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Purgeable Organic Compounds Analysis - EPA Method 524.3

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1 Scope and Application

1.1 This is a general-purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, ground water, and drinking water in any stage of treatment. The method is applicable to a wide range of organic compounds that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures.
The 524.3 THM target list includes the following:

1.1.1

Compound	CAS Number
Dibromochloromethane	124-48-1
Chloroform	67-66-3
Bromodichloromethane	75-27-4
Bromoform	75-25-2

1.1.2 This procedure is restricted to use by an analyst experienced in the operation of GC-MS. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Proficiency, (Initial Demonstration of Capability IDC), verify that all QC acceptance criteria are met, and verify method performance in real sample matrices prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

1.1.3 THMs in drinking water must be analyzed in the full scan detection mode

1.1.3 For the purpose of lab integrity, changes may not be made to sample collection and preservation or to the quality control requirements.

2 Definitions

2.1 Refer to the Georgia EPD Laboratory Quality Assurance Manual for Quality Control definitions. (SOP reference 13.7)

2.2 Analysis Batch- A sequence of samples, analyzed within a 24-hr period,

including no more than 20 field samples. Each batch must include all required QC samples, the QC samples do not contribute to the maximum field sample total of 20. The required QC samples include: LRB, initial low-level CCC, mid-level CCC after 10 samples, high-level CCC after 20 samples, Matrix Spike and Matrix Spike Dup.

2.2.1 A batch is created by the samples based upon the concentrator. If concentrator #1 is used for 20 samples that run on concentrator #1, then it is defined as the batch. If concentrator #2 is used for 20 samples then it is defined as a batch on concentrator #2.

2.2.2 If the GC/MS is used in Dual Mode, the each set of 20 samples run each concentrator will be defined as a batch of 20 samples that ran on either concentrator #1 or concentrator #2. The Ga EPD Lab does not mix samples run between the 2 different concentrators into a single analytical batch is.

2.2.3 If there are more than 20 samples and not enough MS/MSD sample vials for both batches to run MS/MSD, then one concentrator/batch will have the MS/MSD, and the other concentrator/batch will not have an MS/MSD and a corrective action will be created.

2.3 Primary Source, Primary Standard – A standard that is used to make up the primary calibration points of a curve.

2.4 Second Source, Initial Calibration Verification Standard– A standard made from another manufacturer or a different lot number than that of the primary source.

2.5 Desorb Flow Rate- The rate at which gas is passed through the sorbent trap during the desorb cycle.

2.6 Dry Purge Volume- The total volume of purge gas bypassing the sparge tube and passing through the sorbent trap during the dry purge cycle as a moisture control measure.

2.7 Laboratory Reagent Blank(LRB), Method Blank (BK)- An aliquot of reagent water containing the preservatives, internal standards, and surrogate analytes. The LRB is used to determine if the method analytes or interferences are introduced from the laboratory environment, the reagents or glassware. The LRB is also used to test for cross contamination in the purge-and-trap system.

2.8 Laboratory Fortified Blank(LFB), Laboratory Control Sample(LCS)- An aliquot of reagent water to which known quantities of the method analyst are added. The LFB is analyzed in the same manner as a sample. The LFB is used during the IDC to verify method performance for precision and accuracy.

2.9 Laboratory Fortified Sample Matrix(LFSM), Matrix Spike (MS) - A field sample duplicate vial that is spiked at a specific concentration based on the concentration data of the non-spiked field sample.

2.10 Laboratory Fortified Sample Matrix Duplicate(LFSMD), Matrix Spike Duplicate (MSD) - A second field duplicate vial that is treated like the LFSM and spiked at the same concentration level.

2.11 Field Duplicates(FD)- samples taken from the same sampling point and same vial containers that can be processed identically along with the first aliquot. FDs are necessary to conduct repeat analyses due to laboratory error, instrument error, and to use for preparation and analysis of matrix spike and matrix spike duplicate.

2.12 Primary Dilution Standard- A primary source of method analytes prepared from Stock Standard Solutions and diluted as needed to prepare calibration standards and sample fortification solutions.

2.13 Quality Control Sample(also called ICV)- A second source used to verify the

accuracy of the primary calibration standards.

2.14 Internal Standards and Surrogate Standards- Pure compounds added to all standards, field samples, and QC samples in known amounts. The internal standard mixture is prepared using multiple analytes and is used to determine sample concentrations of target compounds. The surrogate standard is used to determine instrument efficiency and the sample analysis process.

2.15 Continuing Calibration Check- A calibration standard analyzed at the beginning, after 10 field samples, and after 20 field samples to verify the accuracy of the existing calibration.

2.16 Minimum Reporting Level – The minimum concentration that can be reported by a laboratory as a quantified value for the method analyte in a sample following analysis.

2.17 Perfluorotributylamine – A compound used to calibrate the mass spectrometer When calibrating PFTBA valve is open. When scanning for air leaks keep PFTBA valve closed.

2.18 Material Safety Data Sheets- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data, storage instructions, spill response procedures, and handling precautions.

2.19 Purge Flow Rate- The rate that the purge gas flows through the sparge tube during the purge cycle

3 Interferences

3.1 During analysis, major contaminant sources are volatile materials in the lab, air, and shipping containers that might permeate the PTFE-lined septa of the vials and collect on the sorbent trap or occupy headspace in the vials. Analyses of laboratory reagent blanks provide information about the presence of contaminants in preservation reagents when new lot numbers are made and impurities in the inert purging gas. Blanks made in an area isolated from VOCs can help identify VOCs contaminants in purging apparatus. Subtracting blank values from sample results is not permitted.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. Carryover is controlled by minimizing the transfer line length from the autosampler to the sparging vessel and optimizing the bake cycle and rinse cycle parameters. Potential carryover is evaluated during instrument initial demonstration where a method blank is run after the highest curve calibration standard of 125ppb.

3.3 Sources of contamination may be found in reagents. All lab reagents must be routinely demonstrated to be free from interferences under the conditions of the analysis. This may be accomplished by analyzing LRBs and meeting the acceptance criterion.

3.3.1 Purge and trap high quality grade Methanol is used with this method. High-purity Helium, gas regulators and a final Helium gas filter are used to minimize traces of VOCs in purge gas and GC/MS system. Purge gas filters are replaced at the intervals specified by the manufacturer or if problems arise.

3.3.2 Traps are evaluated before a batch because when heated the trap will produce small amounts of VOCs. A short bake cycle prior to beginning an analysis is

recommended, the lab runs 2 equilibration blanks at the beginning of each shift to clean the system of trapped VOC in the autosampler, P/T, and GC. If replacing a trap, bake the new trap as recommended by the manufacturer before beginning the sequence.

3.4 A sample that is 'matrix influenced' has contaminants that may interfere with sample analysis. The extent varies depending on nature of the water. Matrix Spikes help provide evidence for the presence (or absence) of matrix effects.

4 Safety

4.1 Refer to Laboratory Safety/Chemical Hygiene Plan and Fire Safety Plan. (SOP reference 13.8). Each lab is responsible for maintaining awareness.

4.2 The autosampler collection containers collects the non-hazardous rinse water and used sample water and is poured down the sink. The water in the container has been measured and determined to be pH=6 which is within sewer water pH limits.

4.3 Pure standard solutions and stock standard solutions should be handled with suitable protection for skin, eyes, etc. Treat each chemical as potential hazard and exposure should be minimized. Expired or left over or unused standards are disposed of in the hazardous waste mixed solvent satellite container located in the fume hood.

4.4 Before inspecting or working on the mass spectrometer, vent and then turn off MS power switch. When work is