MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN SEDIMENT, TISSUE, AND WASTE BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

CHEMISTRY PROGRAM

2600 BLAIR STONE ROAD

TALLAHASSEE, FLORIDA 32399

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN SEDIMENT TISSUE, AND WASTE BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

TABLE OF CONTENTS

1. SCOPE AND APPLICATION 3
2. SUMMARY OF THE METHOD 4
3. APPARATUS AND EQUIPMENT 5
4. REAGENTS AND CHEMICALS 6
5. SAMPLE COLLECTION, PRESERVATION AND STORAGE PROCEDURES 10
6. SAMPLE PREPARATION PROCEDURE 12
7. SAMPLE ANALYSIS PROCEDURE 15
8. INTERFERENCES 20
9. DATA ARCHIVAL, PROCESSING, REVIEW AND REPORTING 21
10. QUALITY CONTROL 21
11. DETERMINATION OF METHOD DETECTION LIMITS 22
12. SAFETY, HAZARDOUS WASTE MANAGEMENT AND POLLUTION PREVENTION 22
13. REFERENCES 23
14. APPENDIX A: SIGNIFICANT CHANGES FROM PRIOR SOP VERSION 24

MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN SEDIMENT, TISSUE, AND WASTE BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1. This method details the analysis of purgeable organic compounds in sediment, tissue, and waste matrices by gas chromatography/mass spectrometry. The procedures describe the operational details needed to perform analysis of sediment, tissue, and waste samples in the Volatiles section of the Florida Department of Environmental Protection (FDEP) laboratory.

1.2. The following compounds may be determined by this method:

acetone
benzene
bromodichloromethane
bromoform
bromomethane
2-butanone (MEK)
carbon disulfide
carbon tetrachloride
chloroethane
chlorobenzene
chloroform
chloromethane
ortho-chlorotoluene
dibromochloromethane
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
dichlorodifluoromethane
1,1-dichloroethane
1,2-dichloroethane
1,1-dichloroethene
c*is*-1,2-dichloroethene
1,2-dichloropropane
trans-1,2-dichloroethene
cis-1,3-dichloropropene
trans-1,3-dichloropropene
ethylbenzene
2-hexanone
methylene chloride
4-methyl-2-pentanone (MIBK)
methyl-*t*-butyl ether (MTBE)
styrene
tetrachloroethene
1,1,2,2-tetrachloroethane
1,1,1-trichloroethane
1,1,2-trichloroethane
trichloroethene
trichlorofluoromethane
toluene
ortho-xylene
meta-xylene/*para*-xylene
vinyl chloride
1,4-dioxane*

*Due to 1,4-dioxane water solubility, it is extracted into water and analyzed as a water sample.

1.3. FDEP Test IDs and equivalent EPA methods covered by this Standard Operating Procedure (SOP):

S-VOC-MS	-	EPA Method 8260D analysis, preserved sediment sample
WAS-VOC-MS	-	EPA Method 8260D analysis, preserved waste sample
TCLP-VOC	-	EPA Method 8260D analysis of TCLP Extract by SOP VO-005
SPLP-VOC	-	EPA Method 8260D analysis of SPLP Extract by SOP VO-005
T-VOC-MS	-	EPA Method 8260D analysis, preserved tissue sample

1.4. Refer to the following Standard Operating Procedures for additional procedural information:

These supporting SOPs contain critical details not fully described within this method SOP. The analyst should be completely familiar with all these SOPs.

1.4.1. *Safety and Waste Management Practices in the Organic Analysis Groups* (SOP **OG-001**).

1.4.2. *Glassware and Equipment Cleaning Procedures* (SOP **VO-007**).

1.4.3. *Data Review/Authorization Procedures for the Volatile Organic Laboratory* (SOP **VO-010**).

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

1.4.4. *Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory* (SOP **VO-001**).

1.4.5. *Non-Conformance Reporting System* (SOP **LB-002**).

1.4.6. *Laboratory Policy Regarding Manual Chromatographic Peak Integration* (SOP **CM-018**).

1.4.7. *Standard Operating Procedure for Reporting Qualified Data* (SOP **LB-027**)

1.4.8. *Standard Operating Procedure for Records Storage and Retention* (SOP **LB-006**)

1.4.9. *Procedure and Policy for Method and Instrument Validation* (SOP **LB-007**)

1.4.10. *Limit of Detection Verification.* **(**SOP **LB-031**).

2. SUMMARY OF THE METHOD

The determination of volatile organic compounds by this method is a multi-step process that depends on the complexity and contamination level in the sediment, tissue, or waste sample. Two of the steps that are common to all samples is the introduction of the compounds by Purge & Trap followed by analysis by gas chromatography/mass spectrometry. More contaminated or complex samples may require an extraction step prior to introduction on the Purge & Trap instrument. Other methods involving direct injections may be more suitable for certain complex samples but are not described in this method.

2.1. Soil and Waste Sample Preparation Methods: The volatile compounds are collected and prepared according to the EPA Method 5035A, SW-846.

2.1.1. Low-Level Samples (<200 µg/kg) are collected in hermetically sealed vials or Encore samplers. The sealed vials are used without opening within a holding time of 14 days. Upon receipt 5 and 1 grams of each sample is weighed separately into 40 mL VOA vials then each covered with about 10 mL of volatile free water. This preparation must be done within 48 hours from the time of collection date. These preserved vials along with applicable QC are then stored below –7 °C the samples have a holding time of 14 days.

2.1.2. High-Level Samples (>200 µg/kg) are collected in Encore samplers or bulk containers and transported to the laboratory within 48 hours at 4 °C. Upon receipt, 5 – 10 grams of samples are extracted into 10 mL of methanol along with appropriate QC, then frozen. These extracts have a holding time of 14 days date of collection when stored below –7 °C. An aliquot of the methanol extract is added to water and purged as a water sample in SOP VO-002. If applicable a 1-5 gram sample can be prepared at the same time as the extract should the sample prove volatile free, with the same requirements as low level samples.

2.1.3. The compound 1,4-dioxane is collected in Encore samplers and bulk containers and then transported to the laboratory at 4 °C. A 10 g portion of the samples are either immediately extracted into 200 mL of water and are frozen in sealed vials within the specified holding time of 48 hours from time of collection and have a holding time of 14 days when stored below –7 °C. Once extracted, the entire 200 mL water extract is treated as a water sample as provided in SOP SV-015.

2.2. Tissue Sample Preparation Method: Tissue samples are prepared using a modified version of EPA Method 5035A, SW846.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

2.2.1. The sample is collected in the field and promptly frozen. The frozen tissue sample has a holding time of 14 days, at ≤ –20 °C. In the laboratory the tissue sample is shaved while frozen and placed into a hermetically sealed VOA vial with a Teflon stir bar, antifoaming agent, and 5 mL of DI water. The sample is then placed onto a shaker table for 30 minutes at 1500 rpm. Once prepared, the hermetically sealed sample has a holding time of 28 days at ≤ –20 °C from the time of sample collection.

