_2Cl_2	100 mL	10.0	.250-.500
Soil/ Sediment (low)	CH_2Cl_2	12.5 g	2.5	0.5-1.0
Soil/ Sediment	CH_2Cl_2	12 g	4.0	1.7-3.3
Soil/ Sediment (med)	CH_2Cl_2	5 g	40.0	20
Tissue	CH_2Cl_2	5 g (wet)	10	5

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

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.

2.2. 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, etc.).

2.2.1. Acid cleanups are sometimes used for non-acid labile analytes, a list of analytes appropriate for acid cleanups is found in Appendix 20.4.

2.3. 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 organochlorine pesticides.

2.4. Following addition of internal standards 1 µL of the extract is injected onto a GC using an auto-sampler and split-less injection technique.

2.5. The injected sample is split onto two columns by passing through a glass Y connector. Analytes are detected and quantified using ECD detectors.

2.6. Identified Target analytes are quantified using an internal standard procedure as described in Section 12.2

3. Definitions

3.1. BNB (1-Bromo-2-Nitrobenzene): Internal standard.

3.2. Initial Calibration Verification (ICV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable.

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

3.4. 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.

3.5. DCBP (Decachlorobiphenyl): Surrogate standard.

3.6. 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.

3.7. HBBP (2,2',4,4',5,5'-Hexabromobiphenyl): Internal standard.

3.8. 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.

3.9. Second Source Calibration Verification Standard (SCVS): 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 vendor than the calibration standard whenever possible.

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. Pesticides (Section 7.1) are the routine BS analytes. All Pesticides must be included in an BS at least once every two years.

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. Pesticides (Section 7.1) are the routine BSD analytes. All Pesticides must be included in a BS at least once every two years.

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. Also referred to as the Minimum Reporting Limit.

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.

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 a matrix like 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. MRL Spike (Method Reporting Limit Spike): A matrix spike prepared at reporting limit, used to determine the MDL and MRL.

3.21. 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.

3.22. 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.

3.23. Target Software: Software used to integrate and reduce raw chromatographic data.

3.24. TCMX (Tetrachloro-m-Xylene): Surrogate standard

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 in pesticide determinations. 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 450^{o}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).

4.2.1.2. Multi-component mixtures such as Toxaphene may interfere with the identification and quantitation of individual chemical compounds.

4.2.1.3. Other organic compounds may be extracted along with the target analytes and interfere with the analysis of pesticides.

4.3. Matrix Interferences

4.3.1.1. High molecular weight materials (waxes, lipids, etc.) and certain co-eluting Organophosphorus pesticides may be eliminated by the Gel Permeation Chromatography cleanup pesticide option (EPA Method 3640).

4.3.1.2. Co-eluting Chlorophenols may be eliminated by Silica Gel (EPA Method 3630), Florisil (EPA Method 3620), or Alumina (EPA Method 3610) cleanup.

4.3.1.3. Co-eluting PCBs, although they are generally not removed by cleanup, may cause interferences that result in raised reporting limits.

4.3.1.4. Phthalate esters may be removed using alumina clean-up (EPA Method 3610.)

4.3.1.5. The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur may be removed using the TBAS method (EPA Method 3660.) as described in ARI SOP 334S. Sulfur contamination should be expected with sediment samples; therefore, all sediment extracts must be treated with TBAS. Sample extracts still requiring additional cleanup for Sulfur interferences can be treated with an additional TBAS clean-up.

4.3.1.6. 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 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. All GC split vents are connected to an exhaust vent.

5.4. Open containers of solvents, reagents or sample extracts must be handled in the fume hoods to avoid exposure to potentially toxic fumes.

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 material safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult with SDS sheets or available online at www.msdshazcon.com for all chemicals handled.

6. Equipment and Supplies

6.1. Gas chromatograph: Analytical systems complete with a temperature-programmable gas chromatograph equipped with a split-less injection system and all required accessories including:

6.1.1. Autosampler

6.1.2. Analytical columns Fused-silica capillary columns - One of the two following column pairs are commonly used. Columns used may vary depending on currently available technology (other column pairs that generate equivalent data may be used):

6.1.2.1. Column 1: Stx-CLP1, 30 m, 0.32 mm ID, 0.50 µm film. Column 2: Stx-CLP2, 30 m, 0.32 mm ID, 0.50 µm film.

6.1.3. Siltek® glass press tight angled y-connectors.

6.1.4. Siltek® coated 5m 0.53 mm ID pre-columns.

6.1.5. ECD detectors

6.2. Data system - A computer system must be interfaced to the GC. The system must allow the recording of instrument response as a function of time

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

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

6.4. Volumetric flasks, Class A - 10 mL to 1000 mL.

6.5. Bottles – amber glass with Teflon-lined screw caps or crimp tops.

6.6. Autosampler vials- amber 2 ml autosampler vials with Teflon-lined crimp caps

7. Reagents and Standards

7.1. Stock standard solutions (1,000-10,000ug/L) – Standard solutions can be prepared from neat standards or purchased as certified solutions. Certificates of analysis for all purchased neat's 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 water (OFW) – 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 (COA).

7.3. Stock Solutions

7.3.1. Prepare stock standard solutions by accurately weighing about 0.2500g of pure material. Dissolve the material in pesticide free grade methylene chloride or other suitable solvent and dilute to volume in a 25ml volumetric flask. When neat compounds are assayed to be 97% or greater purity, their weight may be used without correction to calculate the concentration of a 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. Certificate of Analysis for certified compounds and solutions are stored electronically in Element as a .pdf.

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 must 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 replaced after 1 year or sooner if comparison with quality control check samples indicates they have degraded, or they expire.

7.3.6. Stock standard solutions must be replaced one year after being de-ampullated.

7.3.7. A PDF record of analysis for stock solutions prepared in-house must be attached to the standard registry in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.

7.3.8. Internal Standard Stock Solution - The internal standards employed are 1-Bromo-2-Nitrobenzene and 2,2',4,4',5,5'-Hexabromobiphenyl. Other compounds that meet the method IS requirements may be used.

7.3.8.1. Prepare a stock solution with each IS at a concentration of 1000 µg/ml by dissolving 0.1g of each in a 100 mL volumetric flask and dilute to volume with hexane.

7.3.9. Surrogate Stock Standards- The surrogate standards employed are tetrachloro-m-xylene (TCMX) and decachlorobiphenyl.

7.3.9.1. Prepare a stock solution with each surrogate at a concentration of 1000 ug/mL by dissolving 0.1g of material in a 100 mL volumetric flask and dilute to volume with a hexane.

7.4. Working solutions- working standards are prepared from stock standards or purchased as commercially certified mixtures.

7.4.1. Working standards expire either on the date of expiration of the stock solutions they are made from, or on the manufacturer's certified expiration date or within six months from date of preparation, whichever comes first. They must be replaced at this time.

7.4.2. Working standard solutions must be replaced six months after being de-ampullated.

7.4.3. Working standards must be stored at 0 to 6°C and protected from light.

7.4.4. Working standards must be checked frequently for signs of concentration or degradation.

7.4.5. A PDF record of analysis must be attached to the standard registry (non-virtual only) in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.

7.4.6. Internal Standard Working Solution-

7.4.6.1. Prepare an Internal Standard Working Solution by diluting the Internal Standard Stock Solution such that the concentration of each internal standard is 8µg/mL.

7.4.6.2. Each 0.1mL aliquot of the sample extract undergoing analysis must be spiked with 1µL of the internal standard solution, resulting in a concentration of 80ng/mL of each internal standard (for example, when preparing a sample aliquot of 0.3ml, spike the extract with 3µl of the internal standard working solution).

7.4.7. Working Standards

7.4.7.1. A surrogate spiking standard is prepared by diluting the TCMX and DCBP surrogate stock such that the concentration of each analyte is 2µg/mL. This solution is prepared in Acetone. This solution is used to spike all extracted samples and QC samples with surrogates.

7.4.7.2. Blank Spike Working Standard is used to prepare the BS, and when applicable the BSD.

7.4.7.3. The BS working spike is prepared from commercially certified mixtures.

7.4.7.4. The BS working solution contains those analytes that per Table 05 are curved down to 1.25ng/mL on column at a concentration of 2µg/mL. Those analytes that per Table 5 are curved down to 2.5ng/mL are present in the BS working solution at a concentration of 4µg/mL. Toxaphene is present in the BS working solution at a concentration of 20µg/mL. Methoxychlor, per Table 5 is curved to 12.5ng/mL and is present in the BS working solution at a concentration of 200ug/mL.

7.4.7.4.1. Blank spikes containing nearly all the target analytes that are used.

7.4.7.5. Matrix Spike Working Standards are used to prepare MS/MSD sets.

7.4.7.5.1. Commercially certified solutions are used to prepare the matrix spiking working standards.

7.4.7.5.2. MS/MSD spikes containing nearly all the target analytes that are used.

7.4.7.5.3. MRL spike working standards made from certified solutions are used to prepare MRL spikes.

7.4.8. Calibration working standards- the standards used to prepare calibration curves are purchased as commercially certified mixtures.

7.4.8.1. Prepare calibration working standards by diluting these commercially certified standards such that the concentration of each analyte in each calibration standard corresponds to the concentration found in Table 05.

