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

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

CHEMISTRY PROGRAM

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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
2-chloroethyl vinyl ether
chloroform*
chloromethane
ortho-chlorotoluene
dibromochloromethane*
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
dichlorodifluoromethane
1,1-dichloroethane
1,2-dichloroethane
1,1-dichloroethene
cis-1,2-dichloroethene
1,2-dichloropropane
trans-1,2-dichloroethene
cis-1,3-dichloropropene
trans-1,3-dichloropropene
ethylbenzene
ethyl methacrylate
2-hexanone
methylene chloride
methyl methacrylate
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

*The Tissue Analysis is validated for the designated compounds only.

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

S-VOC-MS - EPA Method 8260C analysis, preserved sediment sample
WAS-VOC-MS - EPA Method 8260C analysis, preserved waste sample
TCLP-VOC - EPA Method 8260C analysis of TCLP Extract by SOP VO-005
SPLP-VOC - EPA Method 8260C analysis of SPLP Extract by SOP VO-005
T-VOC-MS - EPA Method 8260C 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 of 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**).

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

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 injection may be more suitable for certain complex samples, but are not descibed 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 ug/kg) are collected in hermetically sealed vials or Encore samplers. The sealed vials are used without opening. The contents of the Encore is transferred into a hermetically sealed vial in the laboratory within 48 hours at 4 ^{O}C and have a holding time of 14 days stored at < –7 ^{O}C.

2.1.2. High-Level Samples (>200 ug/kg) are collected in Encore samplers or bulk containers and transported to the laboratory within 48 hours at 4 ^{O}C. The high-level samples are either immediately extracted into methanol or are frozen and have a holding time of 14 days when stored at < – 7 ^{O}C. An aliquot of the methanol extract is added to water and purged as a water sample in SOP VO-002.

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

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 ^{O}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 ^{O}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.

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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 8260C, 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 manufactures are followed as provided in the Operator's Manuals. Maintenance contracts, provided by the manufacture, are purchased for the Gas Chromatograph/Mass Spectrometer Systems and Sample Screening System. Documentation of cleaning, maintenance or system modifications are recorded in a maintenance logbook which accompanies each instrument system. Equivalent supply sources or brands for supplys may be used without editting the SOP.

3.1. Syringes, Pipets and Samplers:

3.1.1. Hamilton Microliter/Gastight Syringes: 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 sharps container. The average life expectancy for a syringe that is used daily is typically no more than a few months. Regardless of use, the microliter syringes must be recalibrated or not used for sample or standard measurements after 1 year.

3.1.2. B-D Brand Multifit Reusable Syringes: 5.0 mL, 10 mL, 50 mL. The B-D Brand Multifit syringes are used only in sample screening or transfer applications. This syringe must not be used for the measurement of precise volumes. The B-D syringe is more rugged and can be baked in a low temperature oven at less than 110 °C.

3.1.3. B-D Brand Plastic Disposable Syringes: 5.0 mL. Remove the tip of the syringe with a knife or purchase without a tip. Bake in a low temperature oven at less than 110 °C.

3.1.4. Encore Sampler: 5.0g and 25 g.

3.1.5. Eppendorf Pipetter, 0-50 mL, or equivalent.

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 a Teflon® (PTFE) or pennyhead ground glass stopper.

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

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3.3.2. 2.0 mL vials with Teflon®/silicone/Teflon® septa and polypropylene open-top cap.

3.4. Miscellaneous Supplies:

3.4.1. Stainless Steel Spatula.

3.4.2. Disposable aluminum drying dishes.

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.

3.4.5. Razor or knife dematome tool.

3.5. Solution 2000 Water Purification System.

3.6. Fisher IsoTemp Forced-Air Oven.

3.7. Yamato Forced-Air Oven, Model DN83.

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

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

3.10. Corning pH Meter 340, with a 3-in-1 Combination Electrode and pHydrion pH Paper.

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

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

3.14. Flammable-Rated Freezer, Fisher Scientific Isotemp.

3.15. GlasCol Shaker Table, Model DPM12

3.16. Milestone Ethos Ez Microwave Digestion Labstation

3.17. Gas Chromatograph/Mass Spectrometer Agilent System):

See References 13.3 for Manufacture Operating Manuals.