2.3. Sample Introduction Method: The volatile compounds are introduced into the gas chromatograph by the EPA Purge & Trap Method 5035A, SW-846.

2.4. Quantitation Method: The components are separated *via* gas chromatography and detected using a mass spectrometer, which provides both qualitative and quantitative information. The described quantitative method is based on EPA Method 8260D, SW-846. The procedures described here are designed to meet or exceed the criteria from the EPA methods. Please refer to the EPA methods for additional details.

3. APPARATUS AND EQUIPMENT

The operation, cleaning and scheduled maintenance procedures prescribed by the equipment manufacturers are followed as provided in the Operator's Manuals. Manufacturer maintenance contracts are purchased for the Gas Chromatograph/Mass Spectrometer Systems. Documentation of cleaning, maintenance or system modifications are recorded in a maintenance logbook which accompanies each instrument system. Equivalent supply sources or brands for supplies may be used without editing the SOP.

3.1. Syringes, Pipets and Samplers:

3.1.1. Hamilton Microliter/Gastight Syringes (Class A): 5.0 µL, 10 µL, 50 µL, 100 µL, 500 µL, 1.0 µL, 2.0 µL, 5 mL, 10 mL, 50 mL. The Hamilton syringes are delicate and must be handled with care. Many of the syringes are equipped with Chaney adapters to improve the reproducibility of the injections and to minimize the bending of the plunger. The syringes are cleaned by 10 to 15 rinses with methanol. The Hamilton syringes must never be heated in an oven or damage may result. Damaged or corroded syringes must be cleaned and discarded into the sharp container. The average life expectancy for a syringe that is used daily is typically no more than a few months.

3.1.2. Encore Sampler: 5.0 g and 25 g.

3.2. Volumetric Flasks (Class A) and Graduated Cylinders: 10 mL, 25 mL, 50 mL, 100 mL, 200 mL and 500 mL.

3.2.1. The volumetrics are equipped with Teflon® (PTFE) or penny head ground glass stoppers.

3.2.2. The volumetric flasks and graduated cylinders are cleaned by rinsing with methanol and laboratory reagent water. The volumetrics are dried in a low temperature oven at 105 °C. Never use a brush or strong alkali solution to clean the volumetrics.

3.3. Glass Sample (VOA) and Standard Vials:

3.3.1. 42 mL VOA vials with a Teflon®/silicone septa and polypropylene open-top cap.

3.4. Miscellaneous Supplies:

3.4.1. Stainless Steel Spatula.
3.4.2. Disposable aluminum drying dishes.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

3.4.3. Teflon-coated stir bars, 8 mm x 16 mm.
3.4.4. Glass Jar with Teflon®-liner, 60 mL and 250 mL.

3.5. Solution 2000 Water Purification System.

3.6. Fisher IsoTemp Forced-Air Oven.

3.7. Thermo Heratherm OMH400-SS Mechanical Convection Oven.

3.8. Mettler XS6002S Top-Loading Balance, capable of weighing 0.01 g.

3.9. Denver A-250 Analytical Balance, capable of weighing 0.0001 g.

3.10. Flammable-Rated Refrigerator, Fisher Scientific Isotemp, Model 426-2.

3.11. Flammable-Rated Freezer, Kelvinator Scientific, Model BT30CWFMS-2.

3.12. Flammable-Rated Freezer, Fisher Scientific Isotemp.

3.13. GlasCol Shaker Table, Model DPM12

3.14. Milestone Ethos Ez Microwave Digestion Labstation

3.15. Gas Chromatograph/Mass Spectrometer Agilent System: (Reference 13.4 for Operating Manual.)

3.15.1. Agilent 6890N or 7890 Gas Chromatograph.
3.15.2. Agilent 5975 or 5977 Inert Quadrupole Mass Spectrometer.
3.15.3. Tekmar Atomx Purge & Trap and Autosampler
3.15.5. Personal Computer.
3.15.6. Agilent Enviroquant Computer Software.
3.15.7. Restek RXI-624SIL, 30 m x 0.25 mm ID capillary column, 1.4 µm film, or equivalent.
3.15.8. Supelco High Capacity Gas Purifier or equivalent.

4. REAGENTS AND CHEMICALS

Working with volatile compounds presents several challenges not normally confronted with the handling of most other chemicals. Volatile compounds are easily lost from prepared solutions or when present in the laboratory environment can cross-contaminate other samples. Review the techniques for handling volatile compounds found in **reference 13.1 and 13.2** before attempting to prepare solutions for analysis.

Sources of reagents and chemicals are given in this section, but may change based on availability, quality, and cost. The use of a different source is acceptable without modification of the procedures provided the products are equivalent.

The prepared concentration of standards or reagents may likewise be modified if it is deemed necessary or preferential for a given situation, such as lowering spike levels to achieve a lower minimum detection limit (MDL). Consult your supervisor for approval prior to making concentration modifications.

4.1. Organic Solvents (Purge & Trap grade):

4.1.1. Methanol: CH_3OH - Purge & Trap grade methanol is purchased in 500 mL amber bottles from Fisher Scientific.

4.2. Laboratory Sand:

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Ottowa sand is prepared by rinsing clean, white sand with methanol and laboratory reagent water several times. The rinsed sand is baked in an oven at 105 °C overnight to remove any volatiles and is then stored in the same oven. The heated laboratory sand may be purged with carrier grade nitrogen to facilitate the removal of trapped volatiles.

4.3 Laboratory Reagent Water:

Type 1 laboratory reagent waters are prepared in the laboratory from the municipal water supply. The criteria for laboratory reagent water are that it must not contain any analytes of interest at a concentration greater than 20% of the reporting limit. Other non-target compounds may be detected in the laboratory reagent water but must not interfere with the analysis of the target compounds. Examples of non-target compounds commonly observed are methanol (used in glassware cleaning and standard preparation) and siloxanes (from surfactants, pump oils and column bleed).

4.4.1. Type 1 Laboratory Reagent Water: Municipal water is purified with a Solution 2000 Water Purification System that uses activated carbon cartridges and ion-exchange cartridges to remove impurities. The laboratory reagent water is evaluated every day, when sample data is collected, as a method blank sample.

4.4. Internal Standard and Surrogate Solutions:

4.4.1. 25 ppm or 100 ppm Internal Standard/Surrogate Solution (IS/SURR): An internal standard/surrogate solution is injected into every sample by the autosampler just prior to analysis. The internal standard compounds are fluorobenzene, chlorobenzene-d_5, and 4-bromofluoromethane. The surrogate compounds are dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8 , and 1,4-dichlorobenzene-d_4. These compounds may be purchased in the prepared mixture STM-541 from UltraScientific (or equivalent solution) at a concentration of 5000 µg/mL in methanol.

4.4.1.1. The IS/SURR solution is prepared in P&T grade methanol at a concentration of 100 ppm. This standard is automatically introduced into the sample vials prior to purging by the Autosampler.

