ANALYSIS OF 1,4-DIOXANE IN WATER BY SOLID PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

BUREAU OF LABORATORIES

2600 BLAIR STONE ROAD

TALLAHASSEE, FLORIDA 32399

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

ANALYSIS OF 1,4-DIOXANE IN WATER BY SOLID PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)

TABLE OF CONTENTS

1. SCOPE AND APPLICATION 3
2. SUMMARY OF THE METHOD 4
3. APPARATUS, EQUIPMENT, AND SETTINGS 4
4. REAGENTS AND CHEMICALS 6
5. SAMPLE COLLECTION, PRESERVATION, AND STORAGE PROCEDURES 8
6. SAMPLE PREPARATION PROCEDURE 10
7. SAMPLE ANALYSIS AND CALCULATIONS 13
8. INTERFERENCES 20
9. DATA ARCHIVAL, PROCESSING, REVIEW, AND REPORTING 21
10. QUALITY CONTROL 25
11. DETERMINATION OF METHOD DETECTION LIMITS 25
12. SAFETY, HAZARDOUS WASTE MANAGEMENT, AND POLLUTION PREVENTION .. 26
13. REFERENCES 26
APPENDIX OF CHANGES 28

ANALYSIS OF 1,4-DIOXANE IN WATER BY SOLID PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)

1. SCOPE AND APPLICATION

1.1. This is a gas chromatography/mass spectrometry (GC/MS) method for the determination of the compound 1,4-dioxane in aqueous samples. The method describes the process for using solid phase extraction (SPE) to isolate the compound 1,4-dioxane from ground water, surface water, and waste water. This procedure is based on the drinking water EPA Method 522, which is specifically designed for the analysis of 1,4-dioxane. The Method Detection Limit (MDL) for this method is 0.020 µg/L, where minimal background or matrix interference is present. The Practical Quantitation Limit (PQL) for this method is 0.10 µg/L.

1.2. The operating procedures described here are designed to meet or exceed the QC requirements for EPA Method 522.

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

W-1-4-DIOX - EPA Method 522 Analysis

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

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

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

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

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

1.4.7. Procedure and Policy for Method and Instrument Validation, (SOP **LB-007**).

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

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

1.5. This method is intended for use only by analysts skilled in solid phase extraction (SPE), operation of GC/MS instruments, and skilled in the interpretation of mass spectral data.

2. SUMMARY OF THE METHOD

The determination of 1,4-dioxane by this method is a multi-step extraction and analysis process that depends somewhat on the complexity and contamination level of the water sample. The EPA 522 method was designed for drinking water applications, but has been validated here for use in a wide range of water matrices.

2.1. A water sample is fortified with the isotopically labeled surrogate compound 1,4-dioxane-*d*8 and is then extracted by one of two SPE options.

- Option 1: A 200-mL sample is passed through a Supelco Supelclean ENVI-Carb Plus 400-mg cartridge to extract the method analyte and surrogate.

- Option 2: A 500-mL sample is passed through a Restek 2-gram coconut charcoal SPE cartridge to extract the method analyte and surrogate.

2.2. The compounds are eluted from the 400-mg or 2-gram SPE cartridges with a small amount of dichloromethane (DCM), approximately 1.8 mL or 9.5 mL, respectively. The internal standard, tetrahydrofuran-*d*8 (THF-*d*8), is added and the extract volume is adjusted to 2 mL or 10 mL, respectively. The extract is then dried with anhydrous sodium sulfate.

2.3. Analysis of the extract is performed by GC/MS in the SIM mode for maximum method sensitivity. Sample extract analysis may also be performed in full-scan mode if the sensitivity achieved meets the data user's requirements.

2.4. Each analyst must demonstrate the ability to generate acceptable analytical results with this method and complete required laboratory training requirements prior to reporting data.

3. APPARATUS, EQUIPMENT, AND SETTINGS

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

3.1. Sample Bottles: 1.0 Liter amber glass with Teflon-lined screw caps. Although samples do not need to be collected headspace free, the size of the sample bottle should be selected based upon the sample volume to be extracted.

3.2. Autosampler Vials: 1.5 mL and 0.35 mL glass vials with crimp tops and Teflon-lined septa to fit the Agilent 7683autosampler.

3.3. GC/MS System:

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

3.3.1 Agilent 6890 Series II or 7890A Gas Chromatograph (or equivalent). The GC/MS must be temperature programmable with an injector port designed for split/splitless injection.

3.3.2 Agilent 7683 Autosampler (or equivalent). The autosampler must be capable of 1 to 4 µL injections and equipped with solvent vials for flushing the syringe between injections.

3.3.3 Agilent 5975C or 5973 Mass Spectrometer (or equivalent). The mass spectrometer must be capable of scanning from 35 to 450 amu, utilizing 70 eV (nominal) in the electron impact ionization mode. The instrument must also be capable of full-scan and selected-ion monitoring.

3.3.4. Enviroquant Data System (or equivalent): A computer system must be interfaced to the GC/MS instrument for data acquisition and storage. The instrument software must have the ability to process the GC/MS data files for reporting purposes. See the Enviroquant software manual for details.