Table 05

Compound / Analyte Name	CAS Number	Calibration Standard Concentrations ng/mL						
		1	2	3	4	5	6	7
Routine Analytes								
Aldrin	309-00-2	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Alpha-BHC	319-84-6	1.25	2.50	5.0	10.0	20.0	40.0	80.0
beta-BHC	319-85-7	1.25	2.50	5.0	10.0	20.0	40.0	80.0
delta-BHC	319-86-8	1.25	2.50	5.0	10.0	20.0	40.0	80.0
gamma-BHC (Lindane)	58-89-9	1.25	2.50	5.0	10.0	20.0	40.0	80.0
cis-Chlordane	5103-71-9	1.25	2.50	5.0	10.0	20.0	40.0	80.0
trans-Chlordane	5103-74-2	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Endosulfan-I	959-98-8	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Heptachlor	76-44-8	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Heptachlor epoxide	1024-57-3	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Hexachlorobenzene	118-74-1	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Hexachlorobutadiene	87-68-3	1.25	2.50	5.0	10.0	20.0	40.0	80.0
4,4'-DDD	72-54-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
4,4"-DDE	72-55-9	2.50	5.0	10.0	20.0	40.0	80.0	160.0
4,4'-DDT	50-29-3	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Dieldrin	60-57-1	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endosulfan-II	33213-65-9	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endosulfan Sulfate	1031-07-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endrin	72-20-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endrin aldehyde	7421-93-4	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endrin ketone	53494-70-5	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Methoxychlor	72-43-5	12.5	25.0	50.0	100.0	200.0	400.0	800.0
Additional Analytes								
2,4'-DDD	3424-82-6	2.50	5.0	10.0	20.0	40.0	80.0	160.0
2,4'-DDE	53-19-0	2.50	5.0	10.0	20.0	40.0	80.0	160.0
2,4'-DDT	789-02-6	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Oxychlordane	27304-13-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
trans-Nonachlor	39765-80-5	2.50	5.0	10.0	20.0	40.0	80.0	160.0
cis-Nonachlor	5103-73-1	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Mirex	2385-85-5	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Multicomponent Analytes								
Chlordane (technical)	57-74-9	200						
Toxaphene	8001-35-2	500	1000	2500	5000	10000		

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. 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 in a bin assigned in Element

8.3.3. Extracts must be stored at >0 to 6 ºC and protected from light.

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

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 designated for extract vials. Disposed extracts are now marked in Element as disposed.

9. Quality Control

9.1. ARI in-house Quality control requirements are tabulated in Appendix 20.2.

9.1.1. Acceptance criteria for ARI's routine analyzes 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. 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. Endrin and DDT Degradation

9.2.1.1. Endrin and DDT are especially susceptible to chemical degradation (breakdown) during the gas chromatographic analysis. The degradation generally occurs in the injection port. Endrin may be converted into endrin ketone and endrin aldehyde while 4,4'-DDT may degrade forming 4, 4'-DDE and/or 4, 4'-DDD. The degradation of Endrin and 4, 4'-DDT must be assessed for a given chromatographic system prior to analyses.

9.2.1.2. A Degradation Standard (DS) is analyzed along with all initial calibrations and with each ICV/CCV. The DS contains Endrin and DDT at concentrations of 0.1µg/mL.

9.2.1.3. DDT breakdown is calculated as follows:

DDT % Breakdown = ((DDE + DDD) / (DDT + DDE + DDD)) 100
where:
DDE = chromatographic response for 4,4'-DDE
DDD = chromatographic response for 4,4'-DDD
DDT = chromatographic response for 4,4'-DDT

9.2.1.4. Endrin breakdown is calculated as follows:

Endrin % Breakdown = ((EA + EK) / (E + EA + EK)) 100
where:
E = chromatographic response for Endrin
EA = chromatographic response for Endrin Aldehyde
EK = chromatographic response for Endrin Ketone

9.2.1.5. The breakdown of Endrin and 4, 4'-DDT must each be ≤15% or corrective action is required. Corrective actions are provided in Section 16.

9.2.2. Internal Standard Response

9.2.2.1. For each IS, area and retention time data are evaluated during and/or immediately after the analysis.

9.2.2.2. The response for each of the internal standards must be within the inclusive range of -50.0% to +100.0% of the response of the internal standards in the most recent initial calibration at the CCV level.

9.2.2.3. The retention time shift for each of the internal standards must be within ± 0.02 minutes (1.2 seconds) between the sample and the most recent continuing calibration verification.

9.2.2.4. When the IS criteria are out of control for one column but are acceptable on the other column, the in-control column may be used to quantify analytes without corrective action.

9.2.2.5. Corrective action is required when IS criteria are out of control on both columns and/or any analyte may not be quantified on an in-control column.

9.3. Method Control

9.3.1. Surrogate Standards

9.3.1.1. Surrogate Standards, tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCBP) are added to every sample analyzed including all QA samples.

9.3.1.2. The recovery of spiked surrogate standards is calculated and compared to established control limits.

9.3.1.3. Corrective action is required when a surrogate standard recovery is outside of established control limits.

9.3.2. Method Blanks

9.3.2.1. A method blank (MB) analysis is required for each sample extraction batch. A method blank is a volume of a clean reference matrix (reagent water 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 resulting from the processing and analysis of samples.

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

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

9.3.2.2.2. Each 20 samples in an SDG, 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 extraction batch.

9.3.2.2.3. Each MB must contain all method specific surrogate standards.

9.3.2.2.4. Method blanks must be analyzed on each analytical instrument used to analyze associated samples.

9.3.2.2.5. Target analytes are identified and quantified in the MB.

9.3.2.2.6. Corrective action is required when the concentration of any target analyte in the method blank is greater than half the analyte reporting limit.

9.3.2.2.7. The Method blank may be re-analyzed when the GC instrument is the suspected source of contamination.

9.3.3. Blank Spikes (BS)

9.3.3.1. BS analyses evaluate the accuracy of the analytical method independent of matrix-related effects, a matrix-specific BS must be included in each preparation batch.

9.3.3.2. Spiked target analytes are identified and quantified in the BS.

9.3.3.3. Corrective action is required when the recovery of spiked analytes is outside of established control limits.

9.3.3.4. An associated blank spike duplicate (BSD) may be required to assess method precision.

9.3.3.5. BS and BSD samples must contain all surrogates required for sample analysis.

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

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

9.3.4.2. A client's QA/QC samples (equipment rinses, field/trip blanks etc.) must not be used for MS/MSD analyzes

9.3.4.3. When ARI's client designates a sample to be used as an MS/MSD, that sample must be used. When there is insufficient sample to perform an MS/MSD, then the laboratory may upon consulting with the client, choose another sample for the MS/MSD, reduce the MS/MSD or utilize BS/BSD analysis to assess method precision. The rationale for the choice a sample other than the one designated by the client must be documented in the narrative.

9.3.4.4. Dilution of MS/MSD extracts to get either spiked compounds or target analytes on scale is not required.

9.3.5. Method Reporting Limit Spike (MRL)

9.3.5.1. MRL analyses evaluate the LOD and the MRL of the analytical method independent of matrix-related effects, a matrix-specific MRL may be included in each preparation batch.

9.3.5.2. Spiked target analytes are identified and quantified in the MRL.

9.3.5.3. Corrective action is not required for MRL recoveries.

9.3.5.4. MRL extracts must contain all surrogates required for sample analysis.

9.3.6. 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.

9.3.6.1. 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.

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

9.3.6.3. All analysts using this SOP must use it in conjunction with Control Limit documentation to assess data acceptability and/or the 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 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 in

SharePoint. Each DOC must be documented and stored in the SharePoint/ARIQA/Employee lists directories.

10. Calibration and Standardization

10.1. Prepare calibration standards at the concentrations listed in Table 05. Spike all calibration solutions with Internal Standard as described in Section 11.6.

10.2. Toxaphene is calibrated using a single standard at 2.5 ppm. When Toxaphene is identified in a sample, the sample must be re-analyzed along with a six-point Toxaphene calibration.

10.3. Technical Chlordane is calibrated using a single standard at 0.2 ppm. When Chlordane is identified in a sample above 0.02 ppm, the sample must be re-analyzed along with a six-point Chlordane calibration.

10.3.1. An MRL level Chlordane standard will be run in conjunction to the single standard and evaluated with the main list of pesticide analytes, to Chlordane for the component Chlordane in an MRL level of Chlordane. This MRL level will be compared manually against the method blank and samples and if all analyte hits fall below these MRL levels then a zero will be entered for Chlordane when reporting. If on the other hand there is a hit above the component chlordane MRL levels for any of the identified compounds, then the sample and associated method blank will be quantitated for Chlordane against the single standard to determine if the response is above the MRL for the multi-component analyte.

10.4. Begin the initial calibration sequence by injecting the priming standard. After the priming standard, inject the DS and evaluate it per the criteria found in Section 9.2.1. When the DS meets the acceptance criteria, inject the IB.

10.5. After evaluating the IB for background instrument contamination, analyze 1 µL of each of the initial calibration standards described in Section 10 containing the Internal Standard and tabulate the peak area against the peak area of the internal standard. The injection volume and instrument operating conditions used for the initial calibration must be used for all subsequent sample analysis.