4.4.1.2. Dispense accurately 1 mL of STM-541 to achieve a concentration of 25 ppm (or 4 mL for 100 ppm level) into a 200 mL volumetric flask containing 190 mL of methanol. Fill the volumetric to the volume mark with methanol. The working internal standard is stored at ≤ -20 °C in amber 40 mL vials with Teflon-lined caps. New working standards are prepared from fresh stock solutions every 12 months or before the expiration date of the stock standard.

4.5. Calibration Standards:

The primary and secondary stock calibration standards used for the preparation of the initial calibration and daily quality control (CCV) check standards are purchased from o2si Smart Solutions in P&T methanol as custom mix 124165-01 (100/300 µg/mL). This standard solution includes all the compounds routinely reported by this method. The stock solutions are ready to use as working standards, without dilution, after the stock solution ampules are opened and the contents transferred to a labeled 2 mL vial with a Teflon-lined screw cap. Once opened, the working solutions must be used within 30 days or before the stock standard expires, whichever comes first. All stock and working standards are stored at ≤ -20 °C. A list of the normal calibration levels is given below where a minimum of 5 levels is selected for instrument calibration. Additional calibration levels may be prepared as deemed necessary.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Other compounds that are not routinely reported are spiked only when requested in the test. Additional analytes from the list of compounds found in Method 8260D may be added to this method once initial demonstration and proficiency has been demonstrated through a validation exercise.

The calibration standards must be prepared from the working standards just prior to use in each analysis batch. The calibration standard dilutions must be prepared with Class-A syringes and volumetrics. Mixing the dilutions is accomplished by gently rotating the volumetric flasks slowly 2 times (do not shake!). Transfer the calibration standards to zero headspaced VOA vials immediately after preparation to minimize the loss of volatile compounds. Refer to **reference 13.1** for additional details on the preparation and handling of calibration standards.

4.5.1. Daily Working Calibration Standards:

4.5.1.1. 100/300 ppb o2si 124165-01 Primary Calibration Standard: prepare a 1:1E3 dilution from the 100 µg/mL stock standard. With a 50 µL gastight syringe, add 50 µL of the 100 µg/mL o2si stock standard solution to a 50 mL volumetric flask containing 45 mL of laboratory reagent water. Dilute to final volume and cap flask. This daily working solution must be used within 1 hour after preparation if kept in the volumetric flask. The life of the solution can be extended to 7 days if the solution is zero headspaced and refrigerated.

4.5.2. Initial Calibration Standards:

4.5.2.1. 10/30 ng o2si calibration standard: With a 500 µL syringe inject 100 µL of the 100/300 ppb o2si daily working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.5.2.2. 20/60 ng o2si calibration standard: With a 500 µL syringe inject 200 µL of the 100/300 ppb o2si daily working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.5.2.3. 40/120 ng o2si calibration standard: With a 500 µL syringe inject 400 µL of the 100/300 ppb o2si daily working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.5.2.4. 50/150 ng o2si calibration standard: With a 500 µL syringe inject 500 µL of the 100/300 ppb o2si daily working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.5.2.5. 100/300 ng o2si calibration standard: With a 1.0 mL syringe inject 1.0 mL of the 100/300 ppb o2si daily working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.5.2.6. 200/600 ng o2si calibration standard: With a 2.0 mL syringe inject 2.0 mL of the 100 ppb o2si daily working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.5.3. Daily Quality Control Check Standards:

The working calibration standards used for the preparation of the daily quality control check (CCV) standards contain all the compounds reported for the analysis.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

4.5.3.1. CCV 100/300: A 100/300 ng calibration check sample is prepared from the primary o2si 124165-01 mixture and analyzed every 24 hours of instrument operation when analytical data is being acquired.

4.5.3.3. Calibration checks for other compounds are prepared only for those analytical tests or samples which require the special compounds.

4.6. Laboratory Fortified Blank and Matrix Spike Standards:

The matrix spike standard mixes are used for the preparation of Laboratory Fortified Blanks (LFBs) and sample Matrix Spikes (MS). The second source stock standard is purchased from o2si in the custom mix 124165-01-SS (100/300 µg/mL). All stock and working standards are stored at ≤ -20 °C. The LFB/MS standard solutions are used as a second source to verify the primary calibration standards.

Compounds not routinely reported are spiked only when requested in the test. The calibration standards for these compounds are prepared in a similar fashion to the working standard mixes Additional analytes from the list of compounds found in Method 8260D may be added to this method once initial demonstration and proficiency has been demonstrated through a validation exercise.

The LFB and matrix spike standards must be prepared from the working standards just prior to use in a batch analysis.

4.6.1. 100/300 ppm o2si 122348-01SS Second Source Working Standard: The working matrix spike standard is prepared by simply opening a sealed ampoule of the o2si custom mix 124165-01-SS and transferring the standard solution to a 2.0 mL vial with Teflon screw cap. The working standard solution must be used within 30 days or before the stock standard expires, whichever comes first.

4.6.2. 100/300 ppb o2si 122348-01SS Second Source Daily Working Standard: prepare a 1:1000 dilution of the 100/300 ppm o2si 124165-01-SS working standard. With a 25 µL gastight syringe, add 25 µL of the 100/300 µg/mL o2si custom mix 124165-01-SS working standard solution to a 25 mL volumetric flask containing 20 mL of laboratory reagent water. Dilute to final volume and cap flask. This daily working solution must be used within 1 hour after preparation if kept in the volumetric flask. The life of the solution can be extended to 24 hours if the solution is zero headspaced and refrigerated

4.6.4. 40/120 ng LFB Preparation: With a 500 µL syringe inject 400 µL of the 100/300 ppb o2si daily second source standard solution into a clean soil vial containing 5.0 mL of laboratory reagent water and 5.0 grams of reagent sand. Cap the soil vial immediately. A 40 ng LFB is prepared for every 10 samples.

4.6.5. 40/120 ng Matrix Spike Preparation: With a 500 µL syringe inject 400 µL of the 100/300 ppb 02si daily second source standard solution into a 5.0 gram matrix soil sample vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately. A 40 ng matrix spike check is prepared for every 10 samples (duplicate matrix spikes prepared for every 20 samples meets the 10% requirement).

4.7. Carbopacks – 2 grams Getter Carbopacks, 1500/pail, from Sud Chemie Performance Packaging. The packets are used to trap volatiles in the shipping packages.

5. SAMPLE COLLECTION, PRESERVATION AND STORAGE

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

The collection, preservation and storage of samples begin with the preparation of the sampling kit used to contain the sample. The kits are provided by the laboratory and are prepared based on the sample requests received on a weekly basis.

5.1. Low-Level Soil VOA Vial Preparation: (if used as part of a sampling kit)

The laboratory prepared sampling kits may contain 2 to 3 VOA vials inside of a Ziploc bag. The protocol for cleaning the vials can be found in the cleaning SOP **VO-007**. Instructions for assembling the sample kits are as follows:

5.1.1. Always prepare the VOA vials in batches of 100 or more vials at a time.

5.1.2. Remove clean sample vials, septa, and Teflon-coated stir bars from the low temperature oven (105 °C). Cover the vials and septa with aluminum foil and cool to near room temperature. A box of clean open-top caps will also be needed. Certified precleaned vials may also be used in the place of lab prepared vials.

