MEASUREMENT OF ACRYLONITRILE AND ACROLEIN IN SEDIMENTS AND WASTE BY PURGE & TRAP/GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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TABLE OF CONTENTS

1. SCOPE AND APPLICATION 3
2. SUMMARY OF THE METHOD 4
3. APPARATUS AND EQUIPMENT 5
4. REAGENTS AND CHEMICALS 7
5. SAMPLE COLLECTION, PRESERVATION, AND STORAGE PROCEDURES 10
6. SAMPLE PREPARATION PROCEDURE 13
7. SAMPLE ANALYSIS PROCEDURE 15
8. INTERFERENCES AND CONFORMANCE 21
9. DATA ARCHIVAL, PROCESSING, REVIEW, AND REPORTING 22
10. QUALITY CONTROL 26
11. DETERMINATION OF METHOD DETECTION LIMITS 27
12. SAFETY, HAZARDOUS WASTE MANAGEMENT, AND POLLUTION PREVENTION 28
13. REFERENCES 28
14. APPENDIX OF CHANGES 29

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1. SCOPE AND APPLICATION

1.1. This method details the analysis of acrolein and acrylonitrile in sediment and waste matrix types by heated purge & trap/gas chromatography/mass spectroscopy (P&T/GC/MS). The procedures describe the operational details required to perform heated purge analysis of sediment and waste samples in the Volatiles Section of the Florida Department of Environmental Protection (FDEP) laboratory. These compounds are segregated from the compounds analyzed in the routine sediment and waste EPA Method 8260C analysis due to the poor purging efficiency of the compounds listed in this method.

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

Acrolein Acrylonitrile

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

S-8260C-AA - EPA Method 8260C analysis, preserved sediment or waste sample

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**).

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

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

1.4.9. Routine VOC Instrument Settings and Conditions (OPS **VO-008**)

1.4.10. *Determination of % Dry Solids* (SOP **MT-055**).

2. SUMMARY OF THE METHOD

The compounds acrolein and acylonitrile are not particularly stable in the environment and do not purge well. Consequently, these compounds are included in a separate analysis, apart from the other compounds typically included in a volatile analysis. The determination of volatile organic compounds by this method is a multi-step process depending on the complexity and contamination level in the sediment sample. Two of the steps common to all sediment samples are the introduction of the compounds by Purge & Trap and analysis by gas chromatography/mass spectrometry. More contaminated sediment samples may require an extraction step prior to introduction on the Purge & Trap instrument. Other methods involving direct injection may be more suitable for certain complex samples, but are not described in this method.

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

2.1.1. Low Level Samples (<200 ug/kg) are collected in hermetically sealed vials or Encore samplers. The sealed vials are used without opening. The contents of the Encore is transferred into a hermetically sealed vial in the laboratory within 48 hours at 4 ^{O}C and have a holding time of 14 days stored at –7 ^{O}C in the sealed vials.

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

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

Sample introduction involves passing inert helium gas through a heated (85 ^{O}C) soil sample that has been mixed with enough water to form a slurry. 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 backflushed with helium to desorb the compounds onto a gas chromatographic column.

2.3. Quantitation Method: The components are separated *via* gas chromatography and

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detected using a mass spectrometer, which provides both qualitative and quantitative information. The described quantitative method is based on EPA Method 8260C, SW-846. The procedures described here are designed to meet or exceed the criteria from the EPA method. Please refer to the SW-846 EPA methods for additional details.

3. APPARATUS AND EQUIPMENT

The operation, cleaning and scheduled maintenance procedures prescribed by the equipment manufactures are followed as provided in the Operator's Manuals. Maintenance contracts, provided by the manufacture, are purchased for the Gas Chromatograph/Mass Spectrometer Systems and Sample Screening System. Documentation of cleaning, maintenance, or system modifications must be recorded in a maintenance logbook which accompanies each instrument system.