3.4. Helium, UPC grade carrier gas: The helium is filtered through an oxygen & hydrocarbon cartridge before entering the GC/MS instrument.

3.5. J&W Scientific DB-VRX (122-1534) Capillary column (or equivalent), 30 m x 0.25 mm x 1.4 µm.

3.6. Volumetric Flasks – Class A, various sizes, including 1, 5, and 10 mL for preparation of standards.

3.7. Graduated Cylinders – Glass, various sizes, including 100 and 500 mL for measurement of sample volumes.

3.8. Micro Syringes – Suggested sizes include 10, 25, 50, 100, 250, 500, and 1000 µL.

3.9. Centrifuge Tubes – graduated, with screw cap or ground glass stoppers – 15 mL. Suitable for collection of the eluent from the SPE cartridge after extraction (Calibrate tubes to the required volume and record in the Extraction Log Book).

3.10. Analytical Balance – Capable of weighing to the nearest 0.10 g.

3.11. Solid Phase Extraction (SPE) Cartridges

3.11.1. Option 1: Supelco Supelclean ENVI-Carb Plus 400-mg synthetic carbon (cat. # 54812-U). (Use with samples volumes ≤ 100 mL.)

3.11.2. Option 2: 6-mL polypropylene tubes packed with 2 g coconut charcoal (80-120 mesh, approximately150 µm). Restek Corporation (cat. # 26032). (Use with sample volumes (V) where 100 mL ≤ V ≤ 500 mL)

3.12. Baker Vacuum Manifold (or equivalent) – capable of holding SPE cartridges.

3.13. Glass Beakers, 250, 500 mL

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

3.14. Eppendorf 10 µL to 100 µL Adjustable Pipette (calibrated quarterly).

3.15. Eppendorf 100 µL to 1000 µL Adjustable Pipette (calibrated quarterly).

3.16. Pipette Tips – 200 µL, 30 to 300 µL and 1000 µL.

3.17. 75 mL Polypropylene Sample Reservoirs

3.18. Adapter for 75 mL sample reservoir and SPE Cartridge

3.19. Disposable Plastic Syringe – 5 mL and 10 mL

3.20. Vortex Mixer

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 and reagents. Review the techniques in EPA method 522 for handling the compound 1,4-dioxane 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.

NOTE: Information on all chemical reagents and solvents must be recorded in the LIMS Chemical Standard Preparation Tracker.

4.1. Preparation of Stock Standard Solutions from Neat Materials

4.1.1. Place about 9.8 mL of methanol in a 10 mL volumetric flask. Allow the flask to stand, unstoppered, for several minutes until the alcohol wetted surfaces have dried. Weigh to the nearest 0.10 mg.

4.1.2. Using a precision microliter syringe, quickly add the appropriate volume of neat standard material to the flask. Be sure the standard falls directly into the alcohol.

4.1.3. Quickly reweigh, dilute to volume and mix by inverting the flask several times. Calculate the concentration in µg/mL from the net weight added.

4.1.4. Store the solution in small glass vials with PTFE lined caps with minimal head space.

4.2. Chemical Standards

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

The analytical standards are stored in a freezer at < -20°C and are not stored with samples at any time. Refer to the analytical standard manufacture documentation or laboratory MSDS binder for additional details on safety, handling, and storage.

4.2.1. 1,4-Dioxane (Primary Source): Ultra Scientific Cat# RCC-180. Calibration Standards for 1,4-dioxane are prepared from the neat standard at the following concentration levels: 2, 5, 10, 25, 50, 100, 250 and 500 µg/L in Purge & Trap grade methanol. This standard concentration range corresponds to 0.20 - 20 µg/L in the original samples.

4.2.2. 1,4-Dioxane (Second Source): Sigma Aldrich Cat# 296309. This neat standard is used to verify the primary standard in the calibration verification sample. The standard is prepared at a concentration of 100 µg/L in Purge & Trap grade methanol.

4.2.3. Lab Fortified Blank and Matrix Spike Working Standard: A 1,4-dioxane standard solution is prepared at a concentration of 5 µg/mL using the Primary Source standard.

4.2.4. Tetrahydrofuran-d8 Internal Standard Working Solutions (Neat): Sigma Aldrich Cat# 184314-1G. The neat THF-d8 primary standard is first diluted to an intermediate concentration of 2000 mg/L in methylene chloride. Working Internal Standard solutions of 5.0 µg/mL and 50 µg/L are then prepared in methylene chloride from the 2000 mg/L standard for sample analysis and sample dilution, respectively. Internal Standard solution is added to every sample to a final concentration of 50 µg/L.

4.2.4.1. 2000 µg/mL Intermediate THF-d8 Solution: Add 0.0200 g of neat THF-d8 to a 10 mL volumetric flask containing methylene chloride. Bring the volume up to the mark with methylene chloride and rotate the flask to mix. Transfer the contents to sealed vials.

4.2.4.2. 5.0 µg/mL Intermediate/Working THF-d8 Solution: A working standard at 5.0 ug/mL is prepared by adding 25 µL of the 2000 µg/L intermediate standard to a 10 mL volumetric flask containing methylene chloride. Bring the volume up to the mark with methanol and rotate the flask to mix. Transfer the contents to sealed vials.