5.1.3. Place the vials in cases of 50 to 100 vials.

5.1.4. Add one stir bar in each vial.

5.1.5. Add 5 mL of laboratory reagent water to each vial with a pipetter.

5.1.6. Place a septum on each vial with the Teflon side toward the vials and screw on the open-top cap snugly.

5.1.7. Label the vials with unique, sequential numbers. Label the boxes with a lot ID Number.

5.1.8. Weigh each vial to 3 significant figures on the top loading balance and record the vial ID and weight in the weight notebook.

5.1.9. If purchased vials are not certified pre-cleaned, then submit vials for testing. Quality Control testing of the vials must demonstrate that the vials are free of target analytes to a level less than 20% of the reporting limit. The vials should not be used to prepare kits until the QC testing is complete and documented in the LIMS. The QC approved vials can be stored in the VOC laboratory.

5.2. Sample Kit Assembly:

5.2.1. For Low-Level Soil Tests, place three to four QC-approved vials and 2-gram Carbopack in a 3-mil polyethylene Ziploc bag. Visually inspect the vials as you prepare the kit for anything unusual such as loose caps, inverted septa, or cracked vials.

5.2.2. For all Soil and Waste Tests, add one 25 g Encore samplers into each kit. The Encore should come in a re-sealable foil package.

5.2.3. For all Soil and Waste Tests, add one bulk glass jar container(the bulk jar must accompany the rest of the kit to the field sampling site). This sample portion is used for dry-weight and waste analysis determination.

5.2.4. For the Tissue Test, place a pre-cleaned 60-mL jar with Telon®-lined lid into a 3-mil polyethene Ziplock bag. Visually inspect the jars as you prepare the kit for anything unusual such as loose caps, missing liner, or cracked vials.

5.2.5. Label the outside of the kit container with the vial type and vial Lot ID Number.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

5.3. Sample Collection:

5.3.1. For Low-level Soil Sample Collection:

5.3.1.1. Remove the soil vials from the Ziploc bag. Use all vials in the kit.

5.3.1.2. Use a clean coring device to add a 3.0 cc plug of soil to each soil vial. If the soil is very wet increase the soil plug volume to 4.0 cc. Care must be exercised, when collecting the sample, not to pour out the water in the vial or get soil on the lid or lip of the vial. Also, avoid putting rocks and sticks into the sample.

5.3.1.3. Gently wipe any soil from the lid or lip of the vial.

5.3.1.4. Once the sample is collected, the septa must be placed with the Teflon® side towards the sample and the open-top cap tightened finger tight.

5.3.1.5. After the samples are capped, return them into the Ziploc bag and kit container.

5.3.2. For All Soil and Waste Sample Collection:

5.3.2.1. Remove the Encore samplers from the foil pouch and fill each with a plug of soil as directed in the manufacture instructions.

5.3.2.2. Label the Encore samplers and return them to their re-sealable foil packet.

5.3.2.3. Fill the bulk sample jar with minimal head space. Wipe the lip of the jar and seal the jar tight with the Teflon/silicon septa lid.

5.3.3. For Tissue Sample Collection:

5.3.3.1. Fill the 60 mL jar with a single tissue type, leaving minimal head space at the top of the container. Freeze the sample immediately on dry ice.

5.3.4. The outside of the sample bag and glass bulk jar must be labeled with a field identification. Chain-of-custody labels may be placed across the bag and glass jar lids to give added protection to the integrity of the sample. Fill out all applicable chain-of-custody forms.

5.4. Sample Storage:

5.4.1. Soil vials and Encore samplers may be stored in a flammable-rated refrigerator at 4.0 ± 2 °C for up to 48 hours after sampling. The soil vials and Encore samplers must be analyzed or extracted within 48 hours of sampling to avoid sample expiration. The contents of the Encore samplers must be transferred as soon as possible to a hermetically sealed soil vial or into a methanol extract and stored at < -7.0 °C. The extracted or transferred samples must be analyzed within 14 days of sample collection.

5.4.2. Alternately to 5.4.1, soil and waste collected in hermetically sealed sample vials may be immediately frozen to < -7.0 °C and analyzed within 14 days of sample collection.

5.4.3. Tissue samples must be stored at ≤ 20 °C, prepared within 14 days of sample collection, and analyzed within 28 days of sample collection. The tissue test has been validated for a short subset of compounds with an establish holding time of 28 days.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

6. SAMPLE PREPARATION PROCEDURE

6.1. All glassware must be cleaned according to the glassware cleaning SOP **VO-007**.

6.2. Print out a backlog and determine which samples will be prepared and analyzed. Samples may be assigned by the Section Administrator or Senior Chemists.

6.3. The assigned samples must be checked out from the assigned Receiving room sample refrigerators.

6.4. Each sample must be visually inspected for broken vials, sample headspace, loose lids, upside down septa and chain-of-custody seals (if applicable). Any problems are noted in the sample preparation log.

6.5. The soil VOA vials must be weighed to determine the soil weight added to the reweighed vials.

6.6. <u>High Level Extract Preparation:</u>

A 10-g subsample from one of the Encore samplers is used to prepare an extract for each sample. The sample extract is used for sample screening and high-level soil and waste analysis. Record all preparation information in the Sediment/Waste Sample Preparation Logbook.

6.6.1. Tare a clean, labeled VOA vial on the top loading balance. For 1,4-dioxane analysis use a 250 mL beaker.

6.6.2. Remove approximately 10 g of sample from an Encore sampler or bulk sample container and place it into the sample vial or beaker. The soil sample should be removed from the container as a columnar plug from the center of the sample and care taken not to mix or fragment the soil if possible. If the sample is highly heterogeneous, take several small plugs from more than one area in the sample. Record the sample weight to three significant figures.

6.6.3. For all compounds other than 1,4-dioxane, tare the balance and weigh out approximately 10 g of methanol into the VOA vial. Record the methanol weight in the sample preparation log to three significant figures.

6.6.4. Wipe the rim of the VOA vial to ensure a good seal. Cap the VOA vial finger tight with a Teflon/silicon cap.

6.6.5. The extract must be thoroughly mixed, once the methanol is added and the vial is capped, using a Vortex mixer for up to 1 minute. Recoveries of the more volatile compounds can be severely reduced if the sample is mixed too long or vigorously.

6.6.6. Prepare a methanol extract solvent blank for every batch of extracted samples by adding 20 mL of the methanol into a clean VOA vial and store with the sample extracts. Use the same technique to prepare the blank as used to prepare the samples.

6.6.7. Store the sample extracts in the freezer at < -7 °C for at least 4 hours before analyzing as a high level sample. This will give the sample time to extract into the methanol solvent.

