MEASUREMENT OF NON-HALOGENATED AND POLAR ORGANIC COMPOUNDS IN WASTEWATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

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1. SCOPE AND APPLICATION

1.1. This method details the analysis of polar and non-polar organic compounds in wastewater matrices by heated Purge & Trap/Gas Chromatography/Mass Spectroscopy or by direct aqueous injection. The procedures describe the operational details needed to perform heated purge (HP) analysis of water samples in the Volatiles Section of the FDEP laboratory.

1.2. The following compounds may be determined by this method in addition to the compounds listed in the SOP VO-002:

Acetone
Acrolein
Acrylonitrile
tert-Amyl methyl ether (TAME)
Benzene
1-Butanol (n-Butyl alcohol)
isoButyl alcohol (2-methylpropan-1-ol)
t-Butanol
Butyl acetate
n-Butylbenzene
sec-Butylbenzene
t-Butylbenzene
2-Butanone (MEK)
Carbon disulfide
Cyclohexane
Diethyl ether
Diisopropyl ether (DIPE)
1,4-Dioxane*
Ethanol
Ethyl acetate
Ethyl benzene
Ethyl-t-butyl ether (ETBE)
Ethyl methacrylate
2-Hexanone
Ethylene glycol
Diethylene glycol
Isopentane
Isopropyl acetate
Isopropylbenzene
Isobutyl alcohol
Isopropyl alcohol
n-Propylbenzene
2-Mercaptoethanol
Methanol
2-Methylpentane
Methyl-t-butyl ether (MTBE)
Methyl acetate
Methyl acrylate
Methyl cyclohexane
Methyl methacrylate
Naphthalene
n-Nonane
n-Pentane
1-Propanol (n-Propyl alcohol)
Propyl acetate
Propyl benzene
Propylene glycol
Tetrahydrofuran
Toluene
Triethylene glycol
Styrene
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
2,2,4-Trimethylpentane
m,p-Xylene
o-Xylene

* For 1,4-Dioxane refer to EPA Method 522 and SOP SV-015 for a new preparation and analysis method.

Many of the compounds determined in this method purge poorly and are miscible with water. Consequently, the MDLs are typically higher than for the more non-polar compounds analyzed using the Purge and Trap method in **SOP VO-002**. The instrument conditions are optimized to favor the recovery of these polar compounds. This method is not used for routine VOC analysis because the high purge temperatures tend to damage and contaminate the instrument more quickly.

1.3. FDEP Laboratory Test IDs and equivalent EPA methods covered by this SOP. Refer to the specific laboratory tests for MDL information:

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W-VOC-MS-R	-	EPA Method 8260C analysis, non-preserved water sample
W-VOC-MS-R-A	-	EPA Method 8260C analysis, acid-preserved water sample
W-VOC-MS-HP	-	EPA Method 8260C analysis with heated purge
W-624AA	-	EPA Method 624.1 analysis for Acrolein and Acrylonitrile (A/A)
W-8015C	-	EPA Method 8015C analysis for non-halogenated volatiles

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 should be completely familiar with all of these SOPs.

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

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

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

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

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

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

1.4.7. *Reporting Qualified Data* (SOP **LB-027**)

1.4.8. *Records Storage and Retention* (SOP **LB-006**)

2. SUMMARY OF THE METHOD

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

2.1. Sample Introduction: The volatile compounds are introduced into the gas chromatograph by either direct aqueous injection or by EPA Purge & Trap (P&T) Method 5030C. The P&T method used in this sample introduction is specifically designed for the analysis of polar, water soluble compounds. The procedures described in this method meet the requirements for EPA Methods 624.1, 8015C, and 8260C. Sample introduction by P&T involves passing an inert gas (helium) through 5 or 20 mL of aqueous sample that has been heated to temperatures up to 85 °C. As the helium flows through the sample, the analytes are released into the vapor phase. The vapor is then swept through a sorbent trap where the analytes are trapped. After purging is completed, the trap is heated and back flushed with helium to desorb the compounds onto a gas chromatographic column.

2.2. Compound Identification and Quantitation: The components are separated by gas chromatography and detected using a mass spectrometer, which provides both qualitative and quantitative information. The described quantitative method is based on EPA Methods 624.1, 8015C, and EPA Method 8260C, SW-846. The procedures described here are designed to meet or exceed the criteria from both of these EPA quantitative methods. Please refer to the EPA methods for additional details.