4.2.4.3. 50 µg/L Working THF-d8 Solution: A working standard at 50 ug/L is prepared by adding 100 µL of the 5 µg/mL intermediate standard to a 10 mL volumetric flask containing methylene chloride. Bring the volume up to the mark with methylene chloride and rotate the flask to mix. Transfer the contents to sealed vials.

4.2.5. Bromofluorobenzene (BFB) Tuning Standard: Ultra Scientific 8260C Tuning Standard Mixture STM-541. A solution of tune standard is prepared at a concentration of 20 µg/mL methylene chloride and is used in the preparation of every sample.

4.2.6. 1,4-Dioxane-d8 Surrogate Standard (2000 ug/mL): Restek Catalog # 30614. An intermediate/working standard of 200 ug/mL is prepared from the 2000

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

µg/mL primary standard by diluting 10X with P&T grade methanol. A working standard at 5.0 µg/mL is prepared from the 200 µg/mL intermediate standard with P&T grade methanol. The 5.0 µg/mL and 200 µg/mL working standards are used to fortify 200 mL and 500 mL samples, respectively. The surrogate compound 1,4-dioxane-d8 is added to every sample prior to extraction.

4.3. Organic Solvents

4.3.1. Methylene Chloride, Fisher Scientific HPLC grade (or equivalent).

4.3.2. Methanol, Fisher Scientific P&T grade (or equivalent). An HPLC grade may be used if it is demonstrated not to interfere with the analysis.

4.4. Sodium Sulfate, Anhydrous (CASRN 7757-82-6) Fisher Scientific - Soxhlet extracted with DCM for a minimum of four hours or heated to 400 °C for two hours in a muffle furnace. An ACS grade, suitable for pesticide residue analysis is recommended.

4.5. Sodium Sulfite (CASRN 7757-83-7) Fisher Scientific -Reduces free and combined chlorine in samples that have been disinfected with chlorine and/or chloramine. Dechlorination must be performed prior to the addition of the sodium bisulfate preservative.

4.6. Sodium Bisulfate (CASRN 7681-38-1) Fisher Scientific - Anhydrous, technical grade. Approximately 1.0 gram/L of sodium bisulfate is added to each sample to reduce the pH < 4 as a microbial inhibitor.

5. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Kits used to collect the samples are provided by the laboratory and should contain sufficient bottles to collect samples, blanks, and duplicates. The kits are prepared based on the sample requests.

The Bureau's policy, which is reflected in this SOP, requires that any samples suspected to contain chlorine (e.g. treated wastewater) be checked for residual chlorine in the laboratory prior to analysis. If residual chlorine is present, the sample is dechlorinated and checked again. Samples that are not suspected to contain chlorine (e.g. ambient water) are not checked for residual chlorine in the laboratory prior to analysis.

5.1. Sample Collection:

5.1.1. In order to collect a representative sample it is imperative to flow sufficient sample through the field equipment. Allow enough time for several volumes of water to pass through the equipment and the water temperature to stabilize (typically three to five minutes). Collect samples from the flowing system.

5.1.2. Fill sample bottles, taking care not to flush out the sample dechlorination reagent (if required). Samples collected from treated water supplies will require dechlorination, but surface and ground water samples do not normally require dechlorination. Cap the sample bottle and agitate by hand until the

sodium sulfite is dissolved (if used). Samples do not need to be collected headspace free.

5.1.3. Preserve the sample with sodium bisulfate -. Add enough sodium bisulfate such that the final concentration will be 1.0 g/L. Cap the bottle and mix until dissolved.

5.1.4. Field verification of pH < 4 (optional). It is anticipated that 1.0 g/L of sodium bisulfate will be sufficient to acidify most samples to pH< 4. If there is reason to suspect that more may be needed, the pH can be verified with narrow range pH paper at the time of sample collection. After acidification and mixing, pour a small amount of sample over a strip of the pH paper (do not dip the strip in the sample). Read the result as instructed on the pH paper package. If the pH is ≥ 4, add additional sodium bisulfate until pH < 4 is obtained. Seal the bottle, and keep the sample sealed until extraction.

5.2. Sample Preservation:

Preservation reagents, listed in the table below, are added to each sample at the time of sample collection. Sodium sulfite must be added first and may be placed as a dry material in the sample bottles prior to shipment to the field. Aqueous solutions of sodium sulfite may not be added to sample bottles prior to shipment to the collection site because these solutions are unstable and cannot be relied upon to completely dechlorinate the samples. Sodium bisulfate is added only after the sodium sulfite has been dissolved in the aqueous sample

Table 1. Sample Preservation Criteria

Compound	Amount	Criteria
Sodium Sulfite	50 mg/L	Pass DPD Chlorine Test
Sodium Bisulfate	1.0 g/L (approx)	pH < 4

5.3. Sample Shipment and Storage:

Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Sample temperature must be confirmed to be at or below 10 °C when they are received at the laboratory. Depending upon the water temperature at the time of collection, samples may need to be refrigerated to reduce their temperature before being packed on ice for shipment. Samples stored in the lab must be held at or below 6 °C until extraction, but should not be frozen. Freezing samples may compromise the sealed cap or result in sample bottle breakage.