3.17.1. Agilent 6890N or 7890 Gas Chromatograph.

3.17.2. Agilent 5975 or 5977 Inert Quadrupole Mass Selective Device.

3.17.3. Tekmar Atomx Purge & Trap and Autosampler

3.17.5. Personal Computer.

3.17.6. Agilent Enviroquant Computer Software.

3.17.7. J&W DB-624, 30 m x 0.25 mm ID capillary column, 1.4 μm film, or equivalent

3.17.8. Supelco High Capacity Gas Purifier or equivalent.

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4. REAGENTS AND CHEMICALS

Working with volatile compounds presents a number of challenges not normally confronted in 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 reference 13.2** before attempting to prepare solutions for analysis.

Sources ofreagents 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. Acids and Bases:

4.2.1. Hydrochloric Acid, HCl - Fisher Certified ACS Plus Grade.

4.2.2. Nitric Acid, HNO_3 - Fisher Trace Metal Grade.

4.3. Laboratory Sand:

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 175 ^oC overnight to remove any volatiles and is then store in the same oven. The heated laboratory sand is occasionally purged with carrier grade helium or nitrogen to remove trapped volatiles.

4.4 Laboratory Reagent Water:

Type 1 laboratory reagent waters is prepared in the laboratory from the municipal water supply. The criteria for laboratory reagent water is 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.

4.5. Internal Standard and Surrogate Solutions:

4.5.1. 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-

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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.

4.5.1.1. The IS/SURR solution is prepared in P&T grade methanol.

4.5.1.2. 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 standard is prepared from fresh stock solutions every 12 months or before the expiration date of the stock standard.

4.5.2. Methanol Extraction Surrogate: 2.5 ppm 2-bromo-1-chloropropane may be used as a surrogate for the methanol extraction procedure. This surrogate is purchased as STS-190 from Ultra Scientific (2000 µg/mL in) methanol and is added directly to the bulk methanol that is used to prepare extracts.

4.5.2.1. Dispense accurately 1.25 mL of the stock standard STS-190 (or equivalent solution) into a 1000 mL volumetric flask containing 990 mL of methanol. Fill the volumetric to the volume mark with methanol and cap. Invert the volumetric two times and transfer the solution into a labeled dispensing bottle.The extraction surrogate is stored at ambient temperature in a 1-L dispensing bottle. New working standard is prepared from fresh stock solution every month or before the expiration date of the stock standard, whichever comes first.

4.6. Calibration Standards:

The 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: 47-2981 (100/300 µg/mL mixture), HC-070 (100 µg/mL of 2-chloroethyl vinyl ether), NV-210 (100 ug/mL methyl methacrylate), and NV-170 (100 ug/mL ethyl methacrylate). These standard solutions include all of the compounds 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 are selected for instrument calibration. Additional calibration levels may be prepared as deemed necessary.

The compounds methyl methacrylate and ethyl methacrylate are not routinely reported and are spiked only when requested in the test. The calibration standards for these compounds are prepared in a similar fashion to those prepared for 2-chloroethyl vinyl ether. Additional analytes from the list of compounds found in Method 8260C 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 a batch analysis. The calibration standard dilutions must be prepared with calibrated syringes and volumetrics. Mixing of 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.

4.6.1. Daily Working Calibration Standards:

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4.6.1.1. 100/300 ppb o2si 47-2981 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.

4.6.1.2. 100 ppb HC-070 Primary Calibration Standards: prepare a 1:1E3 dilution from the 100 µg/mL stock standards. With a 50 µL gastight syringe, add 20 µL of the 100 µg/mL HC-070 stock standard solutions 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.

4.6.2. Initial Calibration Standards:

4.6.2.1. 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.

4.6.2.2. 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.

4.6.2.3. 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.

4.6.2.4. 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.

4.6.2.5. 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.

4.6.2.6. 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.

4.6.2.7. 10 ng HC-070 calibration standard: With a 500 µL syringe inject 100 µL of the 100 ppb HC-070 stock working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.6.2.8. 20 ng HC-070 calibration standard: With a 500 µL syringe inject 200 µL of the 100 ppb HC-070 stock working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.6.2.9. 40 ng HC-070 calibration standard: With a 500 µL syringe inject 400 µL of the HC-070 stock working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

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4.6.2.10. 50 ng HC-070 calibration standard: With a 500 µL syringe inject 500 µL of the 100 ppb HC-070 stock working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.6.2.11. 100 ng HC-070 calibration standard: With a 1.0 mL syringe inject 1.0 mL of the 100 ppb HC-070 stock working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.6.2.12. 200 ng HC-070 calibration standard: With 2.0 mL syringe inject 2.0 mL of the 100 ppb HC-070 stock working solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.6.3. 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.