6.6.8. For 1,4-dioxane analysis only - weigh out a 10 g soil sample aliquat and 100 mL of laboratory reagent water into a 250 mL beaker. Record the sample and water weight in the sample preparation log to three significant figures. Stir the soil and water mixture for two minutes and let the sample settle. Once extracted, the entire 100 mL water extract is treated as a water sample. Proceed to SOP SV-015 for the 1,4-dioxane water sample extract preparation and analysis.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

6.7. Low-Level Sediment Preparation:

The low-level EPA Method 5035A method involves purging a heated sediment sample mixed with laboratory reagent water. Record all preparation information in the Sediment/Waste Sample Preparation Logbook.

6.7.1. Weigh out approximately 5.0 g of soil sample into a soil vial.

6.7.2. Record the sample weight in the sample preparation notebook.

6.7.3. Place a magnetic stir bar into the soil vial.

6.7.4. Add 5.0 mL of laboratory reagent water to the vial

6.7.5. Make sure no residual soil is on the vial's sealing surface. Seal the vial with the Teflon/silicone cap. (for samples collected in hermetically sealed VOA vials, steps 1-5 have already been done during field collection).

6.7.6. Prepare a blank sample by weighing ~5.0 g of laboratory sand into the soil vial following steps 1-5 above.

6.7.7. Prepare a Lab Fortified Blank (LFB) sample by weighing ~5.0 g of laboratory sand into the soil vial following steps 1-5 above. If matrix spikes cannot be prepared, then prepare two LFB samples.

6.7.8. Prepare duplicate Matrix Spike (MS) samples by weighing ~5.0 g of a randomly selected sample into the soil vial following steps 1-5 above. If matrix spikes cannot be prepared, then prepare two LFB samples.

6.7.9. For samples collected in the field, record the final sample (weight + vial) and the vial ID number. This information must be matched with the initial pre-weight vial information to determine the final soil mass in each vial. (refer to section 5.1)

6.7.10. Place the soil samples in the refrigerator is they are not going to be analyzed immediately.

6.7.11. The autosampler is equipped to automatically add the surrogates and internal standards.

6.8. Low-Level Tissue Preparation:

The low-level tissue method is a modification of the EPA Method 5035A low-level sediment method. In the laboratory the tissue sample is shaved while frozen and placed into a hermetically sealed VOA vial with a Teflon stir bar, antifoaming agent, and 5.0 mL of DI water. The sample is then placed onto a shaker table for 30 minutes at 1500 rpm. The sealed vial has a holding time of 28 days at ≤ -20 °C from the time of sample collection. Record all preparation information in the Sediment/Waste Sample Preparation Logbook.

6.8.1. Tissue Cooking – use the following steps to cook the tissue sample, otherwise skip to preparation step 6.8.2. Refer to the microwave operation instructions for programming and operational details. The cooking temperature specifications for seafood are provided in this procedure. See the seafood cooking reference for additional details.

6.8.1.1. Weigh out approximately 15 grams of frozen tissue into a clean Teflon® microwave cooking vessel.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

6.8.1.2. Assemble the cooking vessels. One of the vessels must have a lid equipped with a temperature probe sensor port.

6.8.1.3. Assemble the vessels into the microwave carousel and place a thermocouple probe sensor into the probe sensor lid. Place the carousel assembly into the microwave oven.

6.8.1.4. Program the microwave to heat the tissue samples to 71.1 °C slowly on an 8 minute heating ramp and then maintain the heating at 71.1 °C for an additional 8 minutes.

6.8.1.5. Remove and disassemble the vessels once the cooked tissue has cooled to room temperature (about 15 minutes).

6.8.1.6. Place the cooked tissue into a labeled, clean 60 mL Jar with Teflon® septa. If desired, the tissue samples can be weighed out at the same time as sample transfer. Otherwise, return the cooked sample to the freezer storage until ready to further process.

6.8.1.7. Proceed to step 6.8.3.

6.8.2. Shave the frozen tissue into very thin slices using a razor or dermatome tool. The frozen tissue must not be allowed to thaw, so work quickly. Do not allow the original sample to thaw since repeated freeze/thaw cycles can compromise the sample integrity.

6.8.3. Weigh out approximately 1.0 gram of tissue into a soil vial.

6.8.4. Record the sample weight in the sample preparation notebook.

6.8.5. Place a magnetic stir bar into the vial.

6.8.6. Add 5.0 mL of laboratory reagent water to the vial.

6.8.7. Add one drop of Anti-Foam Agent-A to the vial.

6.8.8. Make sure no residual tissue is on the vial's sealing surface. Seal the vial with the Teflon®/silicone cap.

6.8.9. Each preparation batch of samples must include a blank, replicate sample, LFBs, and duplicate matrix spikes.

6.8.10. Place all the tissue sample vials on their side on the shaker table. Shake the samples for 30 minutes at 1500 rpm.

6.8.11. Once the shaker process is complete, place the tissue samples in the freezer if they are not going to be analyzed immediately.

6.8.12. The autosampler is equipped to automatically add the surrogates and internal standards.

6.9. Select a sample for duplicate matrix spikes. The matrix spike sample is selected randomly from the samples in the batch; however, some consideration must be given to the number of available vials or samples. See **Section 4.7.** for matrix spike description and instructions.

6.10. The internal standard and surrogate compounds are automatically added to each sample by the autosampler. The autosampler is equipped with a 1.0 µL loop that rotates into the sample path just prior to sample analysis. The 1.0 µL loop injects 25 ng (100 ng for the high level IS/SURR

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

solution) of each internal standard and surrogate compound and are automatically transferred into the sample vial.

6.11. Laboratory Soil Blank: A laboratory sand preparation is carried through the entire sample and weighing process and is analyzed as a laboratory soil blank. The blank is prepared by adding 5.0 g of sand and 5.0 mL of laboratory reagent water to a clean soil vial.

6.12. Percent Dry Weight: Refer to SOP **MT-055** for the dry-weight determination procedure. The percent dry weight of sediment samples is determined by weighing out 5-10 g of sample into a weighing dish and drying the sample at 103 ± 2 °C overnight for 12 hours minimum. The percent dry weight is equal to the (dry sample weight divided by the wet sample weight) times100. The drying oven must be vented to minimize laboratory contamination and odors. Samples that may pose a fire hazard must not be placed in the oven. Do not measure the dry weight for waste samples since they are reported based on wet weight.

7. SAMPLE ANALYSIS PROCEDURE

7.1. Instrument Conditions: The instrument conditions are set to those given in SOP **VO-008**.

Note: The GC/MS software used by the Finnigan and Agilent instruments is designed to collect MS data, set up calibration files, automatically perform calculations, report pass/fail for tuning, and report detect/non-detect for compound identification based on the method criteria. The chemists, however, should always review carefully data generated by the instruments for accuracy.

7.2. GC/MS instrument file names are generated using the 9-character naming convention **YYMDDI##** where: ## Sequential sample numbers from 01-99.

7.3. GC/MS Tuning: The GC/MS system must be checked to ensure that acceptable performance criteria are achieved for the tuning compound bromofluorobenzene (BFB) at the beginning of each day and every 12 hours thereafter for as long as analysis is to be performed. This performance test must be passed and maintained before any samples or standards are analyzed.