5.4. Sample and Extract Holding Times:

Aqueous samples may be stored as described above for up to 28 days from collection. Sample extracts, as prepared in Section 6, may be stored at -5.0 °C and protected from light for an additional 28 days.

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

6. SAMPLE PREPARATION PROCEDURE

NOTE: Second person must witness the addition of spike standard to the proper samples; verify the correct volume and concentration, verify the LIMS ID number, and initial in the logbook. The record must also include the sample bottle number, if there is more than one, the reagent and solvent lot numbers, bath temperature for extract concentration, balance ID, and calibrated tube IDs.

6.1. Insure all glassware is clean. Thoroughly clean all glassware with Alconox and hot water. Rinse with hot tap water, deionized water and acetone, then baking it in an oven at 550 °C for at least 6 hours.

6.2. Log out the water samples from the receiving room walk-in cooler.

6.3. Remove the spike and surrogate mixes from the standards freezer and bring to room temperature.

6.4. Rinse all glassware with methanol, then rinse with HPLC grade water.

6.5. All Field and QC samples (LRBs and LFBs) must contain the dechlorination agent, sodium sulfite (if applicable). Verify that Field Samples were checked for total chlorine upon sample receipt at the laboratory, and that no chlorine was present if chlorine is suspected. Add sodium sulfite to all LRBs and LFBs according to the sample collection and preservation.

6.6. All Field and QC samples (LRBs and LFBs), must contain the anti-microbial agent sodium bisulfate. Verify that Field Samples were acidified to pH<4 at the time of collection by checking with narrow range pH paper (this verification may take place at sample receipt if preferred by the laboratory). Add sodium bisulfate to all LRBs and LFBs according to the sample collection and preservation instructions.

6.7. Transfer either 200 mL or 500 mL (depending on SPE cartridge type) of sample to a clean glass container with a clean graduated cylinder. Use well water to prepare the laboratory blank and laboratory fortified blanks. Randomly select one of the samples to prepare a duplicate matrix spike. Check the pH of each sample, and record it in the notebook. Alternatively, the sample volume may be calculated by weighing the sample bottle before and after extraction (or sample transfer) and using a density of g/mL.

6.8. For 200 mL of water add 20 µL of the 5.0 µg/mL 1,4-dioxane-d8 surrogate standard to all samples in the set. Add 20 µL of 5.0 µg/mL 1,4-dioxane spike standard to the laboratory-fortified blanks and matrix spikes. If using 500 mL of water for extraction, then increase the spike volumes to 2.5-fold the amount used for the 200-mL sample size.

6.9. Solid Phase Extraction Procedure by Option 1 (Supelco Supelclean ENV1-Carb Plus cartridges):

6.9.1. The SPE cartridges must be conditioned prior to use. Place the SPE cartridges into the vacuum manifold. Label all cartridges with the appropriate sample number, using a permanent marker. Fill the cartridge with approximately 1 mL

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

of dichloromethane solvent, turn on the vacuum, and pull the solvent through, aspirating completely.

6.9.2. Firmly push an adapter into the top of each cartridge, and then attach a 75-mL reservoir to each adapter. Add approximately 2 mL of methanol, turn on the vacuum, and pull the solvent through, aspirating completely.

6.9.3. Fill the cartridge again with approximately 2 mL of methanol and elute with vacuum to just above the top of the cartridge – not allowing the cartridge to go dry at the end. From this point forward do not allow the cartridge to go dry.

6.9.4. Fill the cartridge with 3 mL of reagent water, turn on the vacuum, and pull the water through, without allowing the cartridge to go dry.

6.9.5. Fill each reservoir with the appropriate sample. Open the valves on the vacuum manifold for all cartridges that are in use, and allow the samples to begin passing through the cartridges. The vacuum gauge should not exceed 8-12 inches Hg which corresponds to a sampling rate of about 10mL/min. Do not let any cartridge go dry during sample addition. If a cartridge goes dry during this step, re-extract that sample from the beginning with a new cartridge. If a cartridge becomes clogged, and the sample will not pass through it, proceed to last step in this procedure section for specific instructions. After all the sample has passed through each SPE cartridge, rinse that sample's beaker with 5 mL of HPLC grade water, pour the rinsate into the sample reservoir and allow it to pass through the cartridge, detach the reservoir and draw air through the cartridge for 10 min at full vacuum. Turn off and release the vacuum. Proceed immediately with cartridge elution.

6.9.6. Cartridge elution is accomplished with the solvent dichloromethane. Attach a 5-mL syringe to the adapter on the cartridges. Put 2 mL of dichloromethane into the syringe. Push the dichloromethane through the cartridge using the syringe plunger. Collect each extract in a labeled 15-mL graduated centrifuge tube. If there is any water, remove it carefully with a disposable pipette. Store extracts at 4 °C if not using immediately. Whenever ready to analyze, add internal standard to the extract and add dichloromethane to a final volume of 2 mL. Add a small amount of sodium sulfate, vortex the tube, and transfer the extract to a GC vial. The extract is now ready for analysis by GC/MS using SIM mode.