3.1. Syringes, Pipets, and Samplers:

3.1.1. Hamilton Microliter/Gastight Syringes: 5.0 µL, 10 µL, 50 µL, 100 µL, 500 µL, 1.0 µL, 2.0 µL, 5 mL, 10 mL, 50 mL. The Hamilton syringes are delicate and must be handled with care. Many of the syringes are equipped with Chaney adapters to improve the reproducibility of the injections and to minimize the bending of the plunger. The syringes are cleaned by 10 to 15 rinses with methanol. The Hamilton syringes must never be heated in an oven or damage may result. Damaged or corroded syringes must be cleaned and discarded into the sharps container. The average life expectancy for a syringe that is used daily is typically no more than a few months. Regardless of use, the microliter syringes must be recalibrated or not used for sample or standard measurements after 1 year.

3.1.2. B-D Brand Multifit Reusable Syringes: 5.0 mL, 10 mL, 50 mL. The B-D Brand Multifit syringes are used only in sample screening or transfer applications. This syringe must not be used for the measurement of precise volumes. The B-D syringe is more rugged and can be baked in a low temperature oven at 105 °C.

3.1.3. B-D Brand Plastic Disposable Syringes: 5.0 mL. Remove the tip of the syringe with a knife or purchase without a tip. Bake in a low temperature oven at 105 °C.

3.1.4. Encore Sampler: 5.0 g and 25 g.

3.1.5. Eppendorf Pipetters, 0-50 mL

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

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methanol and laboratory reagent water. The volumetrics are dried in a low temperature oven at 105 °C. Never use a brush or strong alkali solution to clean the volumetrics.

3.3. Glass Sample (VOA) and Standard Vials:

3.3.1. 40 mL VOA vials with a Teflon®/silicone septa and polypropylene open-top cap.

3.3.2. 20 mL VOA vials with a Teflon®/silicone septa and polypropylene open-top cap.

3.3.3. 2.0 mL vials with Teflon®/silicone/Teflon® septa and polypropylene open-top cap.

3.4. Miscellaneous:

3.4.1. Stainless Steel Spatula.

3.4.2. Disposable aluminum drying dishes.

3.4.3. Teflon-coated stir bars, 8 mm x 16 mm

3.4.4. Glass Jar with silicon/Teflon lined septum, 250 mL.

3.5. Corning MP-1 Glass Distillation Unit or Solution 2000 Water Purification System.

3.6. Fisher IsoTemp Forced-Air Oven.

3.7. Yamato Forced-Air Oven, Model DN83.

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

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

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

3.11. 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 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 (P&T) and Autosampler Concentrator.

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3.14.4. Agilent Enviroquant Computer Software.

3.14.5. J&W Scientific DB-624, 30 m x 0.25 mm ID capillary column, 1.4 μm film.

3.14.6. Supelco High Capacity Gas Purifier or equivalent.

4. REAGENTS AND CHEMICALS

Working with volatile compounds presents a number of challenges not normally confronted in the handling of most other chemicals. Volatile compounds are easily lost from prepared solutions or when present in the laboratory environment can cross-contaminate other samples. Review the techniques for handling volatile compounds found in **reference 13.1, 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 (P&T) grade methanol is purchased in 500 mL amber bottles from Fisher Scientific.

4.2. Acids and Bases:

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

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

4.3. Laboratory Sand:

Ottawa sand is prepared by rinsing clean, white sand with methanol and laboratory reagent water several times. The rinsed sand is baked in an oven at 175 ^{o}C overnight to remove any volatiles and is then store in the same oven. The heated laboratory sand is occasionally purged with carrier grade helium or nitrogen to remove trapped volatiles.

4.4. Laboratory Reagent Water:

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

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

4.5. Internal Standard and Surrogate Solutions:

4.5.1. 25 ppm (or 100 ppm) Internal Standard/Surrogate Solution (IS/SURR): An internal standard/surrogate solution is injected into every sample by the autosampler just prior to analysis. The internal standard compounds are fluorobenzene, chlorobenzene-d_5, and 4-bromofluoromethane. The surrogate compounds are dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8 , and 1,4-dichlorobenzene-d_4. These compounds may be purchased in the prepared mixture STM-540 from UltraScientific at a concentration of 5000 µg/mL in methanol.

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

4.5.1.2. Dispense accurately 1 mL (or 4 mL for the 100 ppm level) of STM-540 into a 200 mL volumetric flask containing 190 mL of methanol. Fill the volumetric to the volume mark with methanol. The working internal standard is stored at ≤ -20.0 °C in labeled 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. Enter the standard information into the LIMS standard preparation log.

