MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN WATER 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 water matrices by purge & trap gas chromatography/mass spectrometry. The procedures describe the operational details needed to perform analysis of water samples in the Volatiles section of the 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
chloropicrin
ortho-chlorotoluene
dibromochloromethane
1,2-dibromo-3-chloropropane
1,2-dibromoethane
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
dichlorodifluoromethane (R-12)
1,1-dichloroethane
1,2-dichloroethane
1,2-dichloropropane
1,2-dichloroethane
1,2-dichloropropane
1,1-dichloroethene
cis-1,2-dichloroethene
trans-1,2-dichloroethene
cis-1,3-dichloropropene
trans-1,3-dichloropropene
ethyl acetate
ethylbenzene
2-hexanone
isopropylbenzene
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 (R-11)
1,2,3-trichloropropane
1,1,2-trichlorotrifluoroethane (CFC-113)
1,2,4-trimethylbenzene
1,3,5-trimethylbenzene
toluene
ortho-xylene
meta-xylene/*para*-xylene
vinyl chloride

1.3. FDEP Laboratory Test IDs and equivalent EPA methods covered by this SOP:

This method complies with the requirements of EPA Method 624.1 and Method 8260D for the parameters denoted as such in Table 5.1 of the Laboratory's Quality Manual. EPA Method 624.1 is an approved test procedure of the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) and Method 8260D is listed in the SW-846 publication under Subtitle C of the Resource

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Conservation and Recovery Act (RCRA). Furthermore, the NPDES and RCRA compliant tests employed by the laboratory using these methods are listed below.

Laboratory Test Name	Test Description
W-VOC-MS	EPA Method 624.1 analysis, non-preserved water sample
W-VOC-MS-A	EPA Method 624.1 analysis, acid-preserved water sample
W-VOC-R	EPA Method 8260D analysis, non-preserved water sample
W-VOC-R-A	EPA Method 8260D analysis, acid-preserved water sample
W-FUMGNT	EPA Method 8260D SIM fumigant analysis, non-preserved
W-FUMGNT-A	EPA Method 8260D SIM fumigant analysis, acid-preserved
W-VOC-SIM-A	EPA Method 8260D SIM analysis, acid-preserved water

The acceptance limits, as provided in EPA Methods 624.1 and 8260D, are programmed into the Laboratory's Information Management Systems (LIMS) and applied automatically as part of the data processing, review, and reporting procedures. Table 5.1 of the DEP Laboratory Quality Manual provides information regarding method limits of detection, accuracy, and precision.

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

These supporting SOPs contain critical details not fully described within this method SOP. The analyst must be completely familiar with all of the following 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 and 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**)

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

2. METHOD SUMMARY

The determination of volatile organic compounds by this method is a two-step process where the sample is first concentrated by Purge & Trap and then introduced to a gas chromatography/mass spectrometer instrument for analysis.

2.1. Sample Introduction Method: The volatile compounds are introduced into the gas chromatograph by the EPA Purge-and-Trap Methods 624.1 and 5030C, SW-846.

2.2. Quantitation Method: The analytes 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 624.1 Purgeables, Part 136, Title 40 and EPA Method 8260D, SW-846. The procedures described here are designed to meet or exceed the criteria from both EPA quantitative methods. This is accomplished by meeting the more stringent requirement from both methods. Please refer to the EPA methods for additional details[2,3]

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. Maintenance contracts, provided by the manufacturer, are purchased for the Gas Chromatograph/Mass Spectrometer Systems and Sample Screening System. Documentation of cleaning, maintenance or system modifications is recorded in a maintenance logbook which accompanies each instrument system.

3.1. Syringes:

3.1.1. Hamilton Microliter/Gastight Syringes (Class-A): 5 µL, 10 µL, 50 µL, 100 µL, 500 µL, 1.0 mL, 2.0 mL, 5 mL, 10 mL. The Hamilton syringes are delicate and must be handled with care. Some 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 with methanol rinses. 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's container. The average life expectancy for a syringe that is used daily is typically no more than 6 months. Regardless of use, the microliter syringe calibration and general condition should be verified quarterly.