6.9.7. If during extraction some of a sample will not pass through a cartridge, then pour whatever is left in the reservoir back into the sample beaker. Label a new cartridge with the same sample number and condition it as before. Extract the remaining volume of the sample with the new cartridge. Rinse and vacuum dry both sample cartridges. When eluting the sample, attach the second cartridge to the adapter on the first cartridge and attach the syringe to the adapter on the second cartridge Use only 2 mL of dichloromethane to elute both cartridges simultaneously into the centrifuge tube.

6.10. Solid Phase Extraction Procedure by Option 2: Restek Corporation (cat. # 26032) 6 mL polypropylene tubes packed with 2 g coconut charcoal.

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

6.10.1. The SPE cartridges must be conditioned prior to use. Place the SPE cartridges into the vacuum manifold. Label all cartridges with the appropriate sample number, using a permanent marker. Fill the cartridge with approximately 3 mL of dichloromethane solvent, turn on the vacuum, and pull the solvent through, aspirating completely.

6.10.2. Firmly push an adapter into the top of each cartridge and then attach a 75-mL reservoir to each adapter. Add approximately 2 mL of methanol, turn on the vacuum, and pull the solvent through, aspirating completely.

6.10.3. Fill the cartridge again with approximately 3 mL of methanol and elute with vacuum to just above the top of the cartridge – not allowing the cartridge to go dry at the end. From this point forward, do not allow the cartridge to go dry.

6.10.4. Fill the cartridge with 15 mL of reagent water, turn on the vacuum, and pull the water through, without allowing the cartridge to go dry.

6.10.5. Fill each reservoir with the appropriate sample. Open the valves on the vacuum manifold for all cartridges that are in use, and allow the samples to begin passing through the cartridges. The vacuum gauge should not exceed 8-12 inches Hg which corresponds to a sampling rate of about 10 mL/min. Do not let any cartridge go dry during sample addition. If a cartridge goes dry during this step, re-extract that sample from the beginning with a new cartridge. If a cartridge becomes clogged and the sample will not pass through it, then proceed to final step in this section for specific instructions. After all the sample has passed through each SPE cartridge, rinse that sample's beaker with 5 mL of HPLC grade water, pour the rinsate into the sample reservoir and allow it to pass through the cartridge, detach the reservoir and draw air through the cartridge for 10 min at full vacuum. Turn off and release the vacuum. Proceed immediately with cartridge elution.

6.10.6. Cartridge elution is accomplished with the solvent dichloromethane. Attach a 10-mL syringe to the adapter on the cartridge. Put 10 mL of dichloromethane into the syringe up to 9.5 mL and push the solvent through the cartridge using the syringe plunger. Collect each extract in a labeled 15 mL graduated centrifuge tube. If there is any water, remove it with disposable pipette. Store extracts at 4 °C if not using immediately. Whenever ready to analyze, add internal standard to the extract, making a final volume to 10 mL with dichloromethane. Add a small amount of sodium sulfate and vortex the extract. Transfer the extract to a GC vial and proceed with analysis by GC/MS using SIM mode.

6.10.7. If during extraction some of a sample will not pass through a cartridge, then pour whatever is left in the reservoir back into the sample beaker. Label a new cartridge with the same sample number and condition it as before. Extract the remaining volume of the sample with the new cartridge. Rinse and vacuum dry both sample cartridges. When eluting the sample, attach the second cartridge to the adapter on the first cartridge and attach the syringe to the adapter on the second cartridge Use only 10 mL of dichloromethane to elute both cartridges simultaneously into the centrifuge tube.

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

NOTE: Experiments during method development indicated that this extract cannot be reliably concentrated by nitrogen evaporation because of the volatility of the method analyte. Therefore, extract concentration to enhance sensitivity is not permitted.

7. SAMPLE ANALYSIS AND CALCULATIONS

7.1. Instrument Conditions - (this serves as guideline only, different instruments may have different settings)

Table 2. GC/MS Instrument Settings

Parameter	Setting
Mass Range (Full Scan)	35-450 amu
SIM Mode	m/z 46,78,80 (THF-d8); m/z 58,88 (1,4-dioxane); m/z 62,64,96 (1,4-dioxane-d8)
MS Scan Rate	0.20 seconds/scan
GC Oven Temperature Program	35 °C hold for 2 min.ramp at 7 °C/min. to 90 °C, ramp at 20°C/min to final temp. of 250 °C.
GC Inlet Conditions	Temp: 200 °C; Mode: Splitless; Pressure: Constant Flow ON, 5.0 psi at 35 °C (0.8 mL/min); Purge Time 0.75 min. Purge Flow: 30 mL/min. Total Flow 33.8 mL/min. Gas Saver: ON; Saver Flow 20 mL/min. Saver Time: 2.0 min.
MS Interface Temperature	280 °C
Injection Volume	2 or 4µL
Total Run Time	17.86 min.

NOTE: The GC/MS software used by the Agilent instrumentation is designed to collect MS data, setup calibration files, automatically perform calculations, report pass/fail for tuning, and report detect/non-detect for compound identification based on the method criteria.

7.2. GC/MS instrument file names are generated using the 9-character naming convention **YYMDDI##** where:

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

7.3. GC/MS Tuning: The GC/MS system must be checked to ensure that acceptable performance criteria are achieved for the tuning compound bromofluorobenzene (BFB) at the beginning of each day and every 12 hours thereafter for as long as analysis are to be performed. This performance test must be passed and maintained before any samples or standards are analyzed.

