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

CHEMISTRY PROGRAM

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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 9
7. SAMPLE ANALYSIS AND CALCULATIONS 12
8. INTERFERENCES, MAINTENANCE AND TROUBLE SHOOTING 18
9. DATA ARCHIVAL, PROCESSING, REVIEW, AND REPORTING 19
10. QUALITY CONTROL 20
11. DETERMINATION OF METHOD DETECTION LIMITS 20
12. SAFETY, HAZARDOUS WASTE MANAGEMENT, AND POLLUTION PREVENTION 20
13. REFERENCES 21
APPENDIX OF CHANGES 22

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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 from ground water, surface water, and wastewater. 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 0.040 µg/L, where minimal background or matrix interference is present. The Practical Quantitation Limit (PQL) for this method is 0.20 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 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**).

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.

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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, filtered (if required) through a 0.7µm TCLP filter paper prior to extraction, and is then extracted as follows.

2.1.1. A 200-mL sample is passed through a Supelco Supelclean ENVI-Carb Plus 400-mg cartridge or Phenomenex, Strata Activated Carbon, 400mg Cartridge (CSO-9210) to extract the method analyte and surrogate.

2.2. 1,4-Dioxane is eluted from the 400-mg cartridge with a small amount of methylene chloride, approximately 2.0 mL or 5.0 mL, respectively. Internal standard, tetrahydrofuran-*d*8 (THF-*d*8), is added and the extract volume is adjusted to a final volume of 2.0 mL or 5.0 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.

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-Liter amber glass with Teflon-lined screw caps.

3.2. Autosampler Vials: 1.5 mL and 0.35 mL glass vials with crimp tops and Teflon-lined septa to fit the Agilent 7693 autosampler.

3.3. GC/MS System:

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

3.3.2. Agilent 7693 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.

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3.3.3. Agilent 5975C or 5977B 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. Restek RTX-VRX (19315) 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 (Class A) – Glass, various sizes, including 100 and 500 mL for measurement of sample volumes.

3.8. Micro Syringes (Class A) – Suggested sizes include 10, 25, 50, 100, 250, 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 Logbook).

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

3.11. Solid Phase Extraction (SPE) Cartridge

3.11.1. Supelco Supelclean ENVI-Carb Plus 400-mg synthetic carbon (cat. # 54812-U), or equivalent. Use with samples volumes ≤ 200 mL.

3.11.2. Phenomenex, Strata Activated Carbon, 400mg Cartridge (cat. # CSO-9210)

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

3.13. Glass Beakers, 250 mL and 500 mL, Bake at 150 °C in glassware oven.

3.14. Ceramic Buchner Funnel (90mm), and glass fiber filters (90 mm, 0.70 µm). The funnels and glass-fiber filters are stored in a 150 °C oven until ready to use.

3.15. Eppendorf 10 µL to 100 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 (unfritted and fritted)

3.18. Adapter for 75 mL sample reservoir and SPE Cartridge

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3.19. Luer Lock Syringes – 5 mL and 10 mL

3.20. Vortex Mixer

4. REAGENTS AND CHEMICALS

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 wet 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 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): Agilent Cat # NV150-1 (or equivalent). Calibration Standards for 1,4-dioxane are prepared from the 100 µg/mL standard at the following concentration levels: 5, 10, 25, 50, 100, 250, and 500 µg/L in Purge & Trap grade methanol.

4.2.2. 1,4-Dioxane (Second Source): SPEX Certi-Prep Cat # S-1715(or equivalent). This 1000 µg/mL 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 8 and 20 µg/mL for the LFBs and 20 µg/mL for the matrix spikes 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

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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 µg/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 µg/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 8260D Tuning Standard Mixture STM-541. A solution of tune standard is prepared at a concentration of 20 µg/mL in methylene chloride and is used in the preparation of every sample.

4.2.6. 1,4-Dioxane-d8 Surrogate Standard (2000 µg/mL): Restek Catalog # 30614. An intermediate/working standard of 100 µg/mL is prepared from the 2000 µg/mL primary standard by diluting 10X with P&T grade methanol. A working standard at 5.0 µg/mL is prepared from the 100 µg/mL intermediate standard with P&T grade methanol. The 5.0 µg/mL and 100 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 methylene chloride 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.

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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 Program's policy, which is reflected in this SOP, requires that any samples suspected 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 of containing chlorine (e.g. ambient water) are not checked for residual chlorine in the laboratory prior to analysis.

5.1. Sample Collection:

5.1.1. To collect a representative sample, it is imperative to flow adequate 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 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

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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 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.

6. SAMPLE PREPARATION PROCEDURE

6.1. Ensure all glassware is clean. Thoroughly clean glassware with Alconox, if needed, and rinse with hot water. The cleaned glassware should be further rinsed with reagent water and HPLC grade methanol, followed by baking in an oven at > 105 °C for at least 6 hours (preferably overnight).

6.2. Check out the water samples.

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

6.4. 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.

6.5. 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 takes place at sample receipt). Add sodium bisulfate to all LRBs and LFBs according to the sample collection and preservation instructions.