7.3.1. The internal standard and surrogate solution, which is added automatically by the autosampler, contains BFB as one of the surrogates. Analysis of a laboratory reagent water blank will also serve as a GC/MS performance test.

7.3.2. The GC/MS system is tuned using ≤50 ng bromofluorobenzene (BFB). Obtain a BFB spectra by taking the apex scan or summing the intensities of the m/z's across the GC peak. Background subtraction is allowed by subtracting a single background scan acquired within 20 scans of the elution of BFB. The background subtraction is designed to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak to achieve a passing tune.

The BFB m/z abundance criteria below are used to tune the mass spectrometer prior to other standard, blank, and sample analysis.

Table 1. BFB m/z Abundance Criteria:

Mass, m/z	Abundance Criteria
95	Base peak, 100 %
96	5-9 % of mass 95
173	<2 % of mass 174
174	50-200% of mass 95

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

175	5-9 % of mass 174
176	95 to 105% of mass 174
177	5-10 % of mass 176

7.4. Initial Calibration:

Each instrument is calibrated according to the procedures specified within EPA Method 8260D. Clarification of the calibration requirements and practices of this laboratory are discussed below. Acceptance criteria are tabulated in the QAQC SOP **VO-001**. Refer to the EPA method protocols in **Reference 13.1 and 13.2** for additional detail.

Analytical standards for the initial calibration must be certified and NIST traceable. The standard solutions for the calibration and standard spiking solutions must be from independent sources. The term "independent source" means that the origins of the standard preparations are known to be different from one another. In practical terms this requires that the solutions be prepared by two different suppliers or at a minimum, have different lot numbers from the same supplier.

An initial calibration of the GC/MS instrument is performed whenever the percentage difference or drift for more than 20% of the analytes is more than 20% from the anticipated recovery. The complete list of analytes is contained within the daily quality control check standards.

Five standard concentration levels, with the lowest level equal to the MDL or PQL, are used to create the initial calibration curve. The calibration curve is fit with a linear regression. The correlation coefficient for the linear fit of the calibration curve must be ≥ 0.995 for all target analytes. All quantitations are carried out using the internal standard technique. Paper copies of the calibration and quantitation reports are stored in a file folder using the **YYMDDI##** naming convention described in **Section 7.2.** The initial calibration curve must meet the following criteria:

7.4.1. An average response factor can be calculated for each target compound once the calibration curves satisfy the linearity requirement. The average response factor is calculated as follows:

Average Response Factor $= A_s \times C_{is} / A_{is} \times C_s$

where:
A_s = Peak area of analyte or surrogate
C_{is} = Peak are of internal standard
A_{is} = Concentration of analyte or surrogate
C_s = Concentration of internal standard

7.4.2. The retention time of the target analytes in each calibration standard must agree within with in ± 6 seconds. Late-eluting compounds usually have much better agreement.

7.4.3. A reference mass spectrum library must be generated for all the target compounds. The reference spectra can be extracted from the calibration data, provided that the target compounds do not coelute. In the case of coelution, an individual compound standard analyzed using the same method conditions will be required to produce the reference mass spectrum. The reference spectra will be used for qualitative and quantitative analysis as described later in this section. Refer to the operator manual for each mass spectrometer (**references 13.3 and 13.4**) for procedures on generating a reference mass spectrum library.

7.5. Daily Quality Control Check Standards (CCVs):

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

The daily quality control check standards include all compounds being reported and are used to check the accuracy of the initial calibration curve and to ensure that the standards used to generate the curve have maintained their integrity. A CCV is analyzed every time the instrument is calibrated and every 12 hours of instrument operation. In this method the compounds in the CCV must meet the acceptance criteria as given in EPA Method 8260D. The daily quality control check standard must meet the following criteria:

7.5.1. For the initial calibration to be assumed valid, the percent difference for any one of the CCVs must be less than or equal to 20% from the anticipated recovery based on the last calibration.

7.5.2. All analytes in the CCV must continue to meet the 20% difference criterion as given in EPA method 8260D. Compounds out of the acceptance limits are considered out of control and must be flagged. Given the large number of analytes involved, it is expected that there will be some compounds that do not achieve this criterion on a regular basis. However, if more than 20% of compounds fail the criterion then a new calibration is likely needed.

7.6. PQL or MDL Check Standard:

A sensitivity check sample is analyzed daily at the start of each analytical run. The PQL check standard contains analytes of interest at a concentration level of 1-2X the method PQL. The PQL must meet the accuracy limits established in the QC statistics table given in the LIMS. Alternatively, an MDL level sample may be prepared to verify that the compounds are detected. If the MDL or PQL check standard fails, corrective actions must be taken. The accuracy of the PQL check standard must be in the range of 70-130%. The spiked compounds in an MDL level sample must be detected.

7.7. Internal Standard Retention Time and Internal Standard Response:

The internal standard responses and retention times of each standard and sample analyzed are evaluated after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the retention in the initial calibration, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the extracted ion response for any internal standard varies by more than 50% from the initial calibration, the GC/MS system must be inspected for malfunctions and corrections must be made, as appropriate. Any standard or sample failing these internal standard checks must be re-analyzed. The system may be re-calibrated, if necessary.

7.8. The analysis sequence should be similar to the following:

7.8.1. BFB tune check every 12 hours.

7.8.2. Laboratory reagent water blank (the tune and blank checks can be performed together).

7.8.4. PQL (or MDL) calibration check standard with every sample batch.

7.8.5. 40 ng calibration check standard CCV every 12 hours.

7.8.6. Replicate laboratory fortified blanks (LFB1 and LFB2) every 20 samples.

7.8.7. Replicate matrix spikes every 20 samples.

7.8.8. Laboratory Sand Blank prior to sample sequence.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.8.9. Methanol extract solvent blank (if applicable from waste or high-level soil analysis)

7.8.10. Samples (including duplicate sample).

7.8.11. Laboratory Sand Blank.

7.8.12. 40 ng calibration check standard CCV, if continuing with another sample batch.

7.9. Pre-Analysis Checklist for the GC/MS run sequence:

7.9.1. Check the GC temperature program.

7.9.2. Check the autosampler program.

7.9.3. Check the quantity of internal standard and liquid nitrogen.

7.9.4. Empty the autosampler waste bottle.

7.9.5. Fill the autosampler wash bottle with laboratory reagent water and pressurize it.

7.9.6. Check the purge and trap parameter settings.

7.9.7. Check the job folders and field sheets for any special instructions

7.9.8. Set up the acquisition sequence in the instrument log and in the computer acquisition program.

7.9.9. Check the acquisition parameters in the computer program.

7.9.10. Arrange the sample vials in the autosampler tray.

7.9.11. Double check the order of the sample vials to ensure that it is consistent with the computer acquisition and the instrument log.

7.9.12. Check the volume of internal standard/surrogate standard in the syringe (or vial) on the autosampler.

7.10. Post-Analysis Checklist:

The results of each analytical run must be examined promptly upon completion. The instruments are designed to create both an electronic file and hardcopy for each sample analyzed. The following items must be checked following each batch analysis:

7.10.1. Check all tune blanks for compliance with tuning requirements.

7.10.2. Check to make sure the internal standards and spikes are in the retention time window, and their mass spectra are correct.