4.6. Calibration Standards:

The stock calibration standards used for the preparation of the initial calibration and daily quality control check standards (CCVs) are purchased from Supelco Inc, or equivalent. The catalog numbers are: 4-8501 acrolein (neat, d = 0.839 g/ml), 4-8502 acrylonitrile (neat, d = 0.806 g/ml. The stock solutions must be mixed and diluted into working standards before use. 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 EPA Method 8260C may be added to this method once proficiency has been demonstrated through a validation exercise.

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

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4.6.1. Working and Intermediate Calibration Standards:

4.6.1.1. 200 ppm A/A working calibration standard: With a 10 µL gastight syringe, add 4.70 µL of neat acrolein and 4.96 µL of neat acrylonitrile to a 20 mL volumetric flask containing 45 mL of methanol. Dilute to final volume and cap flask. The working solution must be used within 180 days or by the expiration date of the original material, whichever comes first. Enter the standard information into the LIMS standard preparation log.

4.6.1.2. 100 ppb A/A daily intermediate calibration standard: With a 25 µL gastight syringe, add 25 µL of the 200 µg/mL A/A working calibration standard to a 50 mL volumetric flask containing 45 mL of laboratory reagent water. Dilute to final volume and cap flask. This daily working solution must be used within 1 hour after preparation if kept in the volumetric flask. The life of the aqueous solution can be extended to 24 hours if the solution is zero-headspaced and refrigerated to 4°C.

4.6.2. Initial Calibration Standards:

4.6.2.1. 10 ng A/A calibration standard: With a 500 µL syringe inject 100 µL of the 100 ppb A/A daily intermediate calibration solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap the soil vial immediately.

4.6.2.2. 20 ng A/A calibration standard: With a 500 µL syringe inject 200 µL of the 100 ppb A/A daily intermediate calibration solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap immediately.

4.6.2.3. 40 ng A/A calibration standard: With a 500 µL syringe inject 400 µL of the 100 ppb A/A daily intermediate calibration solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap immediately.

4.6.2.4. 50 ng A/A calibration standard: With a 500 µL syringe inject 500 µL of the 100 ppb A/A daily intermediate calibration solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap immediately.

4.6.2.5. 100 ng A/A calibration standard: With a 1.0 mL syringe inject 1.0 mL of the 100 ppb A/A daily intermediate calibration solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap immediately.

4.6.2.6. 200 ng A/A calibration standard: With a 2.0 mL syringe inject 2.0 mL of the 100 ppb A/A daily intermediate calibration solution into a soil vial containing 5.0 mL of laboratory reagent water. Cap immediately.

4.6.3. Daily Quality Control Check Standards:

The working calibration standard is used for the preparation of the daily quality

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control check standard (CCV).

4.6.3.1. CCV Standard: A 40 ng calibration check sample is prepared from the A/A daily intermediate 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 4.6.2.3.**

4.7. Laboratory Fortified Blank and Matrix Spike Standards:

The compounds contained in the matrix spike standards are used for the preparation of lab-fortified blanks (LFBs) and sample matrix spikes. The stock spike standards are purchased neat from Ultra Scientific, or equivalent. The catalog numbers are: RCC-150 for acrolein and RCC-204 for acrylonitrile. All stock and working standards are stored at ≤ -20.0 °C. The LFB and matrix spike standards must be prepared from the working standards just prior to use in a batch analysis.

4.7.1. 200 ppm A/A working spike standard: With a 10 µL gastight syringe, add 4.70 µL of neat acrolein and add 4.96 µL of neat acrylonitrile to a 20 mL volumetric flask containing 45 mL of methanol. Dilute to final volume and cap flask. The working solution must be used within 180 days after or by the expiration date of the original material, whichever comes first. Enter the standard information into the LIMS standard preparation log.

4.7.2. 100 ppb A/A daily spike standard With a 25 µL gastight syringe, add 25 µL of the 200 µg/mL A/A working spike standard to a 50 mL volumetric flask containing 45 mL of laboratory reagent water. Dilute to final volume and cap flask. This daily working solution must be used within 1 hour after preparation if kept in the volumetric flask. The life of the solution can be extended to 24 hours if the solution is zero-headspaced and refrigerated.