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2.3. Selected Ion Monitoring (SIM) and Full Scan Mass Spectrometry: SIM techniques are particularly useful in the analysis of volatile polar compounds with very poor recoveries (such as 1,4-dioxane). The use of SIM allows for much better detection limits, but does not have the same qualitative value as full scan. Both SIM and full-scan techniques are permitted under EPA Method 8260C and are described in this SOP.

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 that accompanies each instrument system.

3.1. Syringes and Pipettes:

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.

3.1.3. Eppendorf Pipetter, 0-50 mL adjustable pipette and appropriate tips.

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 volumetric containers s 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. These containers are dried in a low temperature oven at less than 120 °C. Never use a brush or strong alkali solution to clean the volumetric containers.

3.3. Glass Sample (VOA) and Standard Vials:

3.3.1. 43 mL glass VOA vials with a Teflon®/silicone septa and polypropylene open-top cap.

3.3.2. 2 mL glass vials with Teflon®/silicone/Teflon® 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. Thermo MP-3A Glass Distillation Unit or AquaSolution 2000 Water Purification System.

3.5. Fisher IsoTemp Forced-Air Oven.

3.6. Yamato Forced-Air Oven, Model DN83.

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3.7. Mettler XS6002S Top-loading Balance, s/n B308057129, capable of weighing 0.01 g.

3.8. Denver A-250 Analytical Balance, capable of weighing 0.10 mg.

3.9. Corning pH Meter 340, with a 3-in-1 Combination Electrode and 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 System (Instrument System 1):

See References 13.4 for Manufacture Operating Manuals.

3.13.1. Agilent 7890 Gas Chromatograph.

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

3.13.3. Tekmar Atomx Autosampler/Purge & Trap

3.14.3.1. Tekmar #9 Proprietary Carbon Trap – Used for routine VOCs
3.14.3.2. Tekmar #1A Tenax TA Trap – Used for Acrolein/Acrylonitrile analysis

3.13.4. Agilent Enviroquant Computer Software.

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

3.13.6. Supelco High Capacity Gas Purifier or equivalent.

3.15. Gas Chromatograph/Mass Spectrometer Agilent System (Instrument System 2):

See References 13.4 for Manufacture Operating Manuals. Instrument system is used for glycol analysis.

3.15.1. Agilent 6890N Gas Chromatograph.

3.15.2. Agilent 5973 Inert Quadrupole Mass Selective Device.

3.15.3. Restek, Stabilwax-MS, 30m x 0.25mm ID x 0.25µm film or equivalent. Cat# 10673

3.15.4. Restek, Open Top Uniliner Liner, Cat# 22272-205

3.15.5. Agilent Enviroquant Computer Software.

5.15.6. 0.45 µm, PTFE syringe type filter.

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

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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 depending 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. The Purge & Trap grade methanol must be used for all applications were the methanol comes into contact with the sample. HPLC grade methanol may be used for cleaning glassware that will be baked overnight before use.

4.2. Hydrochloric Acid Preservation Solution:

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

4.2.1.1. A 6 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 or Type 2 laboratory reagent water is prepared in the laboratory from the municipal water supply. The criteria for laboratory reagent water require that the laboratory blanks 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).

4.3.1. Type 1 Laboratory Reagent Water: Municipal water is purified 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.

4.3.1. Type 2 Laboratory Reagent Water: Municipal water is purified with an in-house DI System that uses ion-exchange cartridges to remove impurities and is then fed into a Thermo MP-3A Glass Distillation Unit. The laboratory reagent water is evaluated every day, when sample data is collected, as a method blank sample.

4.4. Internal Standard, Alternate Internal Standards, and Surrogate Solutions:

4.4.1. 25 or 100 ppm Internal Standard/Surrogate (IS/SURR) Solution: An internal standard/surrogate solution is injected into every sample by the autosampler just prior to analysis. The 25 ppm concentration is used for 5 mL purge samples and the 100 ppm concentration is used for 20 mL purge samples. The internal standard compounds are chlorobenzene-d_5, fluorobenzene and 4-bromofluorobenzene. 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 at a concentration of 5000 µg/mL in methanol.

4.4.1.1. 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

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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 ≤ -10.0 °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.