4.6.3.1. CCV 100/300: A 100/300 ng calibration check sample is prepared from the primary mixture o2si and HC-070 which are analyzed every 24 hours of instrument operation when analytical data is being acquired.

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

4.7. Laboratory Fortified Blank and Matrix Spike Standards:

The compounds contained in the matrix spike standard are used for the preparation of lab fortified blanks (LFBs) and sample matrix spikes (MS). The stock standards are purchased from o2si in their mix 47-2981 second source (100/300 µg/mL) and individual component standards AP-9-105 (100 ug/mL, ethyl methacrylate) and AP-9-131 (100 ug/mL, methyl methacrylate). 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.

The compounds methyl methacrylate and ethyl methacrylate are not routinely reported and are spiked only when requested in the test. The calibration standards for these compounds are prepared in a similar fashion to the standard mix o2si 47-2981 second source. Additional analytes from the list of compounds found in Method 8260C 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.

4.7.1. 100/300 ppm o2si 47-2981 Second Source Working Standard: The working matrix spike standard is prepared by simply opening a sealed ampoule of the o2si 47-2981 second source standard 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.

4.7.2. 100/300 ppb o2si 47-2981 Second Source Daily Working Standard: prepare a 1:1000 dilution of the 100/300 ppm o2si 47-2981 second source working standard. With a 25 µL gastight syringe, add 25 µL of the 100/300 µg/mL o2si 47-2981 second source 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

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4.7.4. 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.

4.7.5. 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).

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

4.9. Antifoaming Agent – Sigma Aldrich Antifoam-A Emulsion

5. SAMPLE COLLECTION, PRESERVATION AND STORAGE

The collection, preservation and storage of samples begins 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 recieved on a weekly basis.

5.1. Low-Level Soil VOA Vial Preparation:

The laboratory prepared sampling kits 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 from the vial oven (105 °C) and remove the septa, plastic syringes 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.

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 the adjustable Eppendorf pipetter. (There is an alternative sample kit which does not contain the 5.0 mL of laboratory reagent water. It appears that the vial can be prepared dry with the same analytical results. We are currently adding water until the new approach is approved)

5.1.6. Place a septa 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.

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5.1.9. If purchased vials are not certified pre-cleaned, then submit a minimum of 2% of the 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 cannot 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 for up to six months.

5.2. Sample Kit Assembly:

5.2.1. For Low-Level Soil Tests, place three to four QC-approved vials and a plastic tipless syringe 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.

5.3. Sample Collection:

5.3.1. For Low-level Soil Sample Collection:

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

5.3.1.2. Use the 5.0 cc plastic syringe 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:

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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 immedately 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.

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 removed from the locked refrigerators. Samples are not checked out once they arrive at the VOC lab since the Chain-of-Custody encompasses the entire volatiles lab until such time that the samples are returned to the main laboratory. Access to the lab is limited to authorized personnel unless accompanied by a supervisor.

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 screening logbook.

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

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

A 10-g subsample from one of the Encore samplers is used to prepare a methanol extract for each sample. The methanol 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 toploading balance.

6.6.2. Remove approximately 10 g of sample from an Encore sampler or bulk sample container and place into the sample vial and wipe the rim of the vial. The soil sample should be removed from the container as a columnar plug from the center of the sample and care

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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. Tare the balance and weigh out approximately 10 g of methanol, containing 2.5 ppm of the surrogate 2-bromo-1-chloropropane (if applicable), into the VOA vial. Record the methanol weight in the sample preparation log to three significant figures.

6.6.4. 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.

6.7. 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/silcone cap. (for samples collected in hermetically sealed VOA vials,steps 1-5 have already been done during fiield 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.

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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 $\leq -20\ ^{O}C$ 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 vessels.

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 a 8 minute heating ramp and then maintain the heating at 71.1 °C for an additional 8 minutes.

6.8.1.5. Remove and dissassemble 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 in 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 orginal 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.

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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 sample. 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 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) times 100. 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 Aglient instruments is designed to collect MS data, setup 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:

YY Year (1999 = 99, 2000 = 00, 2001= 01)
M Month (1 = January, 2 = February, 3 = March, 4 = April, 5 = May, 6 = June, 7 = July, 8 =August, 9 = September, O = October, N = November, D = December)
DD Day (1-31)
I Instrument number (1-3)
Sequential sample numbers from 01-99.