10.6. Calculate a relative response factor (RRF) for each target analyte and surrogate using the formula:

$\mathbf{RRF = (A_X C_{IS}) / (A_{IS} C_X)}$
where:
A_X = Peak area for the 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

10.7. Calculate the average RRF for each peak. The formula is:

Average RRF = Σ 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)

10.8. The relative standard deviation (RSD) for each analyte RRF is determined by dividing the standard deviation of the peak RRFs by the peak's average RRF. The formula is:

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

10.9. Determine the percent relative standard deviation:

$$\%\text{RSD} = \text{RSD} * 100$$

10.9.1. When the %RSD calculated in Section 10.9 is less than 20 for each analyte the Average RRF is used to quantify target analytes. When quantitating toxaphene or other multi-component analytes, choose three to five of the major peaks (the peak height of each of these peaks should be greater than 25% of the peak height of the most intense peak.) Calculate the %RSD for each of these peaks. Each should meet the 20% RSD criteria.

10.9.2. When the %RSD for any analyte is > 20 corrective action is required. Corrective actions are described in Section 16.

10.9.3. When other corrective actions are not effective a linear calibration model may not be appropriate or achievable and alternative calibration models may be employed: Alternate calibration models must not be used in lieu of proper instrument maintenance.

10.9.3.1. Linear calibration using a least squares regression.

10.9.3.1.1. A minimum of 5 calibration concentrations are required.

10.9.3.1.2. The curve must not include the origin, but should be forced through the origin.

10.9.3.1.3. The coefficient of determination, (r^2) must be ≥ 0.990.

10.9.3.1.4. The low point of the curve must be evaluated against the linear regression equation to ensure that the calculated concentrations are not negative.

10.9.3.2. A quadratic regression model may be used to generate a calibration curve when linear calibration models will not yield acceptable results.

10.9.3.2.1. This model requires a minimum of 6 calibration points.

10.9.3.2.2. The curve must not include the origin, but should be forced through the origin.

10.9.3.2.3. The coefficient of determination, (r^2) must be ≥ 0.990.

10.9.3.2.4. The calibration curve should be visually inspected to ensure that there are no parabolas or repeating functions in the calibration range.

10.9.4. All corrective actions and or deviations from use of %RSD to evaluate an initial calibration must be fully documented on the reviewer checklist.

10.10. Retention time windows

10.10.1. ARI uses a default retention time window of ±0.02 minutes. Gas chromatographs equipped with Electronic Pressure Control (EPC) maintains exceptionally constant retention times.

10.10.2. Several years of experience working with difficult matrices have shown that narrower retention time windows often lead to false negatives in samples with high background contamination or with very complex sample matrices. When narrower retention time windows (i.e. 0.03 min.) are required the analyst should still use a window of ±0.02 minutes to evaluate the chromatogram for interferences.

10.10.3. Retention time windows are established for each initial calibration. The retention times of all analytes in all calibration verifications (ICV & CCV) must fall within the retention time windows set by the initial calibration standards.

10.10.3.1. In some instances, it may be appropriate to update the retention times with an opening continuing calibration and documented in the run log and reviewer checklist.

10.10.4. The experience of the analyst must weigh heavily in the interpretation of the chromatogram. In the case of multi-component analytes Toxaphene and Technical Chlordane the analyst must rely primarily on pattern recognition to identify target analytes.

10.11. Initial Calibration Verification – Initial calibrations are verified at the time they are generated by the analysis of an SCV. This is a standard prepared at a similar concentration as the midpoint standard of the curve, but prepared from a source different than the one used to prepare the initial calibration.

10.11.1. Calculate the concentration of each analyte in the SCV.

10.11.2. Calculate the recovery of each target analyte in the SCV using the following formula:

%Recovery = ((ICV/ IC) 100

Where:
IC = Analyte concentration in the initial calibration
ICV = Calculated analyte concentration in the initial calibration verification

10.11.3. The recovery of each analyte in the SCV must be within 80-120% of the true value.

10.11.3.1. When the % recovery is unacceptable corrective action is required. Corrective action may include any of the following:

10.11.3.1.1. Prepare and analyze a second SCV to determine if the first SCV was properly prepared.

10.11.3.1.2. Continue with the analysis following supervisory approval and documentation of the results included with the calibration.

10.11.3.1.3. Recalibration

10.12. An initial calibration must be verified during all sample analytical sequences through the process of continuing calibration verification. This involves analyzing an initial calibration verification (ICV) at the beginning of an analytical sequence and subsequent continuing calibration verification standard (CCV) prepared at the calibration midlevel from the same source as the initial calibration.

10.12.1. ICV/CCVS must be analyzed

10.12.1.1. Prior to sample analysis (ICV) and after every 10 field samples or 12 hours, and at the end of the analysis sequence (CCV).

10.12.1.2. CCVs may be analyzed more often as determined by the analyst.

10.12.1.3. When samples are to be run immediately following an initial calibration, a ICV is not required when the midpoint calibration standard meets the ICV requirements.

10.12.2. To be valid, an ICV/CCV must meet the following criteria.

10.12.2.1. For each analyte, calculate the per cent difference or percent drift (%D) between CCVS concentration and the known concentration using the following formula:

% D = ((CCV – IC) / IC) 100
where:
IC = Analyte concentration in the initial calibration
CCV = Analyte concentration in the continuing calibration

10.12.2.2. The limit on the %D for each compound is ±20%. For multi-component analytes (Chlordane and Toxaphene), calculate the %D for each quantified peak. So long as the average %D of all the quantitation peaks is less than 20%, the multi-component calibration is acceptable.

10.12.2.2.1. When %D is acceptable, proceed with analyzes.

10.12.2.2.2. When the %D is unacceptable corrective action is required. Possible corrective actions are described in Section 16.

10.12.2.3. When any of the CCV criteria are not met, all affected samples must be re-analyzed, except as follows.

10.12.2.3.1. When the concentration of a CCV analyte is > 120% of the expected value, and the analyte was undetected in the samples affected by the CCV, the samples do not need to be re-analyzed. A high CCV indicates that had the analyte been present it would have been detected.

10.12.2.3.2. When the concentration of an analyte with an unacceptable CCV is present in the extract above the linear calibration range, the sample does not need to be re-analyzed. In this case, the extract must be diluted and reanalyzed with an acceptable CCV.

10.12.2.3.3. Any CCV standard that does not meet the ±20% criteria may be re-analyzed if not more than 12 hours has elapsed or 10 field samples run since the injection of the opening CCV for that bracket. If the re-analysis also fails to meet the acceptance criteria corrective action must be performed. No samples may be analyzed without an acceptable opening CCV.

10.12.2.3.4. CCVs with calculated concentrations < 80% of the expected value may be acceptable with written approval by supervisory, management or data review personnel preferably after consultation with the client.

10.12.2.3.5. All CCV exceptions must be clearly documented in the Reviewer Checklist.

10.12.2.4. The retention times for all ICV and CCV compounds must fall within the windows established by the initial calibration or the last updated continuing calibration verification. Retention times may be updated at the beginning of an analytical bracket from the continuing calibration verification that begins that bracket.

11. Procedure

11.1. Essential steps in the analytical procedure are listed in Table 6. Details for each step are provided in the subsequent sections. It is not necessary to perform the procedures in the order given in Table 06.

Table 06

Analytical Procedure

Section:	Procedure
12.2	Examine project and extraction documentation

12.3	Establish appropriate instrument operating conditions
12.4	Prepare or obtain all required standards
12.5	Obtain sample extracts
12.6	Add internal standard
12.7	Load autosampler
12.8	Enter sample sequence into GC data system
12.9	Start analytical instrument run
12.10	Evaluate ICal and ICV or CCV
12.11	Evaluate CCVs during sequence
12.12	Evaluate DS
12.13	Evaluate the Chromatogram for the presence
12.14	Dilute extracts and re-analyze as necessary
12.15	Verify integration and manually integrate as necessary
12.16	Quantify Analytes
12.17	Archive extract vials
12.18	Export Data to ELEMENT
12.19	Prepare & submit analytical documentation

11.2. Examine Project Documentation

11.2.1. Sample receiving documents and Special Analytical Requirements form may contain information affecting the analysis such as unusual analytes, project required data quality objectives, etc.

11.2.2. Organic extraction documents may contain useful sample or extract specific information and includes screening to which may be used to adjust extract concentration prior to analysis.

11.2.3. 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. All associated QA sample (MB, BS, MS etc.) extracts must be included in the cleanup batch.

11.3. The recommended GC operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration). Conditions are instrument dependent and may vary. See Table 07 for typical instrument conditions.

Table 07	
Typical GC Operating Conditions	
Initial temperature:	100°C, hold for 1 minute
Temperature program:	100-230°C at 30C°/min hold 5 mins. 230-315°C at 30°C /min
Final temperature:	315°C, hold for 4 minutes
Injector temperature:	220°C
Detector temperatures:	325°C
Detector make-up gas flows	60 mL/min (front) and 50 mL/min (back)
Column initial flow	4.2 mL/min
Injector:	Grob-type, split-less/split
Injector Pressure	20 psi
Split flow	20 mL/min at 0.5 minutes
Sample volume:	1-2 µL

11.3.1. Make sure the correct GC method is in use

11.4. The following standards or solution must be prepared for the analytical process

11.4.1. Priming Standard

11.4.2. Degradation Standard

11.4.3. Instrument Blank

11.4.4. Calibration standards

11.4.5. Calibration verification standards

11.5. Obtain sample extracts and accept custody by signing the Extract Custody Log Book

11.6. Add internal standard

11.6.1. Measure a 0.3-0.5 ml aliquot of the sample extract obtained from sample preparation. Use a 10 µL syringe to add 1 µL of Internal Standard spiking solution for each 0.1 mL of extract. This results in a concentration of 80 ng/µL of each internal standard in the extract. This aliquot should be prepared in a clear glass autosampler vial and sealed with a crimp cap. Store the un-spiked volume of extracts at >0 to 6°C, protected from light in screw-cap vials equipped with un-pierced Teflon lined septa.