4.4.2. Alternate Internal Standards or Isotope Dilution Standards: Alternate internal standards have proven to be useful for compounds such as 1,4-dioxane that are analyzed by a SIM technique. These alternate standards are typically deuterated analogs of the compounds under investigation. For 1,4-dioxane analysis the internal standard 1,4-dioxane-d8 is purchased from Restek, # 30614, at a concentration of 2000 µg/mL in methanol. The 1,4-dioxane-d8 standard is diluted to 100 µg/mL as a working standard. The working internal standard is spiked directly into sample vials at a final concentration of 50 µg/L.

4.4.3. 100 ppm Internal Standard/Surrogate (IS/SURR) Solution: The internal standard compound is Hexafluoro-2-propanol. The surrogate compound is Hexafluoro-2-methyl-2-propanol. These compounds may be purchased in the prepared mixture M-8260/5031 from AccuStandard at a concentration of 5000 µg/mL in water.

4.5. Calibration Standards:

The acrolein and acrylonitrile (A/A) stock calibration standards used for the preparation of the initial calibration and daily quality control check standards (QCCSs) are purchased from Supelco Inc, or similar. The Supelco catalog numbers are: 4-8501 for acrolein (neat, d = 0.839 g/ml), 4-8502 for acrylonitrile (neat, d = 0.806 g/ml). Acrolein and acrylonitrile are unstable in mixtures with other organic compounds, so it is essential to prepare them in a separate mixture. The neat stock solutions of acrolein and acrylonitrile must be mixed and diluted into a working standard.

The oxygenate compounds are purchased from UltraScientific (NVM-826), AccuStandard (OGAD-001) and Supelco (48367) in prepared stock solutions at a concentration of 2000 µg/mL in water and methanol, respectively. These standards may be exchanged for similar products without notice as long as they meet the same traceability and quality specifications.

The glycol standards and mercaptoethanol are purchased from o2si (G34-111516-05) and Aldrich (neat, 99%), respectively.

All stock and working standards are stored at ≤ -10 °C. A list of the normal calibration levels is given below where a minimum of 5 levels is selected for instrument calibration. Additional calibration levels may be prepared as deemed necessary.

The 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. The standard solutions must be mixed upon preparation 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 13.2** for additional details on the preparation and handling of calibration standards.

4.5.1. Working Calibration Standards:

4.5.1.1. 200 ppm A/A Working Calibration Standard: With a 5.0 µL gastight syringe, add 4.77 µL (4.00 mg) of neat acrolein, add 4.96 µL (4.00 mg) of neat acrylonitrile to a 20 mL volumetric flask containing 15 mL of methanol. Dilute to final volume and cap flask. The working solution must be used within 60 days or by the expiration date of the original material, whichever comes first.

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4.5.1.2. 200 ppm Oxygenate Working Calibration Standard 1: With a 250 µL gastight syringe add 200 µL of the stock standard NVM-826 (2000 µg/mL or equivalent) to a 2.0 mL volumetric flask containing 1.5 mL of reagent water. Dilute to final volume of 2.0 mL and cap the flask. Mix and transfer the working standard to a 2 mL vial. The working solution must be used within 90 days or by the expiration date of the original material, whichever comes first. **This solution must be prepared in reagent water since one of the compounds in the mixture, vinyl acetate, reacts rapidly with methanol.**

4.5.1.3. 200 ppm Oxygenate Working Calibration Standard 2: With a 250 µL gastight syringe add 200 µL of the stock standard OGAD-001 (2000 µg/mL or equivalent) to a 2 mL volumetric flask containing 1.5 mL of methanol. Dilute to final volume of 2.0 mL and cap the flask. Mix and transfer the working standard to a 2 mL vial. The working solution must be used within 90 days or by the expiration date of the original material, whichever comes first.

4.5.1.4. 200 ppm 1,4-Dioxane Working Calibration Standard: With a 250 µL gastight syringe add 200 µL of the stock standard Supelco #48367 (2000 µg/mL or equivalent) to a 2.0 mL volumetric flask containing 1.5 mL of methanol. Dilute to final volume of 2.0 mL and cap the flask. Mix and transfer the working standard to a 2.0 mL vial. The working solution must be used within 180 days or by the expiration date of the original material, whichever comes first.

4.5.1.5. 100 ppm Glycol Working Calibration Standard: With a 250 µL gastight syringe add 100 µL of the stock standard o2si #G34-111516-05 (10,000 µg/mL or equivalent) to a 10 mL volumetric flask containing 9 mL of water. Dilute to final volume of 10 mL cap the flask and mix it. This glycols mix used to prepare calibration standard and as a spiking solution. The working solution must be used within 180 days or by the expiration date of the original material, whichever comes first.