4.7.3. 200 ng LFB Preparation: With a 2.0 mL syringe inject 2.0 mL of the 100 ppb A/A daily spike standard solution into a clean soil vial containing 5 mL of laboratory reagent water. Cap the soil vial immediately. A 40 ng LFB is prepared for every 10 samples.

4.7.4. 200 ng Matrix Spike Preparation: With a 2.0 mL syringe inject 2.0 mL of the 100 ppb A/A daily spike standard solution into a matrix soil sample vial containing 5 mL of laboratory reagent water. Cap the soil vial immediately. A 40 ng matrix spike check is prepared for every 10 samples (duplicate matrix spikes prepared for every 20 samples meets the 10% requirement).

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.

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5.1. Soil VOA Vial Preparation:

The laboratory prepared sampling kits contain 3 to 4 VOA vials inside of a bubble-wrap bag, which in turn is inside Ziploc bag. The protocol for cleaning the vials is in the cleaning SOP **VO-007**. Instructions for assembling the sample kits are as follows:

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

5.1.2. Remove clean sample vials and cans from the vial oven (170 °C) and remove the septa, plastic syringes and Teflon-coated stir bars from the low temperature oven (105 °C). Cover the vials and septa with aluminum foil and cool to near room temperature. A box of clean open-top caps will also be needed.

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

5.1.4. Add one stir bar in each vial.

5.1.5. Add 5.0 mL of laboratory reagent water to each vial..

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

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

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

5.1.9. If purchased vials are not certified pre-clean, then submit a minimum of 2% of the vials for testing. Quality Control testing of the vials must demonstrate that the vials are free of target analytes to a level less than 20% of the reporting limit. The vials cannot be used to prepare kits until the QC testing is complete and documented in the LIMS. The QC approved vials can be stored in the VOC laboratory for up to six months.

5.2. Sample Kit Assembly:

5.2.1. Place two to three QC-approved vials and a plastic tip-less syringe in a 3 mil polyethylene Ziploc bag. Put the Ziploc bag into a baked metal can. Visually inspect the vials as you prepare the kit for anything unusual such as loose caps, inverted septa, or cracked vials.

5.2.2. Add one 25 g Encore samplers into each kit.

5.2.3. Add one bulk glass jar container for each kit.

5.2.4. Trip blanks used in the same soil vials, but only have two vials and do not contain the Encore sampler or bulk jar.

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

5.3. Sample Collection:

5.3.1. Remove the plastic syringe and soil vials from the kit. Use all vials in the kit.

5.3.2. Use the 5 mL plastic syringe to add a 3 mL plug of soil to each soil vial. If the soil is very wet increase the soil plug volume to 4 mL. Care must be exercised, when collecting the sample, not to pour out the water in the vial or get soil on the lid or lip of the vial. Also, avoid putting rocks and sticks into the sample.

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

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

5.3.5. After the samples are capped, return them into the Ziploc bag and metal can.

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

5.3.7. Label the Encore samplers and return them to the kit container.

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

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

5.4. Sample Storage:

5.4.1. Soil vials and Encore samplers are stored in a locked, flammable-rated refrigerator at 4.0 ± 2 °C for up to 48 hours. The soil vials and Encore samplers must be analyzed, extracted, or frozen within 48 hours of sampling to avoid sample expiration. The contents of the Encore samplers must be transferred as soon as possible to a hermetically sealed soil vial or into a methanol extract and stored at ≤ -7 °C. Soil vials or samples frozen at ≤ -7 °C have a holding time of 14 days. The extracted or transferred samples must be analyzed within 14 days of sample collection.

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

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6. SAMPLE PREPARATION PROCEDURE

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

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

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

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

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

6.6. Methanol Extract Preparation: A 10 g subsample from one of the Encore samplers is used to prepare a methanol extract. The methanol extract is used for sample screening and high-level analysis.

6.6.1. Tare a clean, labeled VOA vial on the toploading balance.

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

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

6.6.4. Cap the VOA vial finger tight with a Teflon/silicon lid.

6.6.5. The extract must be thoroughly mixed after using a Vortex mixer for up to 1 minute. Recoveries of the volatile compounds can be severely reduced if the sample is mixed too long or vigorously.