3.2. Volumetric Flasks (Class A): 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 penny head ground glass stopper.

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3.2.2. The volumetric flasks are cleaned by rinsing with methanol and laboratory reagent water. The volumetrics are dried in a low temperature oven at less than 110 °C. Never use a brush or strong alkali solution to clean 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.

3.3.2. 2 mL vials with Teflon®/silicone septa and polypropylene open-top cap.

3.3.3. 2 mL vials with inserts for 300 µL and 900 µL, equipped with a Teflon®/silicone septa and polypropylene open-top cap.

3.4. Aqua Solution 2000 Water Purification System, Type 1 Laboratory Reagent Water or Mega Pure Still MP-3A glass distilled water.

3.5. Fisher IsoTemp Forced-Air Oven.

3.6. Thermo Heratherm OMH400-SS Mechanical Convection Oven.

3.7. Mettler Toledo XS6002S Top-loading Balance, capable of weighing 0.01 g.

3.8. Mettler Toledo XPR205 Analytical Balance, capable of weighing 0.00001 g.

3.9. pH Measuring Equipment:

3.9.1. Hach H-Series Portable pH Meter and ISFET stainless piercing tip microprobe

3.9.2. pHydrion pH Paper.

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. Gas Chromatograph/Mass Spectrometer Agilent Instrument System:

3.13.1. Agilent 6890 or 7890 Gas Chromatograph.

3.13.2. Agilent 5975 or 5977 Mass Spectrometer.

3.13.3. Tekmar Atomx Purge & Trap Sample Concentrator.

3.13.4. IBM-compatible Personal Computer.

3.13.5. Agilent Enviroquant or Mass Hunter Computer Software

3.13.6. Restek Rxi-624Sil MS Column, 30 m x 0.25 mm x 1.4 µm, or equivalent.

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3.13.7. Supelco High-Capacity Gas Purifier or equivalent.

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

3.15. SensSafe Free Chlorine Water Check Strips, P/N 481026, used to evaluate residual chlorine.

3.16. Ziplock style (polypropyelene) sample bags, 3 mil, 6 x10 inch.

4. REAGENTS AND CHEMICALS

Working with volatile compounds presents several unique 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 **references 13.1, 13.2,** and **13.3** before attempting to prepare solutions for analysis.

Sources of the reagents and chemicals are given, 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.

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. Hydrochloric Acid Preservation Solution:

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

4.2.1.1. A 6.0 M HCl solution used for sample preservation is prepared by making a 1:1 dilution of the HCl acid into laboratory reagent water. The expiration date for this solution is 1 year from the time of preparation.

4.3. Laboratory Reagent Water:

Type-1 laboratory reagent water is prepared in the laboratory from the municipal water supply. The criterion 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).

The Type-1 Laboratory Reagent Water is prepared by purifying municipal water with an AquaSolution 2000 Water Purification System that uses activated carbon cartridges and ion-exchange cartridges to remove impurities or prepared using a Mega Pure MP-3A glass still.

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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): A 1-µL volume of internal standard/surrogate solution is injected into every sample by the autosampler just prior to analysis. The internal standard compounds are fluorobenzene, chlorobenzene-d5, and 4-bromofluorobenzene. The surrogate compounds are dibromofluoromethane, 1,2-dichloroethane-d4, toluene-d8, and 1,4-dichlorobenzene-d4. 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 methanol. 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 ≤ -20.0 °C in 20 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, whichever comes first.