4.5.2. Initial Calibration Standards:

4.5.2.1. 2.0 ppb A/A or Oxygenate Calibration Standards: With a 5.0 µL syringe inject 2.0 µL of the 200 ppm working calibration standards into a 200 mL flask containing 200 mL of laboratory reagent water. Invert the volumetric flask slowly two times and transfer the flask contents into a zero-headspace vial. (10 ng on column for a 5.0 mL sample)

4.5.2.2. 4.0 ppb A/A or Oxygenate Calibration Standards: With a 5.0 µL syringe inject 4.0 µL of the 200 ppm working calibration standards into a 200 mL flask containing 200 mL of laboratory reagent water. Invert two times and transfer into a zero-headspace vial. (20 ng on column for a 5 mL sample)

4.5.2.3. 8.0 ppb A/A or Oxygenate Calibration Standards: With a 10 µL syringe inject 8.0 µL of the 200 ppm working calibration standards into a 200 mL flask containing 195 mL of laboratory reagent water. Immediately dilute to final volume, invert two times and transfer into a zero-headspace vial. (40 ng on column for a 5.0 mL sample)

4.5.2.4. 10 ppb A/A or Oxygenate Calibration Standards: With a 10 µL syringe inject 5.0 µL of the 200 ppm working calibration standards into a 100 mL flask containing 95 mL of laboratory reagent water. Immediately dilute to final

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volume, invert two times and transfer into a zero-headspace vial. (50 ng on column for a 5.0 mL sample)

4.5.2.5. 20 ppb A/A or Oxygenate Calibration Standards: With a 10 µL syringe inject 10 µL of the 200 ppm working calibration standards into a 100 mL flask containing 95 mL of laboratory reagent water. Immediately dilute to final volume, invert two times and transfer into a zero-headspace vial. (100 ng on column for a 5.0 mL sample)

4.5.2.6. 40 ppb A/A or Oxygenate Calibration Standards: With a 10 µL syringe inject 10 µL of the 200 ppm working calibration standards into a 50 mL flask containing 45 mL of laboratory reagent water. Immediately dilute to final volume, invert two times and transfer into a zero-headspace vial. (200 ng on column for a 5.0 mL sample)

4.5.2.7. 100 ppb A/A or Oxygenate Calibration Standards: With a 50 µL syringe inject 25 µL of the 200 ppm working calibration standards into a 50 mL flask containing 45 mL of laboratory reagent water. Immediately dilute to final volume, invert two times and transfer into a zero-headspace vial. (500 ng on column for a 5.0 mL sample)

4.5.2.8. 50, 25, 10, 5, 2.0 and 1.0 ppm Calibration standard: 1 mL of each calibration standard were prepared in water. Added 20 µL aliquot of surrogate/IS mix (100 ppm, sec.4.4.3.) at 2 ppm level to each vial. Added appropriate aliquot of glycols mix (100 ppm, sec. 4.5.1.5.) to each vial and rest will be water to make final volume 1 mL.

4.5.3. Daily Quality Control Check Standards:

The working calibration standards used for the preparation of the calibration curve are also used to prepare the daily quality control check standards.

4.5.3.1. QCWAA: A 40 PPB (200 ng) calibration check sample is prepared from the A/A Working Calibration Standard and analyzed every 12 hours of instrument operation when analytical data is being acquired. The preparation of this calibration standard is given in **Section 4.5.2.6.**

4.5.3.2. QCWOX1, QCWOX2, or 14DIOX: A 40 PPB (200 ng) calibration check sample is prepared from the Oxygenate Working Calibration Standard 1, Standard 2 or 1,4-dioxane standard and analyzed every 12 hours of instrument operation when analytical data is being acquired. The preparation of this calibration standard is given in **Section 4.5.2.6.**

4.5.3.3. QCWGLYCOLS: A second source glycols mix were purchased from o2si (G34-111516-05-SS or equivalent) at a concentration of 10,000 ppm. Prepared 100 ppm of intermediate by taking 0.10 mL of aliquot and diluted to 10 mL in water which is used to make CCV at 5.0 ppm level. Surrogate/Internal Standard (100 ppm) added at 2.0 ppm level.