11.7. Load autosampler with the aliquots prepared in Section 12.6.1.

11.8. Enter the analytical sequence into the Chemstation software.

11.9. Begin the analytical sequence.

11.9.1. The injection volume must be the same volume used for the calibration standards.

11.9.2. Recommended GC operating conditions are specified in Section 11.3.

11.9.3. The Chemstation system is used for data acquisition only.

11.9.4. The raw data files are transferred to the Target server for processing.

11.9.5. The "Target" software assigns the chromatographic baseline and integrates the electronic signal producing a chromatogram.

11.10. Evaluate ICal and ICV or CCV

11.10.1. Prior to sample analysis the GC system must have an acceptable initial calibration curve (the requirements for the calibration curve are in Section 10.) The initial calibration must include the analysis of the IB and the DS.

11.10.2. Prior to sample analysis a CCV must be analyzed, and this CCV must meet the criteria found in Section 10. 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.

11.10.3. CCVS must be analyzed every 10 field samples, or every 12 hours whichever occurs first.

11.10.4. Sample analysis may continue if the CCVs meet the criteria in Section 10

11.11. Evaluate CCVs during sequence

11.12. Evaluate DS

11.12.1. Sample analysis may continue as long as the breakdown of both 4, 4'-DDT and Endrin are ≤ 15% each.

11.13. Examine the chromatogram for the presence of elemental sulfur.

11.13.1. If the presence of sulfur interferes with the analysis an extra Sulfur cleanup may 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 12.7.

11.13.2. When there is no evidence of Sulfur in the processed chromatogram proceed to Section 11.8.10

11.14. Dilute extracts and re-analyze as necessary

11.14.1. If the response for any target analyte exceeds the high point of the initial calibration curve, extract dilution must take place. Dilution should occur such that the analytes exceeding the curve range are kept within the upper half of the curve when the dilution is analyzed.

11.15. Verify that the computer has and correctly identified the chromatographic baseline and integrated all peaks correctly.

11.15.1. If corrections are required, manually re-integrate the data file following guidelines in SOP 1021S “Manual Integration of Chromatographic Peaks”.

11.15.2. Manual integrations must be identified on the raw data and explained in the reviewer checklist in the final data package.

11.15.3. Note the manually integrated peaks on a hardcopy of the final chromatogram.

11.15.4. Print before and after chromatograms of the manually integrated sample and when appropriate print magnified chromatograms to demonstrate and justify manual integrations (raw data printouts will include the chromatogram and will show baseline corrections).

11.16. Perform all qualitative and quantitative measurements as described in Section 13.

11.17. Archive the sample extracts at >0 to 6°C and protected from light in Refrigerator 17.

11.18. Following the data analysis, export the final concentration data to the laboratory information management system (ELEMENT) so that final reports may be generated.

11.19. Prepare and submit analytical documentation.

11.19.1. Place copies of all bracketing CCVs, raw data for all the samples and associated QC, the ELEMENT report, manual integration summary report, run log and an analyst’s note form in the project folder.

11.19.2. Make sure the Reviewer checklist include all deviations from standard procedure and any other noteworthy information concerning the project analyzes.

11.19.3. Submit the project file to data review.

12. Data Analysis and Calculations

12.1. Analyte Identification

12.1.1. A sample is tentatively determined to contain a specific analyte when the analyte’s peak falls within the retention time window for the peak determined during the initial calibration on one column.

12.1.2. Positive identification occurs:

12.1.2.1. When a peak is detected in the appropriate retention window on both columns.

12.1.2.2. And the relative percent difference (RPD) between the two responses is < 40%.

12.1.2.2.1. If the RPD is >40% between the responses the analyte may still be reported with a P qualifier at the analysts’ discretion.

12.1.2.3. Calculate the concentration of the analyte for each column using the procedure in Section 12.2.

12.1.2.4. Report the higher of the two calculated concentrations.

12.1.2.5. ARI will report the higher concentration following Method 8000C. 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 concentration as allowed in Method 8000C. This approach is only valid at the discretion of an experienced analyst and must be noted in the analyst's notes and in the project narrative.

12.1.3. When overlapping or co-eluting peaks preclude identification of an analyte on one or both columns:

12.1.3.1. Report the higher of the two column values and qualify the value with a "Y" flag indicating a raised reporting limit.

12.1.3.2. This flag indicates the analyte is not detected at or above the reported concentration. The Y flag is equivalent to the U flag with a raised reporting limit.

12.1.4. When an analyte is identified by the data system in the sample on either column, but the retention time is outside the retention time windows.

12.1.4.1. Report the higher of the two column values qualified with the "Y" flag. Note: the retention time windows in the data system should be intentionally set wide to screen for this type of interference.

12.1.5. When the analyte is present on both columns, within the established retention time windows and the RPD between the two values is ≥ 40%

12.1.5.1. Report the higher value qualified with a "P" flag.

12.2. Analyte Quantitation:

12.2.1. Calculate the concentration of each identified analyte in the sample extract as follows:

12.2.1.1. Water:

Concentration (µg/L) =	$\frac{(Ax)(Is)(Vt)(DF)}{(Ais)(RRF)(Vo)(Vi)}$
Where:	A_X = Peak area of the compound
Is = Amount of internal standard injected (ng).	
Vt = Final Volume of extract	
A_{IS} = Peak area of the internal standard	
RRF = Relative response factor the compound	
C_X = Concentration of the analyte	
Vo = Volume of water extracted (ml)	
Vi = Volume of extract injected (µL)	
DF = Sample Dilution Factor (1 for undiluted samples)	

12.2.1.2. 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 area of the compound	
Is = Amount of internal standard injected (ng).	
Vt = Final Volume of extract	
DF = Sample Dilution Factor (1 for undiluted samples)	
A_{IS} = Peak area of the internal standard	
RRF = Relative response factor for the compound	
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	

12.2.2. Quantitation of Multiple Component Analytes: Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handling Toxaphene and Technical Chlordane.

12.2.2.1. Toxaphene, when identified should be quantitated against a five-point curve using 3-5 major peaks. Note Section 10.2 regarding toxaphene calibration.

12.2.2.2. Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-chlordane (gamma and alpha), respectively, are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

12.2.2.3. The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

12.2.2.4. Unless otherwise requested, chlordane should always be quantitated as alpha-chlordane and gamma-chlordane, not a technical chlordane mixture.

12.2.2.5. When required, the analyst may quantitate technical chlordane residues using 3 to 5 major peaks from a technical chlordane calibration standard.

13. Method Performance

13.1. The QA department measures method performance using a combination of annual method detection limit (MDL) studies, quantitation limit spikes (MRL) studies, performance evaluation samples, and the monitoring of surrogate and spike recoveries.

13.2. Detection limits- detection limits for all analytes quantitated using this SOP are set using the lowest effective point of the initial calibration curve and validated by quantitation limit spike studies.

13.2.1. MDL studies are performed only for major instrument or procedure changes.

13.2.2. LOD and MRL values determined from MRL studies may be found for each analyte in Element.

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

13.3.1. Control limits are calculated from these recoveries.

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

13.3.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found in Element.

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**. In the case of multi-component analytes such as Toxaphene or Technical Chlordane an analyst must rely primarily on pattern recognition to identify target analytes.

13.6. 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 must be documented in the instrument maintenance logbook.

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. Mercury contaminated autosampler vials are placed in the designated container in Fume Hood 34 (satellite accumulation) then transferred to the “Mercury Debris” in the Hazardous Waste Storage Area for pick by.

14.5. 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. Concentrations of target analytes are calculated for both GC columns and compared for consistency.

15.2. When a confirmed analyte’s concentration is less than 1/2 the reporting limit, the analyte is not reported. A confirmed analyte at a concentration greater than 1/2 the reporting limit but less than the reporting limit may be reported with a "J" qualifier at the analyst’s discretion. Project specific requirements may dictate that all confirmed hits above 1/2 the reporting limit in the method blank will be reported.

15.3. If the response of any target analyte exceeds the calibration range of the system, dilute the extract so the analyte concentration falls within the range of the calibration curve and re-analyze. Flag reported concentrations which exceed the curve with an “E” flag on final data reports.

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

15.5. Method Blanks must contain less than 1/2 the reporting limit of the targeted analytes or corrective action is required as described in Section 16.6.

15.6. Internal Standard peak areas must meet the technical acceptance criteria listed in Section 9.2.2 of this SOP.

15.7. Surrogate Recoveries

15.7.1. All samples, method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates, RMs or other samples must have acceptable surrogate recoveries. Surrogate recoveries are considered unacceptable when they fall outside statistically generated control limits found in the ARI’s LQAP.

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

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

15.7.4. 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.

15.7.5. 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.