4.5. Calibration Standards:

The stock calibration standards used for the preparation of the initial calibration and daily quality control (QC) check standards are purchased from O2SI in methanol as a Custom Mix 124165-01 (100/300 µg/mL mixture), AccuStandard M-8015B (10 mg/mL of ethyl acetate), and Ultra Scientific HC-070 (100 µg/mL of 2-chloroethyl vinyl ether), or other equivalent standards. These standard mixtures include 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 solution containing the light gases should be used within 30 days or before the stock standard expires, whichever comes first. The other working standards may be used for up to 180 days or before the stock standard expires, whichever comes first. All stock and working standards are stored at ≤ -20.0 °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. 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 are prepared from the working standards just prior to use in a batch analysis. The calibration standard dilutions are prepared with Class-A 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 head-spaced VOA vials immediately after preparation to minimize the loss of volatile compounds. Alternatively, working standards may be spiked directly into selected VOA vials with a precisely known volume of 42 ± 0.25 mL containing laboratory reagent water determined gravimetrically. The direct injection technique into VOA vials has the advantage of significantly minimizing volatile losses as compared to using volumetrics,

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particularly for the more volatile components. Refer to **references 31.2 and 13.3,** for additional details on the preparation and handling of calibration standards.

4.5.1. Initial Calibration Standards:

4.5.1.1. 0.20/0.60 ppb Custom mix 124165-01 and HC-070 calibration standards: prepare a 1:100 dilution of a solution containing 20 ppb Custom Mix 124165-01 and HC-070. With a 1 mL gastight syringe, add 1 mL of the 20 ppb intermediate calibration solution to a 100 mL volumetric flask containing 95 mL of laboratory reagent water. Dilute to final volume and cap flask.

4.5.1.2. 0.50/1.5 ppb Custom mix 124165-01 and HC-070 calibration standards: prepare a 1:10 dilution of a solution containing 5.0 ppb Custom mix 124165-01 and HC-070. With a 10 mL gastight syringe, add 10 mL of the 5.0 ppb intermediate calibration solution to a 100 mL volumetric flask containing 90 mL of laboratory reagent water. Dilute to final volume and cap flask.

4.5.1.3. 2.0/6.0 ppb Custom mix 124165-01 and HC-070 calibration standards: prepare a 1:10 dilution of a solution containing 20 ppb Custom Mix 124165-01 and HC-070. With a 10mL gastight syringe, add 10 mL of the 20 ppb intermediate calibration solution to a 100 mL volumetric flask containing 80 mL of laboratory reagent water. Dilute to final volume and cap flask.

4.5.1.4. 5.0/15 ppb Custom mix 124165-01 and HC-070 calibration standards: prepare a 1:2E4 dilution from the 100 µg/mL working standards. With a 10 µL gastight syringe, add 5.0 µL of the 100 µg/mL Custom Mix 124165-01 and HC-070 working standard solutions to a 100 mL volumetric flask containing 95 mL of laboratory reagent water. Dilute to final volume and cap flask. This solution will also be used as an intermediate to prepare the 0.50 ppb calibration level.

4.5.1.5. 10/30 ppb Custom mix 124165-01 and HC-070 calibration standards: prepare a 1:1E4 dilution from the 100 µg/mL working standards. With a 10 µL gastight syringe, add 5.0 µL of the 100 µg/mL Custom Mix 124165-01 and HC-070 working standard solutions to a 50 mL volumetric flask containing 45 mL of laboratory reagent water. Dilute to final volume and cap flask.

4.5.1.6. 20/60 ppb Custom mix 124165-01 and HC-070 calibration standards: prepare a 1:5E3 dilution from the 100 µg/mL working standards. With a 25 µL gastight syringe, add 20 µL of the 100 µg/mL Custom Mix 124165-01 and HC-070 working standard solutions to a 100 mL volumetric flask containing 95 mL of laboratory reagent water. Dilute to final volume and cap flask. This solution will also be used as an intermediate to prepare the 0.20 ppb calibration level.

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4.5.1.7. 50/150 ppb Custom mix 124165-01 and HC-070 calibration standards: prepare a 1:2E3 dilution from the 100 µg/mL working standards. With a 25 µL gastight syringe, add 25 µL of the 100 µg/mL Custom Mix 124165-01 and HC-070 working standard solutions to a 50 mL volumetric flask containing 45 mL of laboratory reagent water. Dilute to final volume and cap flask.