4.6. Laboratory Fortified Blank and Matrix Spike Standards:

There are two different matrix spike standards are used for the preparation of lab-fortified blanks (LFBs) and sample matrix spikes. All stock and working standards are stored at ≤ -10 °C. The LFB and matrix spike standards must be prepared from the working standards just prior to use in a batch analysis

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4.6.1. EPA Method 624.1/8260C Acrolein/ Acrylonitrile Spike Solutions:

4.6.1.1. 200 ppm A/A Working Spike Standard: With a 10 µL gastight syringe, add 4.77 µL (4.00 mg) of neat acrolein and add 4.96 µL (4.00 mg) of neat acrylonitrile to a 20 mL volumetric flask containing 15 mL of methanol. Dilute to final volume and cap flask. This working solution must be used within 60 days after or by the expiration date of the original material, whichever comes first.

4.6.1.2. 40 ppb A/A Laboratory Fortified Blank: With a 20 µL syringe inject 20 µL of the 200 ppm A/A Working Spike Standard into a 100 mL flask containing 95 mL of laboratory reagent water. Immediately dilute to final volume, invert two times and transfer into a zero-headspace vial. A set of duplicate LFBs must be prepared for every sample batch. (200 ng on column for a 5.0 mL sample aliquot)

4.6.1.3. 40 ppb A/A Matrix Spike: With a 10 µL syringe inject 8.6 µL of the 200 ppm A/A Working Spike Standard into a 43 mL sample VOA vial. A set of duplicate matrix spikes must be prepared for every sample batch. Duplicate matrix spikes prepared for every 20 samples meet the 10% requirement. (200 ng on column for a 5.0 mL sample aliquot)

4.6.2. EPA Method 8015C/ 8260C Oxygenate Spike Solution:

4.6.2.1. 200 ppm Oxygenate Working Spike Standard: With a 250 µL gastight syringe add 1.0 mL of the UltraScientific stock standard CLP-154 (2,000 µg/mL or equivalent) to a 10 mL volumetric flask containing 8 mL of methanol. Dilute to final volume of 10 mL and cap the flask. Mix and transfer the working standard to five 2 mL vials. The working solution must be used within 1 year or by the expiration date of the original material, whichever comes first.

4.6.2.2. 40 ppb Oxygenate Laboratory Fortified Blank: With a 20 µL syringe inject 20 µL of the 200 ppm Oxygenate Working Spike Standard into a 100 mL flask containing 95 mL of laboratory reagent water. Immediately dilute to final volume, invert two times and transfer into a zero-headspace vial. A set of duplicate LFBs must be prepared for every sample batch. (200 ng on column for a 5.0 mL sample aliquot)

4.6.2.3. 40 ppb Oxygenate Matrix Spike: With a 10 µL syringe inject 8.6 µL of the 200 ppm Oxygenate Working Spike Standard into a 43 mL sample VOA vial. A set of duplicate matrix spikes must be prepared for every sample batch. Duplicate matrix spikes prepared for every 20 samples meet the 10% requirement. (200 ng on column for a 5.0 mL sample aliquot)

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 of a Ziplock bag. The Ziplock bag, in turn, may be placed inside a metal can for added protection.

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The protocol for cleaning the vials and cans can be found in the cleaning SOP **VO-007**. Instructions for assembling the sample kits are as follows:

5.1.1. Always prepare the VOA vials in batches of 1 case or more vials at a time.

5.1.2. Use pre-cleaned vials or remove clean sample vials from the vial 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. Put the vials in cases of 50 to 100 vials.

5.1.4. Acid-preserved samples are not suitable for this analysis if acrolein and acrylonitrile recovery is desired since these compounds will decompose or polymerize at low pH. Do not use acid preserved vials if the recovery of these compounds is desired. A separate vial may be collected for acrolein and acrylonitrile and preserved to a pH of 4-5, otherwise these analytes have a 3-day holding time.

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 vial. Inspect the water-filled vial for air bubbles clinging to the glass surfaces. A gentle tap will usually dislodge any bubbles.

5.1.7. Put septa on each vial with the Teflon side toward the vials and screw on the open-top cap snugly. Inspect the trip blank vials for head space and reject all trip blanks with headspace (bubbles). Reject any vials containing discolored solutions or visible particulates.

5.1.8. Label the boxes as 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 without recertification.

5.2. Sample Kit Assembly:

5.2.1. Prepare the sampling kit by placing three or four QC-approved vials and a 2-gram Carbopack into a 3 mil polyethylene Ziploc bag. The Ziploc bag, in turn, may be placed into a baked metal can if added protection is needed. 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 trip blank vials do not contain air bubbles. Trip blank samples contain only two vials and a 2-gram Carbopack.