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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 are 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 tune analysis must meet the criteria listed in EPA Method 8260C for a 25-ng injection of BFB (bromofluorobenzene). Obtain the BFB mass spectrum and confirm that all of the m/z criteria in Table 1 are achieved. If the criteria are not achieved, the operator must retune the mass spectrometer and repeat the test until all criteria are achieved.

Table 1.-BFB m/z Abundance Criteria

Mass, m/z	Abundance Criteria
50	15-40 % of mass 95
75	30-60 % of mass 95
95	Base peak, 100 %
96	5-9 % of mass 95
173	<2 % of mass 174
174	>50 % of mass 95
175	5-9 % of mass 174
176	>95 % but < 101 % of mass 174
177	5-9 % of mass 176

7.4. Initial Calibration:

Each instrument is calibrated according to the procedures specified within EPA Method 624 and EPA Method 8260C. 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 percent 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:

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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 within ± 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 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 daily quality control check standards include all compounds being reported and are used to check the accuracy of the initial calibration curve and to insure 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 8260C. 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 8260C. 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 on a daily basis 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, a 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.

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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. Laboratoryl blank (the tune and blank checks can be performed together).

7.8.4. 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

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 closing calibration check standard CCV

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. Setup 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.

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7.9.11. Double check the order of the sample vials to insure 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 criterea are tabulated in the LIMS statistics section and are updated quarterly. As a guide, the recovery limits for the surrogates are within 80 to 120%. The recovery limits for the CCV analytes are within 80 to 120 % and the LFB and MS spike compounds are typically within 70 to 130%.

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

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.

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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.

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 8260C 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. In order 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).

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

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:

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

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8. INTERFERENCES

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 from 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.

9. DATA ARCHIVAL, PROCESSING, REVIEW AND REPORTING

9.1. Data Archival

9.1.1. Instrument File Type, Transfer, and Storage:

9.1.1.1. Agilent 5973 or Agilent 5975 GC/MS: The Agilent instruments store the analytical results in data folders with the extension .D. The individual data folders contain the raw results in a file with the extension .MS

9.1.1.2. Raw data files generated from the instruments must be transferred to a network directory for safe keeping.

9.1.1.3. Once the raw data are reviewed and final reports are generated, transfer the files for the instrument to the archival directory.. The data is permanently archived by the Computer Support Group within the Bureau of Laboratories.

9.1.1.4. Contact the System Administrator of the Computer Support Group if raw data files need to be retrieved from archival and identify the files to be retrieved.

9.2. Data Processing

The Quality Control Manager Program is part of our LIMS used for data management, reporting and archival. The QC Manager program includes such operations as converting instrument raw data, loading raw files into the QC-Manager, and performing all routine data calculations within QC Manager. The QC Manager is designed to take a significant amount of information from the data file including the raw data, sample name, analysis date/time, sample type and dilution factor.

9.2.1. Start QC Manager and Load File: Enter into the QC Manager module in the LIMS and choose the laboratory instrument on which the data was collected. Load the .RAW file to be reviewed by choosing the *Open* option from the *Files* menu, select the desired .RAW filename, and click OK.

9.2.2. QC Manager (QCM) Variables:

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Several of the QC Manager variable can be set automatically from information in the data file and other variable must be set manually. Review each column of the sample table to verify that the QC Manager program set the variables correctly. The variables are described below:

9.2.2.1. *Sample Type* - The TYPE column is used to define sample type and is normally set automatically by the sample ID. Use the following guidelines to set the sample type if necessary:

CCV – type used for continued calibration verification.
SAMP - Type used for ordinary samples. Assign this type to all samples that do not fit in another category.
SRM - Assign this type to Standard Reference Materials solutions.
REPL - Assign this type to duplicate and replicate samples.
SPK - Assign this type to spiked samples.
MDL - Assign this type to reagent blank samples.
NONE - Assign this type to samples where calculations are not desired.

9.2.2.2. *Dilution Factor* - The DILUTION FACTOR column should contain the dilution factors used by the instrument and is normally set automatically by information entered into the data comment field. Correct the dilution factor when necessary.

9.2.2.3. *LIMS TEST ID and MATRIX* - Edit the LIMS Test ID for the samples to match the test requested (S-VOC-MS or WAS-VOC-MS), then enter the Matrix type when prompted.

