MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

BUREAU OF LABORATORIES

2600 BLAIR STONE ROAD

TALLAHASSEE, FLORIDA 32399

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

MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

TABLE OF CONTENTS

1. SCOPE AND APPLICATION 3
2. METHOD SUMMARY 5
3. APPARATUS AND EQUIPMENT 5
4. REAGENTS AND CHEMICALS 7
5. SAMPLE COLLECTION, PRESERVATION AND STORAGE PROCEDURES 11
6. SAMPLE PREPARATION PROCEDURE 13
7. SAMPLE ANALYSIS AND CALCULATION PROCEDURES 14
8. INTERFERENCES 20
9. DATA ARCHIVAL, PROCESSING, REVIEW AND REPORTING 20
10. QUALITY CONTROL 24
11. DETERMINATION OF METHOD DETECTION LIMITS 25
12. SAFETY, HAZARDOUS WASTE MANAGEMENT AND POLLUTION PREVENTION 26
13. REFERENCES 27
14. APPENDIX 28

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

MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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
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)
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 is in compliance with the requirements of EPA Method 624 and Method 8260C for the parameters denoted as such in Table 5.1 of the laboratory's Quality Manual. EPA Method 624 is an approved test procedure of the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) and Method 8260C is listed in the SW-846 publication under Subtitle C of the Resource Conservation and Recovery Act (RCRA). Furthermore, the NPDES and RCRA compliant tests employed by the laboratory using these methods are listed below.

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

Laboratory Test Name	Test Description
W-VOC-MS	EPA Method 624 analysis, non-preserved water sample
W-VOC-MS-A	EPA Method 624 analysis, acid-preserved water sample
W-VOC-R	EPA Method 8260C analysis, non-preserved water sample
W-VOC-R-A	EPA Method 8260C analysis, acid-preserved water sample
W-VOC-FM	EPA Method 8260C SIM fumigant analysis, non-preserved
W-VOC-FM-A	EPA Method 8260C SIM fumigant analysis, acid-preserved
W-ETHYL-AC	EPA Method 8260C Ethyl Acetate analysis, acid-preserved

The acceptance limits, as provided in EPA Methods 624 and 8260C, 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 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 these SOPs.

1.4.1. *Safety and Waste Management Practices in the Organic Analysis Groups* (SOP **OG-001-03**).

1.4.2. *Glassware and Equipment Cleaning Procedures* (SOP **VO-007-3**).

1.4.3. *Data Review/Authorization Procedures for the Volatile Organic and Laboratory* (SOP **VO-010-3**).

1.4.4. *Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory* (SOP **VO-001-4**).

1.4.5. *Non-Conformance Reporting System* (SOP **LB-002-1**).

1.4.6. *Laboratory Policy Regarding Manual Chromatographic Peak Integration* (SOP **CM-018-1**).

1.4.7. *Standard Operating Procedure for Reporting Qualified Data* (SOP **LB-027-1**)

1.4.8. *Standard Operating Procedure for Records Storage and Retention* (SOP **LB-006-1**)

1.4.9. *Procedure and Policy for Method and Instrument Validation* (SOP **LB-007**-1)

1.4.10. *Limit of Detection Verification.* **(**SOP **LB-031-1**).

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

2. METHOD SUMMARY

The determination of volatile organic compounds by this method is a two-step process where the sample is first introduced by Purge & Trap concentration and then analyzed by gas chromatography/mass spectrometry.

2.1. Sample Introduction Method: The volatile compounds are introduced into the gas chromatograph by the EPA Purge-and-Trap Methods 624 and 5030C, SW-846.[1]

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 Purgeables, Part 136, Title 40 and EPA Method 8260C, SW-846.[2,3] The procedures described here are designed to meet or exceed the criteria from both of these 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 manufacture, 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: 5 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.

3.2. 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 less than 110 °C. Never use a brush or strong alkali solution to clean volumetrics.

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

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 uL and 900 uL, equipped with a Teflon®/silicone septa and polypropylene open-top cap.

3.4. AquaSolution 2000 Water Purification System, Type 1 Laboratory Reagent Water.

3.5. Fisher IsoTemp Forced-Air Oven.

3.6. Yamato Forced-Air Oven, Model DN83.

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

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

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

3.10. Liquid Nitrogen Dewar, 230 Liter, 50 psi pressure.

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

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

3.13. Flammable-Rated Freezer, Fisher Scientific Isotemp.

3.14. Gas Chromatograph/Mass Spectrometer Agilent Instrument System:

3.14.1. Agilent 6890 or 7890 Gas Chromatograph.

3.14.2. Agilent 5973N or 5975 Mass Spectrometer.

3.14.3. Tekmar Atomx Purge & Trap Sample Concentrator.

3.14.4. IBM-compatible Personal Computer.

3.14.5. Agilent Enviroquant Computer Software Version E.02.02.

3.14.6. J&W Scientific DB-624, 30 m x 0.25 mm x 1 μm, or equivalent

3.14.7. Supelco High Capacity Gas Purifier or equivalent.

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

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 **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.