7.10.3. Check the surrogate and spike recoveries against acceptance limits. The acceptance criteria are tabulated in the LIMS statistics section and are updated quarterly. As a guide, the recovery limits for the surrogates are within 80-120%. The recovery limits for the CCV analytes are within 80-120 % and the LFB and MS spike compounds are typically within 70-130%.

7.10.4. Inspect the vials on the autosampler tray to ensure each was properly sampled.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.10.5. The laboratory soil blanks must be free of target compounds (< 50% MDLs).

7.10.6. Duplicate sample results must be comparable. Reanalyze the sample if the duplicate varies by more than 20%.

7.10.7. All detected target compounds must be within the calibration range. Reanalyze samples at a more appropriate dilution level if compounds are out of range.

7.10.8. For complete reporting procedures, refer to SOP **VO-010** for specific procedures.

7.10.9. Hardcopies of all sample data must be put into the associated job folders.

7.10.10. Hardcopies of the blanks, QC samples, calibration samples, LFBs, matrix spike must be put into the Daily QC folder.

7.11. Qualitative Analysis:

Qualitative identification of each compound is based on retention time and comparison of the sample mass spectrum with characteristic ions in the reference mass spectrum. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest intensity or any ions over 30% relative intensity. Compounds are identified as present when the following criteria are met:

7.11.1. The characteristic ions of a compound maximize in the same scan or within one scan of each other.

7.11.2. The retention time of the compound is within ± 6 seconds of the retention time of the standard component.

7.11.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. The presence of coeluting compounds may alter the relative intensities and complicate the compound identification. Examination of extracted ion current profiles can aid in the selection of spectra and in qualitative identification of compounds.

7.11.4. Structural isomers that produce similar mass spectra and are sufficiently resolved are identified as individual isomers. If the height of the valley between two close eluting isomers is more than 25% of the sum of the two peak heights, then the structural isomers must be identified as isomeric pairs.

7.11.5. A library search must be performed for unknown chromatographic peaks when the total ion chromatogram of the sample contains unknown peaks larger than the internal standard peaks. A tentative identification can be assigned provided that relative intensities of major ions in the library reference spectrum are present in the sample spectrum, and the relative intensities agree within ±20%. Molecular ions must also be present.

7.12. Quantitative Analysis:

7.12.1. The quantitation of identified compounds is based on the integrated abundance of the extracted ion current profile of the primary characteristic ion(s). The internal standard used for quantitation is the one nearest to the retention time of the analyte.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.12.2. The average response factors from the initial calibration are used to calculate the concentration of each compound in the sample. See EPA Method 8260D and reference within for more details.

7.12.3. Solid samples with a significant moisture content (>10%) that are extracted prior to analysis with methanol are diluted by the total volume of the methanol/water mixture. To report this type of sample result on an "as received" basis, the detected concentration must be corrected by the methanol/water dilution factor. See EPA Method 8000C for additional details.

Calculate the total methanol/water extraction volume (V_t) as follows:
Note: All sample weights are in grams (g) and volumes in milliliters (mL).

$$\mathbf{V_t = Vol.\ of\ solvent + \frac{(\%\ moisture \times Wt.\ of\ sample)}{100}}$$

7.12.4. Solid samples, other than waste and tissue, are reported on a dry weight basis. A correction factor for moisture content is applied in the LIMS based on the % moisture measured in the soil sample, as described in SOP MT-005-1.

Calculate the % moisture as follows:

$$\%\ \text{Moisture} = \frac{\text{Wt. of sample} - \text{Wt. of dry sample}}{\text{Wt. of sample}} \times 100$$

Calculate the Moisture Correction as follows:

$$\text{Moisture Corrected Concentration} = \frac{\text{(As received concentration)}}{(100 - \%\ \text{Moisture})} \times 100$$

8. INTERFERENCES, MAINTENANCE AND TROUBLE SHOOTING

Handling difficult samples is a routine part of lab work. However, proper handling can make a significant difference in the analytical results. The procedures below are designed to minimize the impact of difficult sampling situations.

8.1. Submitted sediment samples containing water or excessive amounts of water must be reported to the supervisor to determine the most appropriate test.

8.2. Samples analyzed with an inverted septum or debris under the sealing edge of the septum must have a comment added to the job folder and in the LIMS comment field for the sample.

8.3. Sediment samples containing oil, paint or multiphase waste must be re-logged into the LIMS as waste samples. The receiving room supervisor or section supervisor can change the test.

8.4. Broken, missing or frozen sample vials must be reported to the section supervisor. Also, inform the supervisor immediately if the vials in a sample container do not look similar. The customer must be notified, if possible, prior to sample analysis and informed of the irregularities. Add a comment to the job file and into the LIMS file for the affected sample.

8.5 Follow the routine scheduled maintenance by service engineer all the time.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.6 After the analysis of highly contaminated samples and samples with chlorine, GC-MS and purge and trap may need maintenance. Multiple instrument blanks can remove carry over and injection port service may be indicated. Samples with severe matrices or high levels of free chorine or basic pH can necessitate needing a new column installed, a new transfer line, cleaning the MS, installing a new trap for the Atomix and all samples pathways cleared.

8.7 Replace internal standard and surrogate standard mix when vial volume reaches 50 % or upon expiration date of the standard.

8.8 Careful daily monitoring of instrument performance must be done routinely on every instrument under the responsibility of the analyst. If curves are difficult to pass or if internals and surrogates are problematic, if contamination or interference is suspected the analyst should read the maintenance log of the instrument in question for guidance. Once a direction is chosen to make a detailed record of the steps taken to restore the instrument to control in the maintenance log. This will help analysts conduct trouble shooting and maintenance in the future.

8.9 If any of the above does not work call for service without delay.

9. DATA ARCHIVAL, PROCESSING, REVIEW AND REPORTING

9.1. Archive data to a network directory for safekeeping. Once the raw data is reviewed and final reports are generated, transfer to QC-Manager to perform calculations. When the calculations are finished, review data and report. The Data Review and Authorization process is described in detail in the **SOP VO-010**.

10. QUALITY CONTROL

Quality control procedures for the operation of the GC/MS instruments include:

10.1. The GC/MS system must be tuned to meet the BFB specifications in **Section 7.3**.

10.2. Evaluation of retention time windows to ensure that all compounds are detected within their respective time windows and meet the ± 6 second requirement in **Section 7.4.4**.

10.3. There must be an initial calibration of the GC/MS system as described in **Section 4.6**.

10.4. The GC/MS system must meet the CCV criteria for each 12 hours of instrument operation as described in **Section 7.4**.

10.5. A laboratory reagent water blank (method blank) must be analyzed before the samples in the analytical batch. The blank results must demonstrate that the analytical system contains less than 20% of the reporting level for all target compounds. The analytical system must also be free of contamination that interferes with the analysis of the target compounds.