9.2.2.4. *Preparation Batch Assignments* - A preparation batch is a group of samples including precision and spike recovery samples and all of the associated samples analyzed together by the same method. Highlight the samples and click the header box on the BATCH column to assign a batch ID to that batch.

9.2.2.5. *Spike Code* - Assign the appropriate spike code for the spikes by highlighting all spikes that used a common spike stock solution and clicking on the Spike Code header box and choosing the correct code.

9.2.2.6. *Spike Factor* - Assign spike factors to spiked samples to reflect the amount of spike added to the sample. For instance, a the list normal spike would have a spike factor of '1', a double spike a spike factor of '2' (double amount of spike was added).

9.2.2.7. *Weight Factors* - This is not used for water samples, but is entered using the % dry weights for soils and is entered on a wet weight basis for waste samples.

9.2.2.8. *Analyst* – The Analyst's Name.

9.2.2.9. *Analysis Batch Assignment*- An analysis batch is a group of samples, including the precision and spike recovery samples, analyzed together and fulfills all the method requirements for an analysis batch.

9.2.3. Results Calculations

The QCM program performs calculations based on the data, limits table values and settings.

9.2.3.1. Before calculation, select *Save As* from the *Files* menu . Save the file as a *.REV* file using the same name as the *.RAW* file. Click *OK* to save the file. Perform QC-calculations by choosing the *Begin* option (*F12*) from the *Calculate* menu, select *ALL* to calculate all QC and sample results.

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9.2.3.2. When the calculations are finished, select *Save As* from the *Files* menu and click *OK* to save the file again.

9.2. Data Review

The data review and authorization process is described in detail in the SOP VO-010-3.

9.3.1. Ensure that method blanks, reagent blanks, matrix spikes, duplicate matrix spikes, duplicate samples, and continuing calibration standards are analyzed at the frequency specified in the Comprehensive Quality Assurance Plan.

Type of Check	Frequency Performed
Method Blanks	≥ 10% of samples
Matrix Spikes	≥ 5% of samples
Lab Fortified blanks	≥ 5% of samples
Duplicate Samples	≥ 5% of samples
CCV	Initial and every 12 hour

9.3.2. Blanks must be free of target compounds and interferences. The level of target compounds must be less than 20% of the reporting limit. There are several types of blanks including: Method, Extraction, Trip and Refrigerator.

Type of Blank	Frequency Performed
Method	≥ 10% of samples
Extraction	Every extraction batch
Trip	Every job request

9.3.3. Examine all of the quality control data. The QC code 'P/F' will indicate whether the result is in or out of control limits. Report persistent or unusual problems to the Group Supervisor so corrective action can be taken.

9.3.4. Recovery and Precision (RPD) statistics are determined for samples fortified with known quantities of target analytes. The recovery is an indication of the accuracy of the analytical result. The RPD (relative percent difference) from duplicate fortified samples is an indication of precision. Examine the recovery and precision data to ensure that they are within control limits for the requested analytes. A letter appears in the Pass/Fail column of the component table/baby table of the .REV file. A 'P' indicates the adjacent value passes, an 'F' indicates failure, and a 'Q' indicates a warning value that passes marginally. If the recovery or precision code is 'F', the affected samples should be reanalyzed if possible. Results may be qualified if the 2nd results fail or the samples are expired. Consult the Group Supervisor on the appropriate qualifier and comment.

9.4. Data Reporting by Analyst

9.4.1. Select component results for reporting or upload.

- Highlight a group of samples that share a common set of analytes desired for upload.
- Select the *Change Upload Status by Component* option from the *Options* menu.
- Highlight the desired analytes, and click OK. Repeat this step until all desired analyte rows have a 'Y' Upload Status.
- Transfer the data to the LIMS database via the LIMS Upload function.
- Print out a LIMS report with detects only for each job and put the sheet into the job folder.

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9.4.2. Add appropriate comments whenever results are qualified or comments are otherwise warranted. Indicate all actions taken, such as reanalysis or dilutions, required to resolve a detected problem.

9.4.3. Prepare Job Folders: A job folder contains all data associated with the analysis of samples within a given request. Thus, a folder may contain data acquired on different days, different instruments, or different tests. Every effort must be taken to keep the data complete and orderly.