15.8. Blank Spikes (BS)

15.8.1. Blank spike recovery values must fall within the specified recovery acceptance limits or corrective action is required. If a BSD is performed then relative percent difference (RPD) acceptance limits also apply when available.

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

15.8.3. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet spike acceptance criteria, even when the criteria are labeled as advisory in the reference method.

15.8.4. Spike 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.

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

15.9.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified recovery acceptance limits. When a MSD is performed then relative percent difference (RPD) acceptance limits also apply when available.

15.9.2. MS/MSD recovery and RPD acceptance windows are determined statistically from method and matrix-specific laboratory data and are updated on a periodic basis. Certain methods or clients may require project specific MS/MSD recovery and RPD acceptance limits.

15.10. Holding Times

15.10.1. Extracts must be analyzed within 40 days from the date of extraction.

15.10.2. 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 (seven days for water and fourteen days for unpreserved tissues/solids/soils/sediments) the analyst will analyze and report both extraction sets and distinguish 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.

15.10.3. If any extracts are analyzed after the 40 day extract holding time has elapsed, the analyst must document this in the reviewer checklist accompanying the data so that it may be included in the narrative.

16.11 Analytical Sequences

16.11.1 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.

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 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 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.

16.3. 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 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 17.1, 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 17.1, 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 17.1, based on analyst discretion.

16.7. Blank Spikes (BS)

16.7.1. Control limits for this method are published in Element. If the problem is limited to only a few analytes outside of the allowable control limits the data may be reportable after consultation with the project manager and (or) organics manager.

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

16.7.3. Proceed with any appropriate corrective action from 17.1, 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 must flag all affected analytes with an S flag.

16.9.3.2. 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 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 internal standard out-of-control events.

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

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

17.5. See Section 16.7 for guidance on dealing with blank spike related out-of-control events.

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

17.7. See Section 16.9 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.

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19. Method References

19.1. U.S. EPA, Test Methods for Evaluating Solid Waste (SW-846), Method 8081B, Organochlorine Pesticides By Gas Chromatography, Revision 2, November 2000

19.2. Department of Defense, Quality Systems Manual for Environmental Laboratories, Final Version 4.2, June, 2003

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

20. Appendices

20.1. Acid Lability of Chlorinated Pesticides and PCBs

20.2. Pesticide Quality Control Requirements

20.3. Modifications Required for EPA Method 608

Table 20.1 Acid Lability of Chlorinated Pesticides and PCBs

Acid Lability of Chlorinated Pesticides & PCBs			
Compound	Labile	Partially Stable	Stable
Aldrin			x
Chlordane			x
Dieldrin	x		
4,4'-DDT			x
4,4'-DDE			x
4,4'-DDD			x
α-Endosulfan	x	x	
β-Endosulfan		x	
Endosulfan sulfate			x
Endrin	x		
Endrin Aldehyde	x		
Endrin Ketone	x		
Heptachlor			x
α -BHC			x
β -BHC			x
γ-BHC (Lindane)			x
δ -BHC			x
Toxaphene			x
Archlor - 1016			x
Archlor - 1221			x
Archlor - 1232			x
Archlor - 1242			x
Archlor - 1248			x
Archlor - 1254			x
Methoxychlor	x	x	
Hexachlorobenzene			
Hexachlorobutadiene			
DCBP (surr.)			x
TCMX (surr.)			x

Appendix 20.2: Pesticide Quality Control Requirements

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	DoD-QSM Acceptance	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	QC acceptance criteria published by DoD, if available; otherwise method specified criteria.	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.	Same	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 0.5 minutes	RT width is ± 3 times standard deviation for each analyte RT from 72-hour study.	NA	NA
Breakdown check (Endrin and DDT)	Daily prior to analysis of samples	Degradation < 15% for both Endrin and DDT.	Same	Correct problem and then repeat breakdown check.	Flagging criteria are not appropriate.
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 ± 20% 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.
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.

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	DoD-QSM Acceptance	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	Same	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	No analytes detected > ½ MRL. For common laboratory contaminants, no analytes detected ≥ MRL.	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	QC acceptance criteria specified by DoD	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 reviewer checklist.
Matrix spike (MS)	One MS per preparatory batch per matrix.	ARI MS control limits	For matrix evaluation, use QC acceptance criteria specified by DoD 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 J-flag if acceptance criteria are not met.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	ARI BS control limits	RPD ≤ 30% (between MS and MSD or sample and sample duplicate)	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-flag if acceptance criteria are not met.
Surrogate spike	All field and QC samples	ARI control limits	Analytes identified in DoD-QSM Appendix DoD-D. QC acceptance criteria for BS 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 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-flag if acceptance criteria are not met.
Confirmation of positive results (second column or second detector)	All positive results must be confirmed.		Calibration and QC criteria same as for initial or primary column analysis. Results between primary and second column RPD ≤ 40%.	NA	Apply J-flag if RPD > 40%. Discuss in the reviewer checklist.
Results reported between LOD and MRL	NA		NA	NA	Apply J-flag to all results between LOD and MRL.

Appendix: 20.3 Modifications Required for EPA Method 608

20.3 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 the 5 required in Method 8081B.
20.4.2 Initial calibration RSD for Method 608 must be < 10% with no exceptions.
20.4.3 Continuing calibration RSD for Method 608 must be < 15% with no exceptions.

Standard Operating Procedure

Total Solids

SOP 1023S
Revision 002

Revision Date: 8/22/19
Effective Date: 8/22/19

Prepared by:

Van, Spohn, Dave Mitchell

Approvals:

Bob Congleton
Laboratory / Section Manager

Annual Review

SOP Number: 1023S

Title: Total Solids for Metals & Organics Samples

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

Name	Reviewer's Signature	Date

Standard Operating Procedure: Total Solids

1. Scope and Application

1.1. Analyte concentrations in solid samples are reported on a dry weight basis unless project documentation indicates otherwise. A "Total Solids" (TS) percentage must be determined to correlate analyte concentration with dry weight.

1.1.1. TS are determined by drying a portion of sample at elevated temperature for 12 to 24 hours and calculating percent total solids as outlined below.

1.1.2. TS must be determined immediately before, or immediately after weighting samples for the preparation process.

1.1.3. TS must be determined separately for each sample container and may be used for all analyzes from that container.

1.1.4. When TS must be determined in less than 12 hours, a microwave procedure may be used. The procedure is posted on the microwave oven in the Organics Extraction Laboratory and included as Appendix A of this SOP. The microwave procedure is only for "rush" or emergency situations. Do not use the microwave procedure for routine samples.

1.2. The procedure in this document is used to determine Total Solids (TS) for reporting of data from solid samples (soil, sediment, etc.) on a "dry weight" basis. This SOP is used by the Organics Extraction, Volatile Organics and Metals Laboratories. When TS is specifically requested as a reportable analyte, the TS is determined in ARI's Conventionals Laboratory following SOP 639S "Solids".

2. Summary of the Procedure

2.1. A weighed portion of sample is oven dried and the percent difference between the wet and dry sample calculated.

3. Definitions

3.1. Total Solids. (TS). The total weight of all solid materials (dissolved and particulate) contained per unit weight or volume of sample. For soils or sediments, it is the weight remaining after drying a known weight of sample, usually expressed as a percent.

4. Interferences

4.1. Heterogeneous samples: Samples must be appropriately mixed prior to withdrawing the aliquot for analysis. Anything, including non-representative artifacts, that will interfere with the ability to take a representative sub-sample must be documented on the analysts "Green sheet" and discussed with the Project Manager prior to beginning the analysis. Do not exclude any materials from the sample without discussion with the Project Manager.

4.2. Sample residues for weighing must be at room temperature to avoid convective interference in the balance chamber.

4.3. Constant dry weight is assumed to be reached after the sample has dried for a period of 12 to 24 hours. In the event that the sample has not been dried for the minimum 12 hours, or upon specific request from the client, attainment of constant dry weight must be documented.

5. Safety

5.1. Environmental Samples may contain hazardous materials; treat them as potential health hazards.

5.2. The drying oven must be contained in a hood or vented to prevent potentially toxic fumes from a heavily contaminated sample from entering the laboratory.

5.3. Always wear safety glasses and hand protection when working with hot samples.

6. Equipment and Supplies

6.1. ALUMINUM WEIGHING DISHES.

6.2. DRYING OVENS Gravity convected, adjustable to maintain 104 ± 2 °C. Gravity convection is preferred for the drying of samples since mechanically convected ovens can create drafts that could displace dried materials from their containers. Mechanically convected ovens should only be used for drying of equipment and materials used for the analysis.

6.3. Analytical balance. The balance used must be capable of measurement to 3 places. Balance verification is accomplished using ASTM E 617-97 traceable weights. The calibration weight must return a value within 1 mg or 10% of its known weight, whichever is less.

6.4. Weights for balance verification. Troemner Calibration weights, ASTM E 617-97 traceable (equivalent to old NBS Class S and S-1 standards). Each weight set is certified every 5 years by an outside metrology laboratory. A certificate documenting the "true" weight of each calibration weight accompanies each set.

7. Reagents and Standards

7.1. Not Applicable

8. Sample Collection, Preservation, Shipment and Storage

8.1. Sub-sampling is a critical component of solids analysis. In order to obtain accurate and reproducible results, be certain that the sample is well mixed and that the particulates are uniformly distributed throughout the sample prior to withdrawing the aliquot.