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6.6. 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 laboratory reagent 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 1.0 g/mL.

6.7. 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 by 2.5-fold the amount used for the 200-mL sample size.

6.8. Sample filtration may sometimes be necessary using either a fritted reservoir or a pre-baked ceramic Buchner Funnel (90mm) and glass fiber filters (90 mm, 0.70 µm). If filtration is used, filter all samples, including method blanks and matrix spike samples. Once filtered, rinse the Buchner funnel with two 10-mL volumes of laboratory reagent water. The samples are now ready for solid phase extraction.

6.9. Solid Phase Extraction Procedure using Supelco Supelclean ENV1-Carb Plus cartridges, or equivalent:

6.9.1. The SPE cartridges must be conditioned prior to use. Place the SPE cartridges onto the vacuum manifold. Label all cartridges with the appropriate sample number, using a permanent marker. Pre-rinse each cartridge with approximately 1-mL of dichloromethane followed by 1 mL of methanol solvent, turn on the vacuum, and pull the solvent through, aspirating completely.

6.9.2. Firmly push on an adapter, if required for the SPE cartridge type, into the top of each cartridge and then attach a 75-mL reservoir to each adapter.

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 and let stand momentarily (up to 5 minutes) – not allowing the cartridge to go dry. From this point forward do not allow the cartridge to go dry.

6.9.4. Fill the cartridge with approximately 10-15 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 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, proceed to last step in this procedure section for specific instructions. After all the sample has passed through each SPE cartridge, rinse

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that sample's beaker with 5 mL of reagent 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 3-10 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 glass 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 < -5.0 °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, if necessary. Add a small amount of baked anhydrous sodium sulfate, vortex the tube, and transfer the extract to a GC vial using a disposable glass pipette. The extract is now ready for analysis by GC/MS using SIM mode.

6.9.7. If during extraction some of the samples 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 use 2 mL of dichloromethane to elute both cartridges into the centrifuge tube. Alternatively, the sample volume may be reduced in a new sample aliquot using a new cartridge which will result in an elevated MDL; a comment is added to the affected sample in the LIMS.

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

6.10.1. The SPE cartridges must be conditioned prior to use. Place the SPE cartridges onto the vacuum manifold. Label all cartridges with the appropriate sample number, using a permanent marker. Pre-rinse each cartridge with approximately 1 mL of methanol followed by 1-mL of dichloromethane solvent, turn on the vacuum, and pull the solvent through, aspirating completely.

6.10.2. Firmly push on an adapter, if required for the SPE cartridge type, into the top of each cartridge and then attach a 75-mL reservoir to each adapter.

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 and let stand momentarily (up to 5 minutes) – not allowing the cartridge to go dry. 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 reagent 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 -5.0 °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 the samples 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. Alternatively, the sample volume may be reduced in a new sample aliquot using a new cartridge which will result in an elevated MDL; a comment is added to the affected sample in the LIMS.

NOTE: Experiments during method development indicated that this extract can't be reliably concentrated by nitrogen evaporation because of 1,4-dioxane volatility. Therefore, extract concentration to enhance sensitivity is not permitted.

7. SAMPLE ANALYSIS AND CALCULATIONS

7.1. Instrument Conditions - See Table 2 for general 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	1 or 2 µL
Total Run Time	17.86 minutes

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

7.2. Build GC/MS instrument run sequence by generating 9-character naming convention **YYMDDI##** where ## = Sequential sample numbers from 01-99.

7.3. GC/MS Tuning: The GC/MS system must be checked or HES tuned to ensure that acceptable performance criteria are achieved *after* instrument modification or maintenance and *before* initial calibration as described in EPA Method 522. If using bromofluorobenzene (BFB), tuning criteria are listed below in Table 3. Daily tuning is not required. This performance test must be passed and maintained before any samples or standards are analyzed.

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, which should be less than 5% of ion 69.

7.3.2. The tune analysis must meet the criteria listed in EPA Method 522 for a 2-ng or less injection of BFB solution. Obtain the BFB mass spectrum and confirm that all 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	30-80 % 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

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7.3.3. Check the scan at the apex first. If the tune does not pass a total scan across the entire peak is allowed. Appropriate background subtraction is permitted. Should retuning the instrument fail, maintenance measures are indicated.

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

7.4. Initial Calibration:

The instrument is calibrated according to procedures specified in EPA Method 522. Refer to the EPA method protocols for additional details.

Analytical standards for 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 five or six standard concentration levels, with the lowest level in the MDL to PQL range, 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 initially fit with a linear regression requiring 5 levels but may also be fitted with a quadratic curve requiring 6 levels. The correlation coefficient for the linear or quadratic fit of the calibration curve should be ≥ 0.995 and each point should be within 80-120% of its true value, except the lowest quantitative point which should be within 60-140%. Any point below the PQL should be within 30-200% of its true value. 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 (actual levels may vary somewhat as long as one value is at or below the PQL): 500, 250, 100, 50, 25, 10and 5.0 µg/L. 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

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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
A_{IS} = Peak area of internal standard
C_S = Concentration of analyte or surrogate
C_{IS} = Concentration of internal standard

7.4.4. Retention times for target analytes in each calibration standard must agree within ± 6 seconds. Late-eluting compounds usually have better agreement.