4.5.2. Daily Quality Control Check Standards and PQL Check Standards:

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

4.5.2.1. VOC Mix 47: A 20/60 ppb continued calibration check sample is prepared from the Custom Mix 124165-01 and HC-070 working standard solutions and analyzed every 12 hours of instrument operation when analytical data is being acquired. The preparation of this calibration standard is given in **Section 4.5.1.6.**

4.5.2.2. W-PQL: A PQL calibration check sample is prepared from the Custom Mix 124165-01 and HC-070 working standard solutions and analyzed with the sample batch. The preparation of this calibration standard is given in **Section 4.5.1.3.**

4.5.2.3. Calibration checks for other non-listed compounds are prepared only for those analytical tests or samples that require the special compounds.

4.6. Laboratory Fortified Blank and Matrix Spike Standards:

The matrix spike standard mixes are used for the preparation of both lab-fortified blanks (LFBs) and sample matrix spikes. The following stock standards are purchased from O2SI custom mix 124165-01SS (100/300 µg/mL), Sigma Cat# 34858 (Neat, 99.7%), and AccuStandard M-601C, Restek 8260 MegaMix (30633), or other equivalent secondary standards. All stock and working standards are stored at ≤ -20.0 °C. The matrix spike standards are used as a second source to verify against the primary standards. The O2SI custom mix 124165-01SS matrix spike mix is used alone for spiking unless the individual standard analytes are also requested.

The LFB and matrix spike standards must be prepared from the working standards just prior to use in a batch analysis. Standard dilutions are prepared in class-A volumetric flasks by spiking beneath the water surface (to minimize volatile losses) and mixing by gently rotating the volumetric flasks slowly 2 times (do not shake!). Transfer the standard solutions to zero head spaced VOA vials immediately after preparation to minimize the loss of volatile compounds. Alternatively, working standards may be spiked directly into VOA vials. Multiple measurements of the VOA vials used by the laboratory have demonstrated that the volume of the VOA vials are typically 42 ± 0.5 mL. Variation in vial volume is monitored by routinely comparing the recovery of LFB and MS/MSD duplicate spikes. Direct spiking into the VOA vials has been shown to significantly minimize loss of volatile compounds, particularly the light gases. Refer to **References 13.2 and 13.3** for additional details on the preparation and handling of working standards.

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4.6.1. 100/300 ppm O2SI Custom mix 124165-01SS Working Standard: The working matrix spike standard is prepared by simply opening a sealed ampoule of the O2SI Custom mix 124165-01SS standard and transferring the standard solution to a 2 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 ppm Ethyl Acetate Working Standard: The working matrix spike standard is prepared by diluting the neat compound to make a 2000 µg/mL intermediate, then diluted again to make a 100 µg/L working standard, both in purge and trap methanol. The intermediate standard is prepared by weighing 20 mg of the neat standard into a 10 mL volumetric flask and bringing it to volume with methanol. The working standard is prepared by injecting 5.0 µL of the intermediate standard into a 100 mL volumetric flask and bringing it to volume with methanol. The working standard solution must be used within 180 days or before the stock standard expires, whichever comes first.

4.6.3. Lab Fortified Blank Preparation: A 20/60 ppb LFB is prepared from the second source working standard 124165-01SS for every 10 samples. The LFB is prepared by injecting 20 µL of the 100 ppm O2SI and ethyl acetate working standards as well as 10 µL of the 200 ppm 2-chloroethyl vinyl ether working standard into a 100 mL volumetric flask containing 95 mL of laboratory reagent water. Dilute to final volume, cap flask and mix gently by inverting the flask two times. Immediately pour into VOA vials (zero head space) and close the vials with an open-top cap with Teflon/silicon septa. Alternatively, the LFB may be prepared by injecting 8.4 µL of the 100 ppm O2SI and ethyl acetate working standards as well as 4.2 µL of the 200 ppm 2-chloroethyl vinyl ether working standard into a 42 mL VOA sample vial.