5.2.3. Label the outside of the Ziplock bag or can with the vial type and vial Lot ID Number.

5.3. Sample Collection:

5.3.1. A minimum of three 40 mL VOA vials for each water sample must be collected without headspace (no bubbles). A headspace bubble, the size of a pea (5 mm diameter) will not qualify the data, but any larger headspace will result in volatiles loss and data qualification.

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5.3.2. Care must be taken, when collecting the sample, not to wash out the sample preservative already in the vial.

5.3.3. 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.

5,3,4, More than 1 cm of soil collected in 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.

5.3.5. After the samples are capped, return them into the Ziplock bag and metal can. The outside of the sample container must be labeled with the field identification. Chain-of-custody labels may be placed across the metal can lid 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 stored in a separate refrigerator from the water and soil samples to minimize potential cross-contamination.

5.4.2. Non-preserved water samples have a holding time of 7 days, except for acrolein and acrylonitrile which must be analyzed within 3 days.

5.4.3. Acid-preserved water samples have a holding time of 14 days, but are not suitable for the analysis of acrolein and acrylonitrile (A/A). For A/A preservation the pH must be carefully controlled between pH 4-5.

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 must be checked out from the refrigerators for analysis.in the LIMS. Access to the samples must be protected at all times. Access to the VOC facility and samples is limited to authorized personnel only unless accompanied by a supervisor.

6.4. Each sample must be visually inspected for broken vials, sample headspace, upside down septa and broken chain-of-custody seals. Any problems must be noted in the sample job folder and a non-compliance report prepared, if applicable.

6.5. The sample pH is tested with pH paper to determine the appropriate sample holding time. If the pH is close to 2.0, 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 that 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 sparger, then the sample must be diluted.

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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 screening and preparation.

6.7. Prepare samples by labeling the vials with the sample ID and performing any required sample dilutions. Each sample vial or container must have clear identification. Write the sample ID or number on each sample vial if not already present. Refer to **reference 13.3, Section 5.0** for the handling of volatiles and the preparation of dilutions.

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, R3,

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 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 1.0 μL loop that rotates into the sample path during sample introduction into the Purge & Trap concentrator. There are two IS/SURR standard concentrations, depending if 5.0 or 20 mL samples will be used. For 5.0 mL samples, the 1.0 μL loop injects 25 ng of each internal standard and surrogate compound as a 5 mL aliquot of sample is transferred into the Purge and Trap sparger. For 20 mL samples, the 1.0 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. Regardless of sample volume, the final internal standard and surrogate concentration in the sample aliquot is 5.0 μg/L. The only exception to this is the 1,4-dioxane-d8 internal standard, which has a final concentration of 50 ug/L.

6.10 Sample Preparation for Glycols: Follow Section 6.1 to 6.4. Filter all the samples through 0.45 u filter in to a graduated 10 or 15 mL test tube.

6.10.1. Prepare samples by labeling the vials with the sample ID. Each sample vial or container must have clear identification. Write the sample ID or number on each sample vial if not already present. Matrix Spike Samples: Use Sample ID with suffix SPK1 and SPK2.

6.10.2. 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. The glycol matrix spike level is normally 10 μg/mL, which is prepared by spiking 500 μL of the matrix spike standard solution into each of the two sample duplicate vials. Mix by gently rotating the vials on their side.

6.10.3. The internal standard and surrogate compounds 0.10 mL from 100 ppm are added to each glycol sample at a concentration of 2.0 ppm level. Make the final volume to 5 mL.

6.10.4. Mix the glycol samples using vortex, transfer 1.0 mL sample to 2.0 mL GC vial before analysis.

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7. SAMPLE ANALYSIS PROCEDURE

7.1. Suggested Instrument Conditions: The instrument conditions are given below. Specific instrument conditions may vary slightly, depending on instrument type configuration.