9. Quality Control

9.1. Balance Verification. Each analytical balance is verified against ASTM E 617-97 traceable (NIST equivalent to older NBS Class S and S-1 standards) weights at the beginning each weighing cycle.

9.2. Record which analytical balance and oven are used for the TS determination on the bench sheet

9.3. Verify that the oven used is at 104 ±2° C.

9.4. Record the Oven ID on the TS bench sheet.

10. Calibration and Standardization

10.1. The accuracy of each analytical balance is verified daily against ASTM E 617-97 traceable (NTIS equivalent to old NBS Class S and S-1 standards) weights covering the range of determination.

10.2. The balance verification is documented in a balance specific logbook.

11. Procedure

11.1. Analyte concentrations in solid samples are reported on a dry weight basis unless project documentation indicates otherwise. A “Total Solids” (TS) percentage must be determined to correlate analyte concentration with dry weight.

11.1.1. TS are determined by drying a portion of sample at 104 ± 2 °C for 12 to 24 hours and calculating percent total solids as outlined below.

11.1.2. TS must be determined immediately before, or immediately after weighting samples for the preparation process.

11.1.3. TS must be determined separately for each sample container and may be used for all analyzes from that container.

11.1.4. When TS must be determined in less than 12 hours, a microwave procedure may be used. The procedure is posted on the microwave oven in the Organics Extraction Laboratory. The microwave procedure is only for “rush” or emergency situations. Do not use the microwave procedure for routine samples.

11.1.5. TS determined using this procedure are used to calculate analytes values reported on a dry weight basis. Total Solids as a reported analyte is performed in ARI’s Conventionals Laboratory following SOP 639S “Solids”.

11.2. Obtain a copy of Total Solids Bench Sheet (Form 5050F) and enter the header information, analyst name, date, oven ID, balance ID and ARI sample identification(s).

11.3. Verify that the balance calibration has been documented for the day using bracketing weights. If not, verify and document balance accuracy before proceeding using the procedure described in ARI SOP 1003S.

11.4. Zero the balance.

11.5. Obtain an empty aluminum weighing pan write the sample number on the pan with permanent marker.

11.6. Weigh the empty pan and record its weight to the nearest 0.01 gram in the "Tare Weight" column of the TS bench sheet. Record all digits displayed by that balance. Do not round the numbers.

11.7. Make sure the sample is homogenous by thorough mixing.

11.7.1. Decant and discard any water layer from solid samples to be extracted for semi-volatile organics (SVOA) extractions prior to homogenization.

11.7.1.1. Shared samples (multiple analyses from the same sample container) are not decanted.

11.7.2. Samples for volatile organics analysis (VOA) must not be homogenized in this manner. Ideally a second container which may be homogenized will be collected for VOA TS determination. When the second container is not available the TS determined in another lab section may be used. In this case, the source of the TS data must be clearly identified on the TS bench sheet.

11.8. Weigh 10 ± 5 grams of wet sample into the weighing pan. Record the exact weight to the nearest 0.01 gram in the "Tare + Sample Wet" column of the log form. Using less sample is permissible only when less than 5 g of sample are available.

11.9. Verify and record oven temperature on the TS bench sheet.

11.10. Place the weighing pans in the oven, record the time, and dry at an oven temperature of 102-106°C overnight (12-24 hours) but no longer than 24 hours. If dried for less than 12 hours, it must be documented that constant weight was attained.

11.10.1. To demonstrate that constant weight has been attained, data must be recorded for a minimum of two repetitive weigh/dry/weigh cycles with a minimum of 1-hour drying time in each cycle.

11.10.2. Constant weight would be defined as a loss in weight of no greater than 0.01g between the initial and final weightings of the last cycle.

11.11. Remove pans from the oven and allow them to equilibrate to ambient temperature for no more than one hour.

11.12. Record analyst name, oven temperature, date, and the time of removal on the TS bench sheet.

11.13. Verify the balance accuracy and record the results in the balance specific logbook.

11.14. When cool, weigh and record the exact weight to the nearest 0.01 grams in the "Tare + Sample Dry" column of the log form.

11.14.1. When dry samples cannot be weighed within 60 minutes of removal from the oven, they must be placed in a desiccator to prevent adsorption of moisture from the atmosphere.

11.14.2. When wet samples less than 0.5 g are used, the dry sample must be cooled in a desiccator.

11.15. Data Entry Procedures:

11.15.1. Organics Extraction Laboratory: Enter in Element LIMS using worklist

11.15.2. Metals Preparation Lab: Data is entered into dBase

11.15.3. VOA laboratory: Enter in Element LIMS using worklist

11.16. Place the Total Solids Benchsheet in the appropriate project folder.

12. Review

12.1. Supervisor reviews Service Request and assigns analysis and communicates any special instructions to the analyst as appropriate.

12.2. Analyst reviews Service Request and any special instructions, obtains the appropriate bench sheet and proceeds with the analysis. A handwritten bench sheet is generated, and the data are then entered into the computer for data reduction.

12.3. Creation of Worklists. The final computer-generated result is placed into the method folder in chronological sequence and a copy is placed into the job folder. The data undergo supervisor review and the analysts then enters the data into Element LIMS to create the worklist.

12.4. Distribution of worklists. The supervisor reviews the Element LIMS input, distributes acceptable data and returns the analysis package to analyst for placement in the job folder.

12.5. The completed analysis package is then reviewed by a QA Reviewer and the final report printed.

12.6. The final report is then again reviewed for accuracy and completeness, signed by the QA reviewer and delivered to the Project Manager for final disposition to the client.

13. Data Analysis and Calculations

13.1. TS is a gravimetric determination in which the dry weight of solid residue is expressed relative to the volume or mass of sample used to obtain that residue. Specific calculations are as follows:

13.1.1. Percent solids for reporting chemistry data is calculated by the Element LIMS as follows:

$$\%\ Solids = \left[\frac{(Tare + Sample\ Dry) - Tare}{(Tare + Sample\ Wet) - Tare}\right] * 100$$

14. Method Performance

14.1. Approximately 10 grams of sample are typically taken for analysis. While the balance reports to 0.001 g, a sensitivity of 0.01 g is routinely used to report data. This yields a method sensitivity of 0.1% for TS.

15. Pollution Prevention

15.1. Not Applicable

16. Data Assessment and Acceptance Criteria for Quality Control Measures

16.1. Samples dried less than 12 hours

16.1.1. Demonstrate constant weight as described in Sections 11.10.1 and 11.10.2.

16.2. When samples have dried more than 24 hours

16.2.1. Repeat the TS determination on an additional sample aliquot.

16.2.2. When sample is not available or a repeat determination is not practical, document the excessive weighing time on the TS bench sheet in the comments section.

16.3. When the balance is out of control

16.3.1. Use the corrective action procedures in ARI SOP 1003S to bring balance back in control.

16.3.2. When balance in out of calibration or non-functional use a similar balance from another lab section.

16.4. Oven temperature is out of control

16.4.1. Adjust oven temperature and allow the temperature to equilibrate to required range.

17. Corrective Actions for Out of Control Events

17.1. Not Applicable

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

18.1. Not Applicable

19. Waste Management

19.1. Samples may contain RCRA hazardous constituents and these are screened in ARI's Element LIMS system. Samples which Element LIMS identified as containing one or more hazardous constituents will be segregated into identified waste profiles and disposed of through our RCRA TSD (Treatment, Storage Disposal facility). Samples not having identified hazardous constituents are disposed as routine garbage.

20. Method References

20.1. USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis. ILM05.3 March 2004. Exhibit D.

20.2. USEPA Contract Laboratory Program, Statement of Work for Organic Superfund Methods SOM02.4 October 2016. Exhibit D.

20.3. ASTM D 4643 – Microwave Method of Drying Soils

21. Appendices

21.1. Appendix 20.1 - Total Solids by Microwave Method

Appendix 20.1: Total Solids by Microwave Method

1. Weigh a 100 mL glass beaker to the nearest 0.01 grams
2. Record the weight on the Total Solids Bench Sheet as “Tare Weight”
3. Add approximately 20 grams of sample to the 100 mL beaker
4. Record the weight of the beaker and sample to the nearest 0.01 grams
5. Set the microwave oven in the defrost mode.
6. Place the sample beaker in the microwave oven and heat the sample for 4 minutes in the defrost mode
7. If the sample still appears wet microwave an additional 2 minute in the defrost mode.
8. Repeat the two-minute heating cycles until the sample appears to be dry or mostly dry.
9. When sample is dry or nearly dry remove it from the microwave and use a clean glass stir rod to break up any chunks making sure not to remove any sample from the beaker.
10. Record the sample beaker weight on a separate sheet of paper.
11. Microwave the sample for 2 minutes in the defrost mode and allow it to cool to ambient temperature.
12. Reweight the sample beaker.
13. If the weight is reduced 0.02 or more grams, repeat the Steps 11 and 12 until no weight loss is noted.
14. Record the final weight as “Dry Weight” on the bench sheet.
15. Enter data into ARI’s Element LIMS system.