4.1.2. Ethylene Glycol: $HOCH_2CH_2OH$ - Purge & Trap grade ethylene glycol is prepared by filtering anhydrous ethylene glycol, 99.8% (Aldrich Gold Label), through a 2 cm column of Tenax TA (Supelco). The ethylene glycol is stored in an amber 500 mL bottle with a Teflon-lined cap. Limit the preparation of the Purge & Trap grade ethylene glycol to a quantity that will be used in a period of less than one year. Ethylene glycol is used in the preparation of internal standard when the use of methanol must be minimized.

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 a 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. 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:

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

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-d_5, and 4-bromofluoromethane. The surrogate compounds are dibromofluoromethane, 1, 2-dichloroethane-d_4, toluene-d_8, and 1,4-dichlorobenzene-d_4. These compounds may be purchased in the prepared mixture STM-541 from UltraScientific (or equivalent solution) at a concentration of 5000 µg/mL in methanol.

4.4.1.1. The IS/SURR solution can be prepared in methanol or a 75/25 mixture of ethylene glycol and methanol. The ethylene glycol is used to minimize the amount of methanol introduced into detectors that do not use a split. However, instruments that have a high split ratio can tolerate high methanol concentration and do not need the solvent mixture.

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 or a 25/75 methanol and ethylene glycol. Fill the volumetric to the volume mark with methanol or 25/75 methanol and ethylene glycol. The working internal standard is stored at ≤ -20.0 °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, 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 122981-01 (100 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). These standard mixtures include all of 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 must 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 are selected for instrument calibration. Additional calibration levels may be prepared as deemed necessary. 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 13.3,** for additional details on the preparation and handling of calibration standards.

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

4.5.1. Initial Calibration Standards:

4.5.1.1. 0.20 ppb Custom mix 122981-01 and HC-070 calibration standards: prepare a 1:100 dilution of a solution containing 20 ppb Custom Mix 122981-01 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 ppb Custom mix 122981-01 and HC-070 calibration standards: prepare a 1:10 dilution of a solution containing 5.0 ppb Custom mix 122981-01 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 ppb Custom mix 122981-01 and HC-070 calibration standards: prepare a 1:10 dilution of a solution containing 20 ppb Custom Mix 122981-01 and HC-070. With a 10 mL 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 ppb Custom mix 122981-01 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 122981-01 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 ppb Custom mix 122981-01 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 122981-01 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 ppb Custom mix 122981-01 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 122981-01 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.

4.5.1.7. 50 ppb Custom mix 122981-01 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 122981-01 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 OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

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 ppb continued calibration check sample is prepared from the Custom Mix 122981-01 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. PQLW2: A 2.0 ppb PQL calibration check sample is prepared from the Custom Mix 122981-01 and HC-070 working standard solutions and analyzed with each 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 compounds contained in the matrix spike standard mix are used for the preparation of both lab-fortified blanks (LFBs) and sample matrix spikes. The following stock standard is purchased from O2SI Custom mix 122981-01SS (100 µg/mL), Sigma Cat# 34858 (Neat, 99.7%), and AccuStandard M-601C (200 µg/mL of 2-chloroethyl vinyl ether). All stock and working standards are stored at ≤ -20.0 °C. The standards are used as a second-source to verify against the primary calibration standards.

The LFB and matrix spike standards must be prepared from the working standards just prior to use in a batch analysis. Standard dilutions must be mixed by gently rotating the volumetric flasks slowly 2 times (do not shake!). Transfer the standard solutions to zero headspaced VOA vials immediately after preparation to minimize the loss of volatile compounds. Refer to **Reference 13.3,** for additional details on the preparation and handling of working standards.

4.6.1. 100 ppm O2Si Custom mix 122981-01SS Working Standard: The working matrix spike standard is prepared by simply opening a sealed ampoule of the O2SI Custom mix 122981-01SS 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 ug/mL intermediate, then diluted again to make a 100 ug/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 uL 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.

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

4.6.3. Lab Fortified Blank Preparation: A 20 ppb LFB is prepared from the second-source working standards 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.