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

7.3.1. The GC/MS has an internal tune gas to tune the instrument initially. Using Perfluorotributylamine (PFTBA) and the manual tune section of Chemstation, adjust the tuning lenses so that the PFTBA alignment ions (69, 219, 502) are centered (± 0.10 amu) on their respective amu calibration points and that their widths are 0.45 to 0.55 amu at half height. Print out a tune report from the manual tune section of Chemstation. This is a good time to check for air leaks with ions 18 and 28. These need to be less than 5% of ion 69.

7.3.2. The internal standard solution which is added to each sample may also contain BFB. The tune analysis must meet the criteria listed in EPA Method 522 for a 25-ng injection of BFB (bromofluorobenzene). Obtain the BFB mass spectrum and confirm that all of the m/z criteria in Table 3 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 3: 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

7.3.3. Check the scan at the apex first. If the tune does not pass, then use the auto find BFB feature in the Enviroquant software, which averages 3 scans around the apex. If the tune fails again, then adjust the BFB target tune parameters and perform another test. Clean the ion source and perform other preventative maintenance if the instrument fails to tune after several attempts. Other instrumental problems, which can prevent the mass spectrometer from tuning properly, include a contaminated column, a poorly responding electron multiplier and air leaks. Sample analyses MUST not begin until all the tuning criteria are met.

7.3.4. Place a hard copy of the BFB tuning report(s) in the instrument calibration folder for the instrument that was tuned.

7.3.5. Include a BFB standard injection with each instrument calibration and at least quarterly. If the tune check happens to fail any of the criteria, then reanalyze all samples that were analyzed after the failed tune check standard.

7.4. Initial Calibration:

The instrument is calibrated according to procedures specified in EPA Method 522. Clarification of the calibration requirements and practices of this laboratory are discussed

below. Acceptance criteria are tabulated in the QA/QC SOP **VO-001**. Refer to the EPA method protocols for additional details.

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 is more than 20% from the anticipated recovery for the second source quality control sample or the daily CCC samples do not meet criteria.

A minimum of six standard concentration levels, with the lowest level equal to the MDL or PQL, are used to create the initial calibration curve that covers two orders of magnitude. Three more calibration points are required for each additional order of magnitude included in the 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 daily QA/QC file folder**.** The initial calibration curve must meet the following criteria:

7.4.1. Analyze the 1,4-dioxane calibration standards at the following levels: 500, 250, 100, 50, 25, 10, 5 and 2 µg/L. This standard concentration range corresponds to 0.20 - 20 µg/L in the original samples. At each level, the internal standard (IS) and surrogate (SUR) must be present at 50 µg/L.

7.4.2. For each compound determine the retention time, the primary quantitation ion and two or three secondary ions to use for qualitative identification (Table 4). The primary and secondary ions are already given in the EPA method 522. The major ions (>10% of the most abundant ion) should be present and the relative intensities of the major ions should agree within ±20% of the reference mass spectrum.

TABLE 4: Compound Retention Times and Quantitation Ions

Compounds	Retention Times (min)	Primary Ions (m/z)	Secondary Ions (m/z)
1,4-Dioxane	8.77	88	58
1,4-Dioxane-d8 (SUR)	8.69	96	62, 64
THF-d8 (IS)	6.52	46	78, 80

7.4.3. 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

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

A_{is} = Peak area of internal standard
C_s = Concentration of analyte or surrogate
C_{is} = Concentration of internal standard

7.4.4. The retention time of the target analytes in each calibration standard must agree within ± 6 seconds. Late-eluting compounds usually have much better agreement.

7.4.5. In full scan mode, a reference mass spectrum library must be generated for all the target compounds. The reference spectra can be extracted from the calibration data, provided that the target compounds do not coelute. In the case of coelution, an individual compound standard analyzed using the same method conditions will be required to produce the reference mass spectrum. The reference spectra will be used for qualitative and quantitative analysis as described later in this section. Refer to the operator manual for each mass 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. There are three CCV standard levels used in the analysis of samples, including a low, medium and high level. The CCV concentrations are 5 ug/L (low level), 50 ug/L (medium level) and 500 ug/L (high level). A low level CCV standard is analyzed at the beginning of every analysis batch. Subsequently, the medium and high level CCV standards are analyzed in an alternating fashion after every 10 samples, and after the last sample. The CCV must meet the acceptance criteria as given in EPA Method 522. The daily quality control check standard must meet the following criteria:

7.5.1. Load each batch sequence separately for proper association of CCV data for each sample.

7.5.2. For the initial calibration to be assumed valid, the percent difference for the low level CCVs must be less than or equal to 50% from the anticipated recovery based on the last calibration. All subsequent mid- and high- level CCVs must be ± 30% of the expected value.

7.5.2. The CCV must continue to meet the acceptance criteria. If one of the bracketing CCVs fail, then all samples between the CCVs must be re-analyzed or qualified as no meeting the acceptance criteria.