Standard Operating Procedure

Particle Size Distribution – PSEP Method

Effective Date: 12/06/18

Prepared By:

Harold Benny

Approvals:

Laboratory / Section Manager

Quality Assurance

1.0 PURPOSE AND SCOPE

This procedure describes methods, materials, equipment, and special conditions required to determine the particle size distribution for sediment samples by the PSEP METHOD. Wet sieving separates sample into two size fractions; particle sizes >#230 sieve and particle sizes <#230 sieve. Fine fractions are further subdivided using a pipetted technique that depends on the differential settling rates of different particles.

Particle size determinations can either include or exclude organic material. If organic material is removed prior to analysis, the "true" (i.e., primarily inorganic) particle size distribution is determined. If the organic material is included in the analysis, the "apparent" (i.e., organic plus inorganic particle size distribution is determined).

2.0 EQUIPMENT

2.1 Balance (Capable of precision to 0.1mg)
2.2 Drying Oven – The oven is thermostatically controlled chamber capable of maintaining a uniform and consistent temperature of 90 ± 2° C.
2.3 Mechanical Sieve Shaker – A mechanical device used to spin and vibrate a nest (stack) of sieves at a constant rate and energy level to separate a given sample into the individual particle sizes.
2.4 Sieves – A nest of sieves including #4 (4.75mm), #10 (2.0mm), #18 (1.0mm), #35 (0.500mm), #60 (0.250mm), #120 (0.125mm) and #230 (.063).
2.5 Clock – A suitable timing device capable of measurements to the nearest second
2.6 Sedimentation Cylinders and Rubber Stopper
2.7 Temperature logger for room ambient temperatures
2.8 Desiccator
2.9 25ml in 1/10 Pipette and Rubber Bulb
2.10 Funnel
2.11 Rubber Policeman
2.12 Tare Dishes
2.13 Wire or Bristle Brush and Wax Paper
2.14 Lab Stand with Clamps
2.15 Lab Tape
2.16 Spoons and Spatulas

3.0 REAGENTS

3.1 Solution of SODIUM HEXAMETAPHOSPHATE $Na(PO_2)_6$ – A solution is made by mixing 40 grams sodium hexametaphosphate $Na(PO_2)_6$ in 1000ml of distilled water (0.1 Molar). Mix the solution thoroughly and let stand overnight. Pipette 5, 10 ml aliquots into weighed tares and oven dry. Record the dry weight in the batch notebook. Average the five weights and record average in notebook. The solution expires in one month.

4.0 DEFINITIONS

4.1 Test Environment – A fairly constant temperature of approximately 20° C during analysis. Small fluctuations in temperature may introduce differences that are of practical significance. A data logger will be used to monitor test temperatures.
4.2 Sieve Time – Samples will be sieved for 15 minutes, unless client requests a different time for consistency with previous testing.

4.3 Sieves – Sieves are frames that hold wire cloth that has various size openings. The operator will visually examine the sieves for defects (i.e., tears, plugging, holes) prior to each use. Do not use damaged sieves.
4.4 Flocculation – The process where finely suspended particles agglomerate and settle out of solution

5.0 DOCUMENTATION

5.1 PIPETTE GRAIN SIZE ANALYSIS data sheet 1115F.

6.0 QUALITY CONTROL

6.1 A batch of samples shall not exceed 20 individual samples. If the job has more than 20 samples they may be broken down into batch sizes that are less than 20. One sample from each batch shall be run in triplicate, giving a maximum batch size of 22 samples. The triplicate shall be reported on a separate plot and summary table with all pertinent data that applies to that sample. The average value for each size fraction shall be presented, as well as the relative percent standard deviation for that data point. Usually, a sample is chosen that is representative of the batch. A minimum of 5 grams passing the #230 sieve is required for the pipette portion of the analysis. Sandy samples may not have this much material passing the #230 sieve, and thus are not normally used for the triplicate. If all samples are sandy, then one of these may be used.

6.2 The client usually defines the maximum standard deviation for the project, but if not, a maximum deviation of 5 shall be used. If the triplicate has standard deviations greater than the specified (or lab maximum) then the entire set of samples shall be re-analyzed, unless the samples are non-standard. Non-standard samples may include contaminated samples, i.e., samples contaminated with diesel, or other tarry materials that would cement particles together. Samples that have been frozen prior to receipt by the lab would also be considered non-standard.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Remove the samples from the cooler/refrigerator and allow them to warm to room temperature. This ensures that the samples are not frozen. Check the HLB sample numbers against the client numbers to verify that they are correct. Notify supervisor for ID discrepancies.

7.1.2 Label and pre-weigh two tare dishes, one for the total solids portion of the sample and one for the wet sieving portion.

7.1.3 Carefully homogenize the sample to incorporate any overlying water.

7.1.4 Remove the total solids portion of the sample (approximately 25 grams), weigh it in the labeled tare dish, and record weight on the data sheet to the nearest 0.1mg. Dry the sample in oven for a minimum of 16 hours (overnight) or until completely dry, cool it in a desiccator, weigh, and record the weight on the data sheet.

7.1.5 Remove wet the sieve portion of sample (approximately 40 to 150 grams), weigh it in a labeled tare dish, and record the weight on the data sheet to the nearest 0.1mg. The critical factor for the sample size determination is the weight of the fine-grained material that will be used for the pipette analysis. Ideally, the total dry weight of fine-grained material in the 1000 ml-graduated cylinder should equal approximately 15 grams. Estimate the fraction of material finer than the #230 sieve, along with the moisture content (i.e., if the moisture content is 100%, and the percent finer than the #230 is estimated at 50%, an acceptable sample size could be approximately 80 grams).

7.1.6 Clean workstation when sample preparation is finished. Initial and date data sheet.

7.2 Wet Sieving

7.2.1 Label cylinders with sample number by using lab tape.

7.2.2 Place a #230 sieve in the funnel over a 1,000 ml cylinder using lab stands with clamps. Moisten sieve using a light spray of distilled water.

7.2.3 Add 20-30mls of distilled water in sample tare dish and stir to suspend the fine-grained material.

7.2.4 Pour sample and water onto sieve and gently agitate sieve to separate fractions. Aggregated clumps of sediment can be gently broken down with a rubber policeman. For sample spillage, see 9.0 CORRECTIVE ACTION.

7.2.5 Continue washing sample with a fine spray of distilled water until only clear water passes through sieve. See 9.0 CORRECTIVE ACTION if liquid passes 1000ml mark.

7.2.6 Rinse all remaining material off the #230 sieve back into the tare dish. Place sample in oven, minimum of 16 hours (overnight) until a constant weight is obtained.

7.2.7 Clean workstation when wet sieving is finished. Initial and date data sheet.

7.3 Sieving the Sand-Gravel Fraction

7.3.1 Remove plus #230 material tare dish from the oven and cool in a desiccator to room temperature.

7.3.2 Set up a nest of sieves with the coarsest on the top and grading down to the finest on the bottom over a sieve pan. This set of sieves will include the #4, #10, #18, #35, #60, #120, and #230. Clean any dirty sieves with a wire or bristle brush and tap sieve on table with all edges evenly to remove debris.

7.3.3 Weigh the sample and tare dish and record the weight on the data sheet to the nearest 0.1mg.

7.3.4 Add the sample to the uppermost (#4) sieve in nest. Use a brush to clean the entire sample from the tare dish and gently break up any agglomerations of material that may have formed due to drying.

7.3.5 Place the nest of sieves in mechanical sieve shaker and place the metal lid on the top of the stack. Set timer for 15 minutes, and close the door to the shaker. Remove the nest of sieves when shaker is finished.

7.3.6 Empty the top sieve by inverting it over a glossy piece of paper or tag board. Run a bristle brush over bottom of sieve to remove all particles. Tap sieve evenly on table.

7.3.7 Carefully pour sample from the paper into the tare dish, weigh it to the nearest 0.1mg, and record the weight on the data sheet.

7.3.8 Repeat 6.3.6 and 6.3.7 with each remaining sieve. Tare out the weight of an empty foil pan on the balance and pour the contents of the sieve pan into it. Weigh and record the weight of the < #230 material and record this on the data sheet. Empty the contents of the foil pan into the silt-clay fraction in the cylinder. Compare the total weight retained with the original dry weight to ensure that no material was lost in the sieving process. If weights are significantly different, see section 9.0 CORRECTIVE ACTION. Note large amounts of organic material (e.g., wood debris, grass, shells) or unusual material in any size fraction on the data sheet.

7.3.9 Clean workstation when work is finished. Initial and date the data sheet.

7.4 Pipetting the Silt-Clay Fraction

7.4.1 Add 10ml of $Na(PO_2)_6$ dispersant to each silt-clay fraction cylinder and fill to the line with distilled water. Record the batch number of dispersant used on data sheet.

7.4.2 Using a #13 rubber stopper, mix suspensions by inverting cylinder end over end for 60 cycles.

7.4.3 Allow the mixed suspension to stand for 2-3 hours and check for signs of flocculation. See 9.0 CORRECTIVE ACTION if flocculation occurs.