7.1.1. Tekmar Atomx Autosampler Settings (typical):

• Internal Standard: yes	• Pre-Purge = 0.0 min.
• Flow Rate = 40 cc	• Purge Time = 11 min.
• Dilution Factor = 1	• Flush Vol = 5.0 or 20 ml
• Line Heat = 120 ºC	• Sparger Flushes: 2 times
• Sample Heat ºC = 28, 60 (HP), 85 (A/A)	• Syringe Flush: 1 time
• PreHeat = 0.20 min.	• Desorb time: 0.50 min.
• Sample Volume = 5.0 or 20 ml	• Soil Stir = No

7.1.2. Tekmar Atomx Purge and Trap Conditions (typical):

• Line Temp = 120 ºC	• CryoFocus Temp = ------
• Valve Temp = 120 ºC	• Inject Time = -----
• Purge Ready Temp = 30 ºC	• Cryo Inj Temp = -----
• Purge Temp ºC = 28, 60 (HP), 85 (A/A)	• Desorb Preheat = 245ºC
• Mount Temp = 90ºC	• Desorb Time = 2.0 min.
• MCS Line Temp = 120ºC	• Desorb Temp = 250ºC
• MCS Des Temp = 40ºC	• Sample Drain = off
• Sample Fill = 0	• Bake Time = 15 min.
• Purge time = 11 min.	• Bake Temp = 260ºC
• Drypurge Time = 2.0 min.	• BGB = off
• GC Start = DesEnd	• Delay = 2.00 min.
• Cryo Focuser = off	• MCS Bake Temp = 250ºC
• GC Cycle Time = 0 min.	• Sample Heater = on
• Cryo Standby = ----	• Sample Temp = 85ºC

7.1.3. Agilent 5975 or 5977 Inert GC/MS Conditions (typical):

• Initial temperature = 35ºC	• Final temperature (B) = 200ºC
• Initial time= 3.0 min.	• Final time (B) = 0 min.
• Ramp rate (A) = 6.0ºC/min.	• Carrier Flow = 1.5 mL/min
• Final temperature (A) = 100ºC	• Total Run Time = 20.15 minutes
• Final time (A) = 0 min.	• GC/MS Transfer Line Temp = 180ºC
• Rate (B)= 19ºC/min	• Helium Split Ratio = 1:30
• Final temperature (B)= 200ºC	• Column Flow = 1.2 mL/min

7.1.4. Agilent 5973 or 5975 Inert GC/MS Conditions (typical) for Glycols:

• Initial temperature = 60ºC	• Average velocity = 40 cm/sec
• Initial time= 4.0 min.	• Spitless mode
• Ramp rate (A) = 15.0ºC/min.	• Carrier Flow = 1.5 mL/min
• Final temperature (A) = 225ºC	• Total Run Time = 18.00 minutes
• Final time (A) = 3 min.	• GC/MS Transfer Line Temp = 230ºC
• Injection temperature = 225ºC	• Helium
• Injection volume = 2 µL	• Column Flow = 1.2 mL/min

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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.

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 performance test.

7.3.2. The tune analysis must meet the criteria listed in EPA Method 8260C for a 25-ng injection of BFB (bromofluorobenzene). Obtain a background subtracted BFB spectra by taking the apex scan or average of three scans (apex scan and the preceding and following scans) and subtract 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. Confirm that 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 Methods 8015C and 8260C. Clarification of the calibration requirements and practices of this laboratory are discussed below. Acceptance criteria are tabulated in the QAQC SOP **VO-001**. Refer to the EPA Method protocols in **Reference 13.1 and 13.2** for additional detail.

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

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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 (QCWAA, QCWOX1 or QCWOX2).

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

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

Average Response Factor $= A_S \times C_{IS} / (A_{IS} \times C_S)$

where:

A_S = Peak area of analyte or surrogate

C_{IS} = Peak are of internal standard

A_{IS} = Concentration of analyte or surrogate

C_S = Concentration of internal standard

7.4.2. The retention time of the target analytes in each calibration standard must agree within ± 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 for procedures on generating a reference mass spectrum library.

7.4.4. When using Selected Ion Monitoring (SIM), a full scan is first acquired to determine the best mass ions to use. Normally only the primary ion and 1or 2 secondary ions are selected. The primary ion is used for quantitation and the secondary ions are typically used only for identification purposes. While SIM can provide 1-2 orders of magnitude better detection limits, it must be used with caution due to the lower qualitative value of the data.

7.5. Daily Quality Control Check Standards (QCCS):

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

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

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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 Check Standard (PQL Check):

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 QCCS in the most recent 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 last QCCS, 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 is re-analyzed. The system is re-calibrated, if necessary.

7.8. The analysis sequence must 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. Calibration Check Standard (CCV) initially and every 12 hours.

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

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**).

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 Calibration Check Standard (CCV) at the end of the batch sequence.