4.6.4. Matrix Spike Preparation: A 20/60 ppb matrix spike check is prepared from the 100 ppm 124165-01SS working standard for every 10 samples. Duplicate matrix spikes prepared for every 20 samples meet the 10% requirement. The matrix spike and matrix spike duplicate are prepared by injecting 8.4 µL of the 100 ppm O2SI and ethyl acetate working standards as well as 4.2 µL of the 200 ppm 2-chloroethyl vinyl ether working standard into each of the 42 mL VOA sample vials.

5. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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. Sample Vial Preparation:

The laboratory prepared sampling kits containing 3 to 4 VOA vials and a 2-gram Carbopack inside a polyethylene bag. The protocol for cleaning the vials is described in the cleaning SOP **VO-007**. Instructions for assembling the sample kits are as follows:

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

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5.1.2. Remove clean sample vials and septa 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 case units of 50 to 100 vials.

5.1.4. To preserve vials, add 200 µL of the 6 M HCl solution to each vial with a micropipetter. HCl is added for sample preservation.

5.1.5. For non-preserved vials do not add the HCl solution.

5.1.6. For trip blank vials add 200 µL of the 6 M HCl solution to each vial with a micropipetter. Fill the vial with laboratory reagent water. Take care not to overfill the vials.

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

5.1.8. Label the boxes of preserved, non-preserved or trip blank vials with a Lot ID Number If the vials are not purchased certified clean, submit vials for testing. QC testing of the vials demonstrates 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.

5.2. Sample Kit Assembly:

5.2.1. Prepare the sampling kit by placing three or four QC-approved vials and a 1-gram Carbopack into a 3-mil polyethylene 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. Make sure that the zero head spaced blanks used in the trip blank samples do not contain air bubbles. Trip blank samples contain two vials and a 1-gram Carbopack.

5.2.3. Label the polyethylene bags with the vial type and vial Lot ID Number.

5.3. Sample Collection:

- A minimum of three 40-mL VOA vials for each water sample should be collected without headspace (no bubbles). Bubble size must not to exceed 5-6mm or 1/4” - roughly the size of a pea.
- Care must be taken, when collecting the sample, not to wash out the sample preservative already in the vial (if present).
- Once the sample is collected, the septa must be placed with the Teflon side towards the water sample and the open-top cap tightened finger tight.
- More than 1 cm of soil collected in the bottom of the VOA vial may compromise the water analysis. Also, a multi-phase or pure product sample must not be collected in the VOA vials used for water analysis.

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- After the samples are capped, label each vial with a unique identification. And return them into the polyethylene bag. The outside of the sample containers must also be labeled with distinguishable field identification.
- Chain-of-custody labels may be placed across the bag opening 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. Samples are stored in a locked, flammable-rated refrigerator at 4.0 ± 2 °C until time for analysis. Waste samples are double bagged and stored in a separate refrigerator from the water and soil samples to prevent potential cross-contamination.

5.4.2. Non-preserved water samples have a holding time of 7 days, and acid-preserved samples have a holding time of 14 days from collection time.

5.4.3. The refrigerator units may be monitored with a refrigerator blank on a weekly basis. Refrigerator blanks should stay in the refrigerator for a minimum of seven days and then be analyzed as a sample. The criterion for the refrigerator blank is the same as the laboratory reagent water blank.

6. SAMPLE PREPARATION PROCEDURE

6.1. All glassware should 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 restricted-access refrigerators in the Receiving room. Once the appropriate sample vials have been collected for analysis, the remaining sample vials must be promptly returned to the receiving room storage to maintain Chain-of-Custody.

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

6.5. Preservation Verification: (Normally performed after the analysis to minimize sample loss.)

6.5.1. The sample pH is tested with pH paper or pH meter to determine the appropriate sample holding time. If the pH is close to 2, then a more precise pH meter is used. Samples analyzed within 7 days do not require pH<2 preservation, but unpreserved samples analyzed beyond this time must be properly qualified.