10.6. The laboratory must fortify all samples with surrogate standard solutions and calculate the percent recovery of each surrogate compound. The surrogate recovery data is uploaded with the daily check data into the QC database of the LIMS. The control limits are set at **Avg.** +/- 3**Std**, where **Avg.** is the average recovery and **Std** is the standard deviation. Appropriate corrective measures must be taken if the surrogate recovery values are outside of these limits and the affected sample(s) must be reanalyzed.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

10.7. The laboratory must analyze a duplicate matrix spike sample for every batch of up to 20 samples. Batch matrix spikes and replicates shall be prepared separately for each main quality system matrix group identified by NELAP (see Section 11 for definition of matrix groups). These groups represent the minimum matrix distinctions matrix quality control samples where there is evidence that the accuracy and precision will not be affected by sub-matrix distinctions within this group, Otherwise, batch matrix quality control samples shall be prepared separately for each matrix type. Where a suitable quality system matrix cannot be found for preparing batch method blanks, a substitute matrix may be used or sometimes no matrix may be appropriate. Inappropriate background analyte levels in a quality system matrix may be one reason for substituting or excluding a matrix in a method blank for some quality system matrix batches

The QC measures for matrix spikes must include the following:

- Include at least one set of matrix spikes in every sample batch.
- The accuracy (%Recovery) and precision (%RPD) are calculated for every pair of spikes and a statistical analysis is performed quarterly on the last 20 points to calculate and update the quality control tables in the LIMS.
- The control limits are then set at **R** +/- 3**s**, where **R** is the average of %Recovery (for precision it is the average of %RPD) and **s** is the standard deviation.
- Appropriate corrective measures must be taken if the analyte recoveries or RPDs are outside of these limits and the affected samples must be reanalyzed.
- The spike recoveries and statistical analysis are uploaded into LIMS and printed in the final report for the job.

10.8. For more specific information regarding QA/QC measures, see **Reference 13.2** and SOP **VO-001**.

11. DETERMINATION OF METHOD DETECTION LIMITS AND DEMONSTRATION OF CAPABILITY

Refer to the SOP **LB-007** *Procedure and Policy for Demonstration of Capability for Method, Instruments and Staff* and refer to SOP **LB-031** *Limit of Detection Verification* for procedural details

12. SAFETY/HAZARDOUS WASTE MANAGEMENT

12.1. Review the Laboratory Safety SOP Manual and the Contingency Plans and Emergency Procedures for a Hazardous Waste Generator. See Safety SOP, **OG-001**.

12.2. Safety equipment must be used when appropriate and must be maintained in good operating condition. Safety glasses, long pants, and closed-end shoes must always be worn in the Laboratory.

12.3. Store any wastes that cannot be disposed of down the sink in 4 L bottles or other approved containers (properly labeled with **Hazardous Wastes** labels). These wastes must be disposed of in the appropriate waste storage container found in the Hazardous Waste storage room in Bldg. C. Waste from the VOC lab includes chemical standards, used pump oil, methanol extract waste, hazardous sample and oily sample waste.

12.4. Non-hazardous wastewater can be disposed of into the municipal waste stream if the pH range is 5-10. If it is not, then the wastewater must be neutralized prior to disposal.

13. REFERENCES

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

13.1. "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8260D, Revision 4, June 2018.

13.2. "Closed-System Purge & Trap and Extraction for Volatile Organics in Soil and Waste Samples", *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 5035A, Revision 1, July 2002.

13.3. "Determinative Chromatographic Separations", *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8000D, Revision 4, March 2018.

13.4. Agilent 5975C Inert Mass Selective Detector, EnviroQuant Software, G1701EA, Rev. E.02.02, 2010.

13.5. Tekmar Atomx Automated VOC Sample Prep System TekLink Software, Version 1.1.3965.21095, Nov. 2010.

13.6. Comprehensive Quality Assurance Plan, Chemistry Section, Bureau of Labs, DEP.

13.7. Florida Department of Environmental Protection, Standard Operating Procedure **OG-001** *Safety and Waste Management Practices in the Organic Analysis Groups*.

13.8. Florida Department of Environmental Protection, Standard Operating Procedure **VO-010** *Data Review/Authorization Procedures for the Volatile Organic Laboratory*.

13.9. Florida Department of Environmental Protection, Standard Operating Procedure **VO-007** *VOC and Methyl Mercury Glassware and Equipment Cleaning Procedures*.

13.10. Florida Department of Environmental Protection, Standard Operating Procedure **VO-001,** *Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory*

13.11. Florida Department of Environmental Protection, Standard Operating Procedure **CM-018**, *Laboratory Policy Regarding Manual Chromatographic Peak Integration*.

13.12. Florida Department of Environmental Protection, Standard Operating Procedure **LB-002** *Non-Conformance Reporting System*.

13.13. Florida Department of Environmental Protection, Standard Operating Procedure **LB-027** *Standard Operating Procedure* for Reporting Qualified Data.

13.14. Florida Department of Environmental Protection, Standard Operating Procedure **LB-006** *Standard Operating Procedure for Records Storage and Retention.*

13.15. Florida Department of Environmental Protection, Standard Operating Procedure **LB-007** *Procedure and Policy for Demonstration of Capability for Methods, Instruments, and Staff.*

13.16. Florida Department of Environmental Protection, Standard Operating Procedure **LB-031** *Limit of Detection Verification.*

13.17. Florida Department of Environmental Protection, Standard Operating Procedure **MT-055** *Determination of Percent Dry Weight.*

13.18. *NOAA Guidance on Sensory Testing and Monitoring of Seafood for Presence of Petroleum Taint Following an oil Spill.* Technical Memorandum NOS OR&R 9, Seattle Washington August 2001.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

APPENDIX A: SIGNIFICANT CHANGES FROM PRIOR SOP VERSION

02/09/2012	Updated the equipment section.
10/23/2012	Updated tissue preparation and analysis procedure; corrected typos.
12/09/2013	Updated Sample Preparation section to include specific instructions for the preparation and record keeping for blanks, LFBs, and matrix spikes.
12/02/2014	Updated the equipment, sample collection, and reference sections. The sample collection section was updated to more concisely conform to EPA Method 5035A. Calculations were added to section 7.12.
12/07/2015	Updated logo, analytical standards, removed obsolete equipment, and updated references.
12/12/2017	Corrected typos and updated references.
01/04/2019	Updated the equipment section, MDL determination section, and references.
01/24/2020	Updated the equipment section, MDL determination section, and references.
02/10/2020	Updated BFB tuning section.
02/10/2021	Updated equipment section, corrected typos, and updated references.
01/20/2022	Updated equipment section, preservation options, and updated references.
03/04/2022	Corrected typos, clarified preservation options, and updated references.
04/26/2023	Updated scope and application section, summary section, equipment section, reagents section, sample preparation section, and waste management section.
02/20/2024	BFB abundance criteria updated to match EPA Method 8260D.
02/11/2026	Added a section on Maintenance and Troubleshooting

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.