7.8.12. Laboratory reagent water blank.

7.9. Pre-Analysis Checklist for the GC/MS Run Sequence:

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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 (if applicable).

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 computer acquisition program.

7.9.9. Check the acquisition parameters in the computer program.

7.9.10. Arrange the sample vials in the autosampler tray.

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

7.9.12. Check the volume of internal standard/surrogate standard in the syringe or vial on the autosampler. The autosampler adds the internal standards and surrogates to the sample automatically.

7.10. Post-Analysis Checklist:

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

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

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

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

7.10.3. Check the surrogate and spike recoveries against acceptance limits. The recovery limits for the surrogates are within 70 to 130%. The recovery limits for the CCV analytes are within 80 to 120 % and the LFB and MS spike compounds are typically within 70 to 130%.

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

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

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

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

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

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

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

7.11. Qualitative Analysis:

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

7.11.1. The characteristic ions of a compound maximize within one scan of each other.

7.11.2. When using selected ion monitoring (SIM), there will normally be one primary ion used for quantitation and only 1 or 2 additional secondary ions for qualitative identification. The secondary ion(s) must be evaluated closely to make sure they are present and in the correct ratio with the primary ion.

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

7.11.4. 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.

7.11.5. 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.

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

7.12. Quantitative Analysis:

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

7.12.2. The average response factors from the initial calibration are used to calculate the concentration of each compound in the sample. See **Reference 13.3** for the equations describing internal standard calibration.

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8. INTERFERENCES

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

8.1. 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 5mm 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. Instrument File Types, Transfer, and Storage:

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

9.1.1.2. Raw data files generated from the instruments must be transferred to a network directory for safe keeping, as established for each instrument.

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 program 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.

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9.2.1. Start QC Manager and Load File: Load the QC Manager program from 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 variable must be set manually. Review each column of the sample table to verify that the QC Manager program set the variables correctly. The variables are described below:

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

CCV – type used for continued calibration verification.

SAMP - Type used for ordinary samples. Assign this type to all samples that do not fit in another category.

SRM - Assign this type to 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.

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), 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 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.

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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
Lab Fortified blanks	≥ 5% of samples
Duplicate Samples	≥ 5% of samples
CCV	Initial and every 12 hours
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 analytical 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 must 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

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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.

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 folder.
- 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 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.

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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 7.2**.

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 7.3.4**.

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 7.5**.

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

10.8. For more specific information regarding QA/QC measures, see **Reference 13.1, 13.3,** and the **SOP VO-001**.

11. DETERMINATION OF METHOD DETECTION LIMITS

11.1. 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 and 13.3**.

11.2. Seven replicate samples are analyzed near the MDL.

11.3. The MDL is the concentration of analyte at which there is analyte present with 99% confidence.

11.4. The results of the seven replicate data sets are tabulated and the statistical calculations are performed electronically on at least a semi-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**.**

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12. SAFETY/HAZARDOUS WASTE MANAGEMENT

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

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

12.3. Use **CAUTION** with strong irritants such as acids and bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals. Avoid contact of these irritants with skin and clothing by appropriate use of gloves, apron, face mask and hood shield.

12.4. Store any wastes that cannot be disposed of down the sink in 4 L bottles or other approved containers (properly labeled with **Hazardous Wastes** labels). These wastes must be 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. All the non-hazardous waste water can be dumped into sink if its pH range is 5-10. If it is not, the waste water must be neutralized before dumping.

13. REFERENCES

13.1. Non-Halogenated Organics by Gas Chromatography, *Test Methods for Evaluating Solid Wastes, SW-846,* Method 8015C, Revision 3, August 2006.

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

13.3. *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8000C, Revision 3, March 2003.

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

13.5. Agilent 5975 Series Inert Mass Selective Detector Operator's Manual. G3170-90036, June 2012.

13.6. Teledyne 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, 2018.

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

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

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

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

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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. EPA Method 8430: Identification of Bis(2-chloroethyl) ether and hydrolysis products by direct aqueous injection GC/FT-IR. Payne, W.D. and Collette, T.W., J. of High Res. Chrom., 12, 693-696, 1989.

13.17. Techniques for Optimizing GC Analysis of Ethylene Glycol in Water, Restek , www.restek.com

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

14. SUMMARY OF THE CURRENT SOP VERSION EDITS

14.1. Updated SOP version number and date.
14.2. Updated for Method 624 to 624.1 transition.
14.3. Updated References.

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