- Place hardcopies from the sample screening in the job folders (if applicable)
- Hardcopies of all sample data must be put into the associated job folders. This is normal done as part of the post-analysis check.
- Hardcopies of the blanks, QC samples, calibration samples, LFBs, matrix spike must be put into the Daily QC folder. This is normal done as part of the post-analysis check.
- Place a copy of the analysis sequence into each job folder.
- Complete the VOC QC Batch Information Sheet with all the QC elements and standard serial numbers filled in. Comment any unusual issues, failures, or problems. Place the completed form into the daily QC folder for the corresponding instrument.
- Date and sign the file folder to indicate the initial data review is complete.
- Check the front of the job folder a final time for special directions and completeness.
- Double check the LIMS calculations and final reported values.
- Give the complete job folders to the senior chemist or supervisor for data review and authorization.

9.5. Data Reporting by Supervisor:

- Review each job folder and associated LIMS entries according to the criteria found in **Section 9.4**.
- Make note of any necessary corrections and return to the analyst. The analyst must make all corrections and review a second time before resubmitting.
- Sign and date the front of each job folder, once corrections are done, to indicate the review is complete.
- Return the job folders to the analyst for archival.
- Report to the Environmental Manager that the job is complete and ready for final review.

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**.

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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 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 contaminates that interfere 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.

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 these 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 the 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 the 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 the SOP **VO-001**.

11. DETERMINATION OF METHOD DETECTION LIMITS AND DEMONSTRATION OF CAPABILITY

Refer to the SOP **LB-007-1** *Procedure and Policy for Method and Instrument Validation* and refer to SOP **LB-031** *Limit of Detection Verification* for specific procedural details

The LOD and demonstrations of capability (DOCs) shall be determined for each main quality system matrix group identified by NELAP (air, drinking water, non-potable water, biological materials and solids/chemical materials). These groups represent the minimum matrix distinctions for LOD

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determinations and DOCs where there is evidence that the the method performance will not be affected by sub-matrix distinctions within these group, Otherwise LODs and DOCs shall be determined separately for the quality system matrix sub-groups listed below. Where a suitable matrix cannot be found for preparing samples for LOD determinations or DOCs, another similar matrix type may need to be used or samples may need to be prepared in the absence of a matix (e.g. method blanks). Reasons for matrix substitution may include (but are not limited to): inappropriate background analyte levels in the matrix for the intended study, no analyte-free matrix is available for method blanks, no reference materials are available for a matrix, etc,

11.1 Quality System Matrices:

11.1.1. Chemical Waste – a product or by-product of an industrial process that results in a material not defined elsewhere. Because of unanticipated matrix effects from unknown materials of this nature, it is anticipated that deriving LODs for this sub-matrix category would be pursued upon client request only for well-defined projects and materials.

11.1.2. Non-aqueous Liquid – an organic liquid with <15% solids; Because of unanticipated matrix effects from unknown materials of this nature, it is anticipated that deriving LODs for this sub-matrix category would be pursued upon client request only for specific well-defined projects and materials.

11.1.3. Solids – includes soils, sediments, sludges and other materials with > 15% settable solids.

11.2 MDL Determination Procedures

11.2.1. The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register. Refer to **SOP LB-007 for additional details.**

11.2.2. A minimum of seven replicate blank samples and seven replicate spiked samples are prepared and analyzed over three days, spread across all instruments used to perform the test, The spiked samples must be prepared between the MDL and PQL. The MDL is the concentration of analyte at which there is analyte present with 99% confidence.

11.2.3. The results from a minimum of seven replicate data sets are tabulated and the statistical calculations are performed initially and on a quarterly basis thereafter to update the MDLs and PQLs for each analyte and matrix.

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 be worn in the Laboratory at all times.

12.3. Use **CAUTION** with strong irritants such as acids and 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 and hood shield.

12.4. 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 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.

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

13. REFERENCES

13.1. "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8260C, Revision 3, August 2006.

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 8000C, Revision 3, March 2003.

13.4. Agilent 5973N Inert Mass Selective Detector Operator's Manual, EnviroQuant Software, Manual Number G2589-90075, Manual Date: August 2003.

13.5. Tekmar Stratum Purge & Trap Concentrator Teklink and User Manual; Version 3.2.5257; Document Part Number: 14-9800-075 Rev D; Jan 9, 2008.

13.6. Comprehensive Quality Assurance Plan, Chemistry Section, Bureau of Labs, DEP, 2018.

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.*

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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 Petroleumn Taint Following an oil Spill.* Technical Memorandum NOS OR&R 9, Seattle Washington August 2001.

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.

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