4.6.4. Matrix Spike Preparation: A 20 ppb matrix spike check is prepared from the 100 ppm M-601 working standard for every 10 samples. Duplicate matrix spikes prepared for every 20 samples meet the 10% requirement. The matrix spike is 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 one of the 42 mL VOA sample vials. Direct spiking into the vials minimizes loss of the volatile compounds. Multiple measurements of the VOA vials used by the laboratory has demonstrated that the volume of the VOA vials is 42 ± 0.5 mL. Volatile loss is minimized by directly injecting the sample vials. Variation in the vial volume can be monitored by comparing the recovery of the LFB and matrix spike duplicates.

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

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 received on a weekly basis.

5.1. Sample Vial Preparation:

The laboratory prepared sampling kits contain 3 to 4 VOA vials and a 2-gram Carbopack inside a Ziploc 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.

5.1.2. Remove clean sample vials from the high temperature oven (160 °C) and remove the 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.

5.1.3. Place the vials in case units of 50 to 100 vials.

5.1.4. To preserve vials, add 130 µL of the 6 M HCl solution to each vial with a hand held micropipetter. The HCl is added for sample preservation.

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

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

5.1.6. For trip blank vials add 130 µL of the 6 M HCl solution to each vial with a hand held micropipetter. Fill the vial with laboratory reagent water. Take care not to overfill the vials.

5.1.7. Put 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 and submit a minimum of 2% of the vials for testing. QC 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. Prepare the sampling kit by placing three or four QC-approved vials and a 1-gram Carbopack into 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. Make sure that the zero headspaced blanks used in the trip blank samples do not contain air bubbles. Trip blank samples contain only two vials and a 1-gram Carbopack.

5.2.3. Label the outside of the Ziploc 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 must be collected without headspace (no bubbles).
- 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.
- After the samples are capped, label each vial with a unique identification. And return them into the Ziplock 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:

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

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 must be monitored with a refrigerator blank on a weekly basis. The refrigerator blank must 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. The refrigerator blank must not contain any analytes of interest at a concentration greater than 20% of the reporting limit.

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 complex. 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, upside down septa and chain-of-custody seals (if applicable). Any problems are noted in the sample screening logbook.

6.5. 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.

6.6. All samples other than blanks and duplicates must be bubble tested prior to analysis. The bubble test is designed to identify samples that foam excessively during the purging process and may present a risk to the Purge & Trap instrument.

6.6.1. Place a 5 mL aliquot of sample into a sparge tube which is connected to a 40 mL/minute air flow and observe the amount of foam generated. If the foam from the sample approaches the top of the test sparger, then the sample must be diluted.

6.6.2. Record the dilution factor (DF) required to pass the bubble test. This DF will be used as a starting point for sample preparation.

6.7. 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 **reference 13.3,** for the handling of volatiles and the preparation of dilutions.

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

6.7.1. Duplicate Sample: Use Sample ID with suffix _DUP

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

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

6.8. 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.

6.9. 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, setup 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:

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.

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.

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

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 serve as a GC/MS blank performance test.

7.3.2. The tune analysis must meet the criteria listed in EPA Methods 624 and 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-001-4**. 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 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.

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

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

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 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 13.4 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 is achievable by full-scan GC/MS (such as the fumigant tests W-VOC-FM and W-VOC-FM-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 insure 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:

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

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. 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.

7.7. Internal Standard Retention Time and Internal Standard Response:

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

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

7.8.1. BFB tune check every 12 hours.

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

7.8.3. 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.

7.8.7. Laboratory reagent water blank.

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

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

7.8.9. Samples (including duplicate sample).

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

7.8.11. Closing Blank and Calibration Check Standard (CCV) at the run end.

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.

7.9.11. Double check the order of the sample vials to insure 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 the 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.

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, CCV and spike recoveries against acceptance limits. The recovery limits for the surrogates are 80 to 120%. The recovery limits for the CCV

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

analytes are also 80 to 120 %. The recovery limits for the LFB and MS spike compounds are typically 70 to 130%.

7.10.4. Inspect the vials on the autosampler tray to insure 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.

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

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

7.11. Qualitative Analysis:

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

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

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

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

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

7.11.5. A library search must be performed for unknown chromatographic peaks when the total ion chromatogram of the sample contains unknown peaks larger than the internal standard peaks. A tentative identification can be assigned provided that

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

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.

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. Water samples with excessive soil or suspended particulates may be centrifuged and transferred to a zero headspaced 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.

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 air bubble with a 5 mm diameter (pea size) or less does not require commenting.

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.