7.4.4 Label and pre-weigh all fraction tares to the nearest 0.1mg and record on data sheet.

7.4.5 Print out a set of withdrawal time stickers on the computer. Attach stickers to the corresponding data sheets.
7.4.6 Verify that the temperature logger is functional, and record the initial temperature.
7.4.7 Use rubber stopper and mix suspensions by inverting cylinder end over end approximately 60 times per one minute. For sample spillage see 9.0 CORRECTIVE ACTION.
7.4.8 After 20 seconds, withdraw a 20ml aliquot from a depth of 20 cm below the surface of the suspension using a 25ml 1/10 pipette with rubber bulb. It is critical that the solution be disturbed as little as possible when the pipette aliquots are taken.
7.4.9 Transfer aliquot to pre-weighed tare and rinse pipette by drawing approximately 20ml distilled water into pipette and transferring rinse into the same tare.
7.4.10 Withdraw another 20ml aliquot at the depth of 10 cm below the surface of the suspension at the appropriate time as listed in TABLE 1 according to the average room temperature. For missed pipetting times see 9.0 CORRECTIVE ACTION.
7.4.11 Dry all aliquots in oven to a constant weight at 90°C.
7.4.12 Cool dried samples to room temperature in a desiccator, weigh to the nearest 0.1mg, and record on data sheet.
7.4.13 Keep workstation clean. Initial and date the data sheet.

TABLE 1. Withdrawal Times for Pipette Samples

Diameter Finer (phi)	Diameter Finer (um)	Withdrawal Depth (cm)	Elapsed Time for Withdrawal of Sample in Hours (h) Minutes (m) and Seconds (s)						
			18°	19°	20°	21°	22°	23°	24°
4.0	62.5	20	20s	20s	20s	20s	20s	20s	20s
5.0	31.2	10	2m	1m 57s	1m 54s	1m 51s	1m 49s	1m 46s	1m 44s
6.0	15.6	10	8m	7m 48s	7m 36s	7m 25s	7m 15s	7m 5s	6m 55s
7.0	7.8	10	31m 9s	31m 11s	30m 26s	29m 41s	28m 59s	28 m 18s	27 m 39s
8.0	3.9	10	2h 8m	2h 5m	2h 2m	1h 59m	1h 56m	1h 53 m	1h 51 m
9.0	1.95	10	8h 32m	8h 18m	8h 6m	7h 56m	7h 44m	7h 32 m	7h 22 m
10.0	0.98	10	34h 6m	33h 16m	32h 28m	31h 40m	30h 56m	30h 12 m	29h 30 m

8.0 CALCULATIONS

8.1 MOISTURE CONTENT and TOTAL SOLIDS

Total solids content is determined as follows:

$$\text{Percent Solids} = \frac{(A - B)(100)}{(C - B)}$$

Where: A = weight of tare and dry sample residue
B = weight of tare
C = weight of tare and wet sample

8.2 SAND and GRAVEL FRACTION

The sand and gravel fractions of the sample are reduced as follows:

Percent retained (for a given sieve)= C/D * 100

Where: C = cumulative weight retained for a given sieve
D = total dry sample weight

8.3 SILT and CLAY FRACTION

The total weight of the phi-sized interval in the 1000ml graduated cylinder is determined as follows:

Phi weight = 50 ((E -G) - (F - G))

Where: E = weight of residue in a 20ml aliquot for a given phi size boundary
F = weight of residue in a 20ml aliquot for next larger phi size boundary
G = weight of dispersant and dissolved salt in a 20ml aliquot

9.0 SAFETY

9.1 Lab wear including a lab coat, safety glasses, and gloves should be worn at all time.
9.2 Care should be taken not to inhale fine dust while sieving. A dust mask should be worn when sieving.
9.3 The sieve shaker is loud, and the lid should be closed while in operation.
9.4 Keep workstation clean at all times. Wipe any spills to avoid safety hazards.

10.0 CORRECTIVE ACTION

10.1 Sample loss during wet sieving - If sample is spilled on table, use distilled water to wash spillage into tare dish. If sample is lost on the floor, see supervisor. A significant loss may result in a redo.
10.2 Excess wash volume – If wash volume exceeds 1000ml mark during wet sieving, let sample evaporate to obtain an acceptable volume.
10.3 Sample loss during sieving – Attempt to brush spilled sample into tare dish prior to weighing. It is extremely important to keep worktables and floor clean prior to sieving in case a spill occurs.
10.4 Sample Flocculation – Flocculation results in a curdling and rapid settling of lumps of particles or by the presence of a thick, soupy layer on the bottom of the cylinder passing abruptly into clear water above. When flocculation occurs, add dispersant in 10ml increments until no noticeable flocculation is observed. Record the total volume of dispersant added on the data sheet.
10.5 Sample spillage during cylinder mixing – If rubber stopper is not tight on cylinder and spillage occurs, continue pipetting procedure. Note approximate amount of spilled liquid on data sheet.
10.6 Missed pipetting aliquots – If withdrawal is missed the suspension may be re-mixed and the missed aliquot can be taken at the appropriate time. It is not necessary to take the initial 20ml aliquot for this corrective action.

11.0 REFERENCES

11.1 Folk, Robert L., 1978, The Petrology of Sedimentary Rocks, Hemophile Publishing Co., Austin TX

11.2 USACOE 1995, Puget Sound Estuary Protocols, U.S. Army Corps of Engineers, Seattle WA

Laboratory Data Consultants, Inc. (LDC)

SOP #14.0.0 REV 1.0
January 16, 2020

STANDARD OPERATING PROCEDURE
FOR DATA REVIEW/
DATA VALIDATION PROCESS

Approved / Date
Stella Cuenco 1/16/20

Stella Cuenco
Operations Manager/
Principal Chemist

1.0 PURPOSE

The data review and validation level of effort required for the Scope of Work outlined for any project will encompass several activities. The steps are categorized below. To perform the tasks, LDC will not use subcontractors since they would reduce the quality and control of the work product.

2.0 CUSTOMER Data Packages delivered via email or CD/DVD or LDCAdvantage.

Data deliverables are delivered to the Data Control Manager. The data is copied to \\LDCArchive and saved under the date received folder by Client Name and project on the LDC file server network. Data deliverables are printed for Login.

If the Data arrived via CD/DVD, the original media is placed with the hardcopy data package on the shelf after printing and saving data to the \\LDCArchive folder.

3.0 SAMPLE LOGIN

All samples submitted for data validation are entered into the LDC Log-in system. The system generates various spreadsheets for sample tracking, listings of laboratory and client identifications, sampling dates, analysis requested, matrix, and project due date. These tracking documents are distributed to all data validation, QA and project management staff.

4.0 DEFINITIONS

The following definitions are provided for this SOP.

Definitions

LDC Number	-	Project number given to a Group of SDG numbers to form a batch.
SDG Number	-	Data package number given to a Group of samples by the analytical laboratory.

5.0 PRE SCREENING OF DATA PACAKGES

The pre-screening is performed concurrently with the sample log-in process. This task verifies sample chain-of-custody, data package completeness, and concurrence with the authorized delivery order.

6.0 DATA VALIDATION

The execution of the data review task requires the highest level of effort. The review process will be handled in a stepwise fashion including manual and automated data review. The validator will use manual review to document each finding on a Validation Findings form. Along with the finding, the reviewer will document the date of the occurrence, the lab reference identification, the validation criteria, the associated samples, and the qualification of the data. A Validation Checklist form is marked noting if validation criteria was met or exceeded. A Validation Checklist is enclosed for review (Exhibit A). These checklists are used as an inventory sheet to assure all samples were reviewed for each criteria. The findings documented on the Validation Findings form will be transcribed into the final summary report. Examples of recalculation and findings worksheets used for Level 4 validation are available for review upon request.

All initial validation performed by Laboratory Data Consultants, Inc. has a secondary peer review. All final reports will be reviewed by a Senior Chemist or Principal Chemist.

7.0 LDC Validation Data Packages

LDC Validation Data Packages are processed and stored in the archive room 2D.
Once the LDC Validation report has been delivered to client, the ST (Attachment 1: Sample Table) is pulled from active job file.

8.0 FIRST REPORT REVIEW

The first review of the data validation report verifies that all findings and data qualification has been accurately transferred from the data validation worksheets. All sample identifications, methods, formatting, and general text are reviewed.

9.0 SENIOR REPORT REVIEW

The senior review of the data validation report verifies that all findings, data qualification, and professional judgments previously integrated into the reports reflect the overall quality of the data. Any additional comments required to enhance the usability of the report will be inserted at this time.

10.0 QA REPORT REVIEW

A QA check of selected data validation reports within an individual delivery order will be reviewed by the QA department. A formal nonconformance report will be generated for any identified deficiencies. The deficiency will be addressed with the appropriate staff and corrected prior to submittal to senior management for final review and signature.

11.0 SENIOR MANAGEMENT REVIEW

The program/technical manager will perform an overall review of the final reports. He will sign the report cover letter and submit the report to the sample custodian for shipment to the client.

12.0 Archived Data Packages

LDC Validation Packages Archive Boxes are labeled as follows:

1. Box number is assigned in chronological order
2. LDC job number – Client/Project

12.1 Holding times for archived material

1. Data Packages received from client as hard copy will be held for 3 months.

2. Data Packages received from client electronically will be held for 30 days.

3. Data Packages where client has requested Data to be returned, the data packages will be returned to client upon completed validation.

13.0 Electronic Data Deliverables (EDD)

This process will be initiated at step 1 with the receipt of disks or from the client or loading EDDs to LDC's secured Internet portal LDCAdvantage. After automated verification of the EDD format, content, and fields, the EDD will be populated with the manual review for importing of the final data qualifiers. The final approval of qualifiers will occur after step 5.