6.5.2. Check for residual chlorine in the analyzed vial using the SensSafe chlorine strips. Samples with residual chlorine above 0.20 ppm must be properly qualified.

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6.6. Prepare the water samples by verifying the vial sample ID and performing any required sample dilutions. Write the sample ID on the vial if not already present. Refer to **references 13.2 and 13.3** for the handling of volatiles and the preparation of dilutions.

6.6.1. Duplicate Sample: Use Sample ID with suffix _DUP

6.6.2. Matrix Spike Samples: Use Sample ID with suffix SPK1 and SPK2

6.6.3. Reanalysis Samples: Use Sample ID with suffix R1, R2, …

6.7. 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. Also, samples with headspace must not be used for the matrix spikes. The matrix spike level is normally 10 µg/L, which is prepared by spiking 4.3 µL of the matrix spike standard solution into each of the two sample duplicate vials. Mix well by gently rotating the vials on their side.

6.8. The internal standard and surrogate compounds are automatically added to each sample by the autosampler. The autosampler is equipped with a 1 µL loop that rotates into the sample path during sample introduction into the Purge & Trap concentrator. The 1 µL loop injects 100 ng of each internal standard and surrogate compound as a 20 mL* aliquot of sample is transferred into the Purge and Trap sparger. The final internal standard and surrogate concentration in the sample aliquot is 5 µg/L.

* Other volumes may be used in the sparger (typically 5 to 20 mL), provided the instrument has been recalibrated for the volume used.

7. SAMPLE ANALYSIS AND CALCULATIONS 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 Agilent instrumentation 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.

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 solutions are added automatically by the autosampler and contain BFB as one of the surrogates. Analysis of a laboratory reagent water blank will serve as a GC/MS blank performance test.

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

† Based on EPA Method 8260D.

7.3.3. Acceptable system performance may also be demonstrated by meeting manufacturer specifications for mass resolution, mass accuracy, and sensitivity using an internal calibrant (e.g. PFTBA). A passing High Efficiency Source Autotune is sufficient for the Agilent 5977 series MSD.

7.4. Initial Calibration:

Each instrument is calibrated according to the procedures specified within EPA Method 624.1 and 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-001-4**. Refer to the EPA method protocols in **Reference 13.2 and 13.3** 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.

A minimum of 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 fits with a linear regression, except in situations where the analyte response is clearly non-linear. A quadratic

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curve using six standard concentration levels may be used in the case of a non-linear response. The correlation coefficient for the 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 ± 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 13.4 and 13.5**) for procedures on generating a reference mass spectrum library.

7.4.4. Selected-Ion Monitoring (SIM) Tests – SIM may be used for analytical tests requiring lower detection limits than can be achieved by full-scan GC/MS (such as the fumigant tests W-VOC-FM and W-VOC-FM-A or the tracer test W-VOC-SIM-A). However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. Using the primary ion for quantitation and two secondary ions for confirmation, set up the collection groups based on their retention times. One secondary ion will suffice in cases where there are not two secondary ions available but be aware of potential false positives. The use of a secondary ion for quantitation is permitted only if the primary ion has a common interference.

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 ensure 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

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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 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. 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 each internal standard must be within 50% to 200% (1/2 to 2x) of its respective response in the mid-point calibration standard. If any internal standard recovery exceeds these limits 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).

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

7.8.4. Calibration Check Standard (CCV) initially and every 12 hours.

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

7.8.6. Replicate matrix spikes for every 20 samples.

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7.8.7. Laboratory reagent water blank prior to sample sequence.

7.8.8. Methanol extract solvent blank (if applicable from waste or high-level soil analysis (See **SOP VO-003**).

7.8.9. Samples (including duplicate sample).

7.8.10. Additional Laboratory reagent water blank for rinsing purposes as needed during run sequence.

7.8.11. Closing Blank and new Calibration Check Standard (CCV), if continuing.

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 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. The Atomx autosamplers add internal standards and surrogates to the sample automatically.