7.6. Internal Standard Retention Time and Internal Standard Response:

7.6.1. Each sample extract must contain 50 µg/L of internal standard. The extracts should be diluted as deemed necessary. The concentration of internal standard must remain at 50 µg/L when diluting samples by using the Internal Standard solution (50 µg/L) as diluting agent.

7.6.2. The internal standard responses and retention times must be evaluated after data acquisition. If the retention time for any internal standard changes by

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

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.

7.7. The analysis sequence batch should be similar to the following:

7.7.1. BFB tune check for every calibration and at least once per quarter.

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

7.7.3. Calibration Check Standard (CCV) analyzed at the low level initially, followed by mid-level CCV analysis (after 10 samples).

7.7.4. Single or Replicate laboratory fortified blanks (LFB1 and LFB2) for every 20 samples.

7.7.5. Replicate matrix spikes for every 20 samples.

7.7.6. Laboratory reagent water blank.

7.7.7. Samples (including duplicate sample).

7.7.8. Subsequent CCVs after every 10 samples, alternating between medium and high level.

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

7.7.10. Closing Calibration Check Standard (CCV) at the batch end.

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

7.8.1. Check the GC temperature program.

7.8.2. Check the autosampler program.

7.8.4. Empty the autosampler waste vial.

7.8.5. Fill the autosampler wash bottle.

7.8.6. Check the job folders and field sheets for any special instructions.

7.8.7. Setup the acquisition sequence in the computer acquisition program.

7.8.8. Check the acquisition parameters in the computer program.

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

7.8.9. Arrange the sample vials in the autosampler tray.

7.8.10. Double check the order of the sample vials to insure that it is consistent with the computer acquisition log.

7.9. 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:

7.9.1. Check all tunes and blanks for compliance with requirements.

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

7.9.3. Check the CCV, surrogate, and spike recoveries against acceptance limits. The initial low-level CCV must have a recovery within 50% to 150%. The recovery limits for the surrogates must be within 70 to 130%. The recovery limits for the med- and high-level CCV analytes are within 70 to 130 % and the LFB and MS spike compounds are within 70 to 130%.

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

7.9.5. The laboratory reagent water blanks must be free of target compounds (< 30 % MDLs).

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

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

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

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

7.9.9. Hardcopies of the blanks, QC samples, calibration samples, LFBs, and matrix spikes must be placed into the Daily QC folder.

7.10. 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 (in full-scan mode). Compounds are identified as present when the following criteria are met:

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

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

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

7.10.3. 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.

7.10.4. 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.

7.10.5. For data collected in full scan mode, 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.

7.11. Quantitative Analysis:

7.11.1. 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.

7.11.2. The average response factors from the initial calibration are used to calculate the concentration of each compound in the sample. See EPA Method 522 and reference within for more details.

7.12. Concentrations (Cs) of each compound and surrogate identified should be calculated as follows (the computer program will automatically calculate the concentrations for water samples, including any dilution factors entered):

$$Cs = \frac{(A_S)(I_{IS})(V_T)(DF)}{(A_{IS})(RF)(V_{H2O})}$$

where:

A_S is the corrected area of the compound peak
I_{IS} is the concentration of the appropriate internal standard (in µg/mL)
V_T is the total volume of the extract (usually 1 mL)
DF is the appropriate dilution factor (i.e., 1:10 dilution = a DF of 10)
A_{IS} is the corrected area of the internal standard
RF is the response factor for the compound being measured

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

V_{H2O} is the volume of water extracted

8. INTERFERENCES:

Handling difficult sampling situations 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. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interference. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

8.2. Contamination by carryover can occur whenever high-level and low-level samples are analyzed together. To reduce carryover, rinse the syringe several times with solvent between samples. In extreme cases, it may be necessary to analyze a solvent blank between samples.

8.3. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary.

8.4. Purge and trap grade methanol must be used for all steps where methanol is used in this method. Other grades of methanol contain numerous low molecular weight compounds that contain interfering ions which may prohibit accurate identification and quantitation of the analyte, surrogate, and internal standard.

8.5. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water.

8.6. Preservatives are added to samples to ensure sample stability during shipping and storage prior to analysis. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of LRBs, particularly when new lots of reagents are acquired.

8.7. Solid phase extraction cartridges may be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

8.8. High laboratory background levels of 1,4-dioxane have been reported to be associated with air contamination. If 1,4-dioxane is detected in LRBs, room air should be considered as a possible source.

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

8.9. Non-aqueous or multiphase samples must be re-logged into the LIMS as waste samples. Please refer this problem to the receiving room supervisor or section supervisor.

9. DATA ARCHIVAL, PROCESSING, REVIEW AND REPORTING

9.1. Data Archival: Instrument File Type, Transfer, and Storage

9.1.1. Agilent 5973 or 5975A 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

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

9.1.3. 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.

9.1.4. 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 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.

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

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-1-4-DIOX) and enter the Matrix type "Water" when prompted.

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

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

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

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

9.3. Data Review

The Data Review and Authorization process is described in detail in the **SOP VO-010**.

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

Type of Check	Frequency Performed
Method Blanks	Initial, minimum of 1 per batch of 20 samples
Matrix Spikes	Duplicate spikes for every batch of up to 20 samples
Lab Fortified blanks	One per batch of up to 20 samples
Duplicate Samples	One per batch of up to 20 samples
CCV	Initial, every 10 samples and at end of batch.
SRM Standards	Initial and every new calibration

9.3.2. Blanks must be free of target compounds and interferences. The level of target compounds must be less than 30% of the reporting limit. There are several types of blanks including: Method, Extraction, and Trip blanks..

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

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

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

9.4. Data Reporting by Analyst

9.4.1. Select component results for reporting or upload.

- Highlight a group of samples that share a common set of analytes desired for upload.
- Select the *Change Upload Status by Component* option from the *Options* menu.

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

- 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 folders
- Hardcopies of all sample data must be put into the associated job folders. This is normal done as part of the post-analysis check.
- Hardcopies of the blanks, QC samples, calibration samples, LFBs, matrix spike must be put into the Daily QC folder. This is normal done as part of the post-analysis check.
- Print out the QC pass/fail sheet with all components listed for the samples analyzed. Highlight the components that failed and indicate any anomalies for any reported components. Put the printout into the daily QC folder for the corresponding instrument.
- Write the name of the review file (.REV file) and SOP used on the Analysis Sequence Logbook. Date and sign the files to indicate initial data review is complete. Put a copy of the analysis sequence into each job folder.
- Check the front of the job folder a final time for special directions and completeness.
- Double check calculations and final reported values.
- Give the complete job folders to the senior chemist or supervisor for data review and authorization.

9.5. Data Reporting by Supervisor:

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

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

- 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 are summarized here. Additional details may be found in the Quality Assurance/Quality Control SOP **VO-001**:

10.1. The GC/MS system must be tuned to meet the BFB specifications with each initial and new calibration.

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**.**

10.3. There must be an initial calibration of the GC/MS system.

10.4. The GC/MS system must meet the CCV criteria for EPA Method 522. The initial low-level CCV must have a recovery within 50% to 150%. The recovery limits for the med- and high-level CCV analytes are within 70 to 130 % and the LFB and MS spike compounds are within 70 to 130%.

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 30% 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 recovery limits for the surrogates must be within 70 to 130%. 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. 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.

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. See Table 5 for the results of the initial demonstration of capability.

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

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

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

TABLE 5: MDLs and PQLs for 1,4-Dioxane in Water

Analyte	MDL (µg/L)	PQL (µg/L)	Accuracy Range Water (%)	Precision (% RPD)
1,4-Dioxane	0.020	0.10	70-130	<30

12. SAFETY, HAZARDOUS WASTE MANAGEMENT AND POLLUTION PREVENTION

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

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

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

12.4. Store any wastes that cannot be disposed of down the sink in 4 L bottles or other approved containers (properly labeled with **Hazardous Wastes** labels). These wastes should be dumped in the appropriate waste storage container found in the Hazardous Waste Storage Room in Bldg. C. Chemical wastes for this analysis may include chemical standards, used pump oil, methanol waste, hazardous sample and oily sample waste.

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

13. REFERENCES

13.1. *Determination of 1,4-Dioxane in drinking water by Solid Phase Extraction and Gas Chromatography/Mass Spectrometry with Selected Ion Monitoring*, Method 522, Version 1, National Exposure Research laboratory, US EPA, Cincinnati, OH 45268, September 2008.

13.2. Winslow, S.D., Pepich, B.V., Martin, J.J., Hallberg, G.R., Munch, D.J., Frebis, C.P., Hedrick, E.J. and R.A. Krop, *Statistical Procedures for Determination and Verification of Minimum Reporting Levels for Drinking Water Methods.* Environ. Sci. Technol., **40**, (2006) 281-288.

13.3. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A. and W.L. Budde, *Trace Analyses for Wastewaters.* Environ. Sci. Technol., **15**, (1981) 1426-1435.

13.4. Kadokami, K., Koga, M. and Otsuki, *Gas Chromatography/Mass Spectrometric Determination of Traces of Hydrophilic and Volatile Organic Compounds in Water after Preconcentration with Activated Carbon.* Analytical Sciences, **6**, (1990) 843-849.

13.5. Isaacson, C., Mohr, T.K.G. and J.A. Field, *Quantitative Determination of 1,4-Dioxane and Tetrahydrofuran in Groundwater by Solid Phase Extraction GC/MS/MS.* Environ. Sci. Technol., **40**, (2006) 7305-7311.

13.6. USEPA, *2006 Edition of the Drinking Water Standards and Health Advisories.* APA #822-R-06-013.

13.7. *Carcinogens - Working With Carcinogens.* Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

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

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

13.10. Florida Department of Environmental Protection, Standard Operating Procedure **CH-008** *SOP for Reporting Qualified Data*.

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

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

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

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

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, "Comprehensive Quality Assurance Plan" (2015).

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

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

APPENDIX OF CHANGES

10/05/2011	Added text explaining relationship between calibration concentration and sample concentration in sections 4.2.1 and 7.4.1.
10/02/2013	Updated reference section.
11/07/2013	Updated the SOP MDLs and standard spike levels.
10/20/2014	Updated the SOP section 3,6,7 and 9.
12/07/2015	Minor typo corrections, logo update, and reference section updates.

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