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

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

6.7. Low-Level Sediment Sample Preparation:

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

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

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

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

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

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

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

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

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

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

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

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

6.8. Percent Dry Weight: Refer to SOP **MT-055** for the dry-weight determination procedure. The percent dry weight of sediment samples is determined by weighing out 5-10 g of sample into a weighing dish and drying the sample at 103 ± 2 °C overnight for 12 hours minimum. The percent dry weight is equal to the (dry sample weight divided by the wet sample weight) times 100. The drying oven must be vented to minimize laboratory

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contamination and odors. Samples that may pose a fire hazard must not be placed in the oven. Do not measure the dry weight for waste samples since they are reported based on wet weight.

7. SAMPLE ANALYSIS PROCEDURE

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

Note: The GC/MS software used by the 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 = Jan, 2 = Feb, 3 = Mar, 4 = Apr, 5 = May, 6 = Jun, 7 = Jul, 8 =Aug, 9 = Sep, O = Oct, N = Nov, D = Dec)
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 blank performance test.

7.3.2. The tune analysis must meet the criteria listed in EPA Method 8260C for a 25-ng injection of BFB (bromofluorobenzene). Obtain the BFB mass spectrum and confirm that all of the m/z criteria in Table 1 are achieved. If the criteria are not achieved, the operator must retune the mass spectrometer and repeat the test until all criteria are achieved. The apex peak scan or ± 1 scans from the apex may be used to demonstrate tuning by using a single scan. Alternately, the average of these three scans (peak apex plus immediately preceding and following scans) may be used to meet the tuning m/z criteria.

Table 1.-BFB m/z Abundance Criteria

Mass, m/z	Abundance Criteria
50	15-40 % of mass 95

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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 8260C. Clarification of the calibration requirements and practices of this laboratory are discussed below. Acceptance criteria are tabulated in the QAQC SOP **VO-001**. Refer to the EPA method protocols in **Reference 13.1 and 13.2** for additional detail.

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

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

Six or seven 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 or non-linear fit. A minimum of 5 calibration points is required for a linear calibration curve and 6 calibration points for a non-linear calibration curve. Removal of calibration points at the extremes of the calibration curve is allowed, provided is can still achieve the method calibration requirements. Hoever, calibration points in the middle of the curve must not be removed without clear justification and documentation (consult supervisor for removal of intermediate calibration levels). 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 = $(A_S \times C_{IS}) / (A_{IS} \times C_S)$

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where:

$\mathbf{A_S}$ = Peak area of analyte or surrogate

$\mathbf{C_{is}}$ = Peak are of internal standard

$\mathbf{A_{is}}$ = Concentration of analyte or surrogate

$\mathbf{C_S}$ = 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 (**References 13.4 and 13.5**) for procedures on generating a reference mass spectrum library.

7.5. Daily Quality Control Check Standards (CCVs):

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

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

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

7.6. PQL or MDL Check Standard:

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

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7.7. Internal Standard Retention Time and Internal Standard Response:

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

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

7.8.1. BFB tune check every 12 hours.

7.8.2. Laboratory reagent 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. A laboratory fortified blank (LFB1) for every 20 samples. Prepare duplicate LFBs if duplicate matrix spikes are not available.

7.8.6. Replicate matrix spikes for every 20 samples.

7.8.7. Laboratory reagent sediment 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 blank for rinsing purposes as needed during run sequence

7.8.11. Closing 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.

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

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

7.10.5. The laboratory reagent sediment 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.

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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, LFB, and matrix spikes must be put into the Daily QC folder.

7.11. Qualitative Analysis:

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

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

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

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

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

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

7.12. Quantitative Analysis:

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

7.12.2. The average response factors from the initial calibration are used to calculate the

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concentration of each compound in the sample. See EPA Method 8260C and reference within for more details.