9. DATA ARCHIVAL, PROCESSING, REVIEW AND REPORTING

9.1. Data Archival

9.1.1. <u>Instrument File Type, Transfer, and Storage:</u>

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

9.1.1.1. Agilent 5973 or 5975 GC/MS: The Agilent MSD 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 manipulations 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 Calculator and Load File: Load the QC Manager program 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:

Several of the QC Manager variables can be set automatically from information in the data file and other variables 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 all 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 all reagent blank samples.

NONE - Assign this type to all samples where calculations are not desired or meaningful.

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

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 (W-VOC-MS, W-VOC-MS-A, W-VOC-R or W-VOC-R-A, ect.), 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 prepared 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 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.

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

9.3. Data Review

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

9.3.1. Ensure that method blanks, reagent blanks, matrix spikes, duplicate matrix spikes, duplicate samples, continuing calibration standards and SRM check 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

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

Lab Fortified blanks	≥ 5% of samples
Duplicate Samples	≥ 5% of samples
CCV	Initial and every 12 hour
SRM Check Standards	Initial and every 12 hours

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
Refrigerator	Every 7 days

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.

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

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.

- Make copies of the field sheets for each job folder
- Put hardcopies from the sample screening in the job folders
- 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.
- Print out the QC pass/fail sheet with all components listed for the samples analyzed. Highlight the components that failed and indicate any anomalies for any reported components. Put the printout into the daily QC folder for the corresponding instrument.
- Write the name of the review file (*.REV file) and SOP used on the Analysis Sequence Logbook. Date and sign the files to indicate initial data review is complete. Put a copy of the analysis sequence into each job folder.
- Check the front of the job folder a final time for special directions and completeness.
- Double check 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.

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

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.

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

- 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 13.3** and the SOP **VO-001-4**.

11. DETERMINATION OF METHOD DETECTION LIMITS AND DEMONSTRATION OF CAPABILITY

Refer to the SOP **LB-007** *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 Demonstration 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 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:

- Aqueous – all aqueous samples excluding drinking water (see below) and salt or estuarine waters;
- Drinking Water – water from a designated potable source;
- Saline/Estuarine – an aqueous sample from an ocean or estuarine. The effects of this matrix type may from analysis to analysis and with salt content. Therefore, the decision to what extent if any this matrix has on the LOD and what salt levels may affect the LOD is left to the discretion of experienced supervisory staff;

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. Also refer to **References 13.1., 13.2. and 13.3**.

11.2.2 Seven replicate samples are analyzed near the MDL. The MDL is the concentration of analyte at which there is analyte present with 99% confidence.

11.23 The results of the seven replicate data sets are tabulated and the statistical calculations are performed electronically on at least an annual basis to establish or update the MDLs and PQLs for each analyte and matrix. A list of MDLs is given in the Laboratory Comprehensive Quality Control Plan, see **Reference 13.9.**

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

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 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 sample and oily sample waste.

12.5. Non-hazardous wastewater can be disposed 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, Vol. 49, No. 209*, Method 624: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, 1984.

13.3. USEPA *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8260C, Revision 3, August 2006.

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

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. Comprehensive Quality Assurance Plan, Chemistry Section, Bureau of Labs, DEP, 2016.

13.8. Florida Department of Environmental Protection, Standard Operating Procedure, **OG-001-3** Safety and Waste Management Practices in the Organic Analysis Groups.

13.9. Florida Department of Environmental Protection, Standard Operating Procedure, **VO-010-3** *Data Review/Authorization Procedures for the Volatile Organic Laboratory*.

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

13.10. Florida Department of Environmental Protection, Standard Operating Procedure **VO-007-3** VOC and Methyl Mercury Glassware and Equipment Cleaning Procedures.

13.11. Florida Department of Environmental Protection, Standard Operating Procedure **VO-001-4** *Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory*

13.12. Florida Department of Environmental Protection, Standard Operating Procedure **CM-018-1**, *Laboratory Policy Regarding Manual Chromatographic Peak Integration*.

13.13. Florida Department of Environmental Protection, Standard Operating Procedure **LB-002-1** Non-Conformance Reporting System.

13.14. Florida Department of Environmental Protection, Standard Operating Procedure **LB-027-1** *Standard Operating Procedure* for Reporting Qualified Data.

13.15. Florida Department of Environmental Protection, Standard Operating Procedure **LB-006-1** *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-031-1** *Limit of Detection Verification.*

14. APPENDIX

14.1 SOP Update Revision Summary:

The following revisions were made to this SOP from the prior version:

1. Incremented revision number and date.
2. Updated list of equipment in the Equipment section.
3. Updated list of analytes and standards in the Reagent and Chemicals section.
4. Updated References.

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