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.

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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 internal standard, surrogate, CCV, and spike recoveries of all samples against acceptance limits:

- Each internal standard must be 50% to 200% (1/2 to 2x) of its respective response in the mid-point calibration standard
- Surrogate limits are 80 to 120%.
- CCV analyte recovery limits are 80 to 120 %.
- LFB and MS spike compound recovery limits are typically 70 to 130%.

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

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

7.10.5. Duplicate sample results must have similar chromatogram profiles and have comparable recoveries. Reanalyze the sample if the duplicate recoveries vary by more than 20%.

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

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

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 may be identified and reported as individual isomers. Isomers are considered

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resolved if the peaks are at least 50% resolved where the height of the valley between two close eluting isomers is ≤50% of the average of the two peak heights, as verified on the mid-point concentration of the initial or on-going calibration verification. Otherwise, the structural isomers must be identified and reported as isomeric pairs.

7.11.5. A library search should 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 Methods 8260D, 624.1, and references for more details.

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. Water samples with excessive soil or suspended particulates may be centrifuged and transferred to a zero headspace VOA vial. Water from more than one vial will be required to do this. Make a note explaining what was done in the data folder and in the LIMS comment field for the sample. An NCR should be created.

8.2. Samples analyzed with headspace or an inverted septum must have a comment added to the job folder and in the LIMS comment field for the sample. An NCR should be created and the results Y qualified. Small air bubbles 5 mm in diameter (about pea size) or less do not require action.

8.3. Non-aqueous or multiphase samples 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 Foaming samples or samples with strong coloration or odor should be screened prior to analysis or diluted significantly for the initial analysis.

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

8.7 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.

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

8.9 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 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.

8.10 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.**

10.3. There must be an initial calibration of the GC/MS system as described in **Section 4.5**.

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.

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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 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 the SOP **VO-001.**

11. DETERMINATION OF METHOD DETECTION LIMITS AND DEMONSTRATION OF CAPABILITY

The Method Detection Limit (MDL) and Practical Quantitation Limit (PQL) are also referred to as Limit of Detection (LOD) and Limit of Quantitation (LOQ), respectively. Refer to the SOPs **LB-007** *Procedure and Policy for Demonstration of Capability for Method, Instruments and Staff*, and SOP **LB-031** *Limit of Detection Verification* for procedural details.

12. SAFETY/HAZARDOUS WASTE MANAGEMENT

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

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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. 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, aprons, 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 Waste labels). These wastes should be dumped 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 samples, and oily sample waste.

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

13. REFERENCES

13.1. USEPA *Purge-and-Trap for Aqueous Samples, SW-846,* Method 5030C, Revision 3, May 2003.

13.2. *Code of Federal Regulations, Title 40, Part 136*, Appendix A; Method 624.1: Purgeables by GC/MS, 2016.

13.3. USEPA *Test Methods for Evaluating Solid Wastes,* Fourth Edition, SW-846*,* Method 8260D, Revision 4, June 2018.

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

13.6. Tekmar Atomx Automated VOC Sample Prep System Teklink Software, Version 1.1.3965.21095, Nov. 2010.

13.7. Florida Department of Environmental Protection, Quality Manual, Bureau of Laboratories.

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

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

13.10. Florida Department of Environmental Protection, Standard Operating Procedure **VO-007** *Volatiles Glassware and Equipment Cleaning Procedures*.

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

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

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

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

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

13.16. Florida Department of Environmental Protection, Standard Operating Procedure **LB-007** *Procedure and Policy for Method and Instrument Validation.*

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

Appendix of Significant Changes

02/15/2023 Equipment and Reagent updates in Sections 3 and 4. Sample analysis clarifications in section 7.

01/25/2024 Test IDs updated for fumigants. Bubble test removed from section 6.

11/18/2024 BFB abundance criteria updated to match EPA Method 8260D.

12/30/2025 Added Maintenance and Troubleshooting

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