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

Calculate the total methanol/water extraction volume (V_t) as follows:

$$V_t = Volume\ of\ solvent\ (ml) + \frac{(\%\ moisture \times Weight\ of\ sample\ (g))}{100}$$

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

Calculate the % moisture as follows:

$$\%\ Moisture = \frac{(Weight\ of\ sample\ (g)) - (Weight\ of\ dry\ sample\ (g))}{Weight\ of\ sample\ (g)} \times 100$$

Calculate the Moisture Correction as follows:

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

8. INTERFERENCES AND NON-CONFORMANCE

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. Difficult or non-compliance samples are normally identified during sample preparation. Non-compliance samples must be clearly identified on the sample screening log, job file, and final report. The screen log has a footnote containing numerical codes for the more common non-compliance problems encountered.

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

8.3. Non-aqueous or multiphase samples, such as oil or paint, 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,

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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. Initiate a non-conformance report and add a comment to the job file and into the LIMS file for the affected sample.

8.5. Sediment samples containing excessive amounts of water must be reported to the supervisor to determine the most appropriate test.

8.6. 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 Type, Transfer, and Storage:

9.1.1.1. Agilent 5973 or 5975 GC/MS: The Agilent GC/MS stores 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 variable must be set manually. Review each column of

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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 (S-8260B-AA, S-VOC-MS, WAS-VOC-MS, or S-VOC-MS-X), 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.

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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, and continuing calibration standards are analyzed at the frequency specified in the Comprehensive Quality Assurance Plan.

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

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

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

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

9.3.4. Recovery and Precision (RPD) statistics are determined for samples fortified with known quantities of target analytes. The recovery is an indication of the accuracy of the analytical result. The RPD (relative percent difference) from duplicate fortified samples is an indication of precision. Examine the recovery and precision data to ensure that they are within control limits for the requested analytes. A letter appears in the Pass/Fail column of the component table/baby

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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 *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.

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

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- Give the complete job folders to the senior chemist or supervisor for data review and authorization.

9.5. Data Reporting by Supervisor:

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

10. QUALITY CONTROL

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

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

10.2. Evaluation of retention time windows to ensure that all compounds are detected within their respective time windows and meet the ± 6 second requirement in **Section 7.4.**

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

10.4. The GC/MS system must meet the CCV criteria each 12 hours of instrument operation as described in **Section 7.5**.

10.5. A laboratory reagent 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 analyzed. 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

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deviation. Appropriate corrective measures must be taken if the analyte recoveries or RPDs are outside of these limits and the affected samples must be reanalyzed. The spike recoveries and statistical analysis are uploaded into the LIMS and printed in the final report for the job.

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

11. DETERMINATION OF METHOD DETECTION LIMITS

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

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

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

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

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

11.2 MDL Determination Procedures

11.2.1 The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register. Refer to **Reference 13.2**.

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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.

11.2.3 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.

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 waste that cannot be disposed down the sink (see Laboratory Safety SOP Manual) in 2 L bottles (properly labeled with **Hazardous Wastes** labels). These wastes must be disposed in the appropriate waste storage container found in the Hazardous Waste storage room in Bldg. C of the Main Laboratory Complex. Waste from the VOC lab includes chemical standards, used pump oil, methanol extract waste, hazardous samples, and oily sample waste.

12.5. All non-hazardous wastewater can be disposed into the municipal waste stream if the pH is in the 5 to 10 range. If not, the wastewater must be neutralized before disposal.

13. REFERENCES

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13.2. "Determinative Chromatographic Separations", *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8000C, Revision 3, March 2003.

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

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

13.5. Tekmar Atomx TekLink Software Manual, Version 1.1.3965.21095, 2010.

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13.6. Comprehensive Quality Assurance Plan, Chemistry Section, Bureau of Labs, FDEP, December 2014.

13.7. FDEP Laboratory Safety SOP Manual **OG-001**.

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

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

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

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

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

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

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

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

13.16. Florida Department of Environmental Protection, Standard Operating Procedure **VO-008** Routine VOC Instrument Settings and Conditions.

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

14. APPENDIX OF CHANGES

12/17/2014 Updated version number and date, Instrument Section 3, Reagent Section 4, Section 6 for sample preparation, Section 7 addressing the sample analysis procedures, Section 8 discussing interferences, Section 9 for data review, Section 11 for the determination of MDLs, and References in Section 13.

12/07/2015 Updated logo, removed obsolete reagent solvents, updated sampling container, and reference section.

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