7.4.5. In SIM mode, a reference mass spectrum library must be generated for the target and surrogate compounds. The reference spectra can be extracted from the calibration data, provided that the 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.

7.5. Daily Quality Control Check Standards (CCVs or CCCs):

The daily quality control check standards include all compounds being reported and are used to check the accuracy of the initial calibration curve and to ensure that the standards used to generate the curve have maintained their integrity. There are two CCV standard levels used in the analysis of samples, including a low and medium level. The CCV concentrations are 8.0 g/L (low level) and 50 µg/L (medium level). A low level CCV standard is analyzed at the beginning of every analysis batch. Subsequently, the low and medium 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 percentage difference for the low level CCV must be 50-150% of the expected value. All subsequent mid-level CCVs must be ± 30% of the expected value.

7.5.3. The CCV must continue to meet the acceptance criteria. If one of the bracketing CCVs fails, then all samples between the CCVs must be re-analyzed or qualified as not meeting the acceptance criteria.

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7.6. Internal Standard Retention Time and Internal Standard Response:

7.6.1. Each sample extract should contain 50 µg/L of internal standard. Sample extracts may require dilution, depending on the analyte concentration in the sample matrix. The concentration of internal standard should 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 the 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 made, as required. If the extracted ion response for the internal standard varies by more than 50% from the mean initial calibration value or 30% from the most recent CCV, then the GC/MS system must be inspected for malfunctions and corrections be made, as appropriate. Any 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 (tune and blank checks can be performed together).

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

7.7.4. Every extraction batch contains one Laboratory reagent water method blank, laboratory fortified blanks (LFB) and Replicate matrix spikes for up to 20 samples.

7.7.5. Replicate matrix spikes for every 20 samples.

7.7.6. Subsequent CCVs after every 10 samples, alternating between the low and medium levels.

7.7.7. Samples (including duplicate sample).

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

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

7.8. Prepare GC/MS Run Sequence and start run

7.9. Post-Analysis Checklist:

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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 mid-level CCV analytes must be 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 ensure each was properly sampled.

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

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

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

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

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:

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.

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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
V_{H2O} is the volume of water extracted

8. INTERFERENCES, MAINTENANCE AND TROUBLE SHOOTING

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 these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

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.

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

8.9 Follow the routine scheduled maintenance recommended by instrument manuals and service engineers at all times.

8.10 When the ratio of the primary to secondary ions of the target analyte (m/z 88 and 58) falls out of range, especially for a lower calibration standard, it indicates a possible source of contamination, usually in the reagent methylene chloride.

8.11 Do not proceed without determining the source of the contamination.

8.12 Perform injection service when the area counts for the target analyte, internal standard and/or surrogate standard fall out of routinely expected values. Clean the injection port, change septa cut and remove a one-foot section from the front (injector) end of column.

8.13 If peak tailing occurs at the start of the peak, then perform injection service and cut and remove a one-foot section from the front end of the column.

8.14 If there is still no change, replace the column with the new column and do clean the source. Also change the oil in the vacuum pump.

8.15 Make a detailed record of the steps taken to restore the instrument in the maintenance log. This will help analysts conduct trouble shooting and maintenance in the future.

8.16 If any of the above does not work, contact Agilent for instrument service without delay.

9. DATA ARCHIVAL, PROCESSING, REVIEW AND REPORTING

9.1. Archive data to a network directory for safekeeping. Once the raw data is reviewed and final reports are generated, transfer to QC-Manager to perform calculations. When the calculations are finished, review data and report. The Data Review and Authorization process is described in detail in the **SOP VO-010**.

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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 mid-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 contamination that interferes 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 LIMS and printed in the final report for the job.

11. DETERMINATION OF METHOD DETECTION LIMITS

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

12. SAFETY, HAZARDOUS WASTE MANAGEMENT AND POLLUTION PREVENTION

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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 always worn in the Laboratory.

12.3. Use **CAUTION** with strong irritants such as acids and bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals. Avoid contact with these irritants with skin and clothing by appropriate use of gloves, aprons, face masks 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 of into the municipal waste stream if the pH range is 5-10. If it is not in this range, then the wastewater must be neutralized prior to disposal.

13. REFERENCES

13.1. *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.

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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".

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

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.
12/20/2017	Minor typo corrections.
01/04/2019	Updated the equipment section, clarified sample filtration procedure, updated MDL determination section, and references.
01/28/2020	Updated SOP version number and date. Removed instructions from MDL/PQL Determination Section and reference applicable SOPs. Clarify minor processes.
03/23/2021	Updated SOP version number and date. Updated equipment in Section 3, clarified sample preparation procedures in Section 6, and updated references in Section 13.
03/24/2022	Updated SOP version number and date. Minor typo corrections were made.

04/26/2023	Updated SOP version number and date. Minor equipment updates.
06/06/2024	Clarified tuning check procedure.
12/29/2025	Added a section on scheduled maintenance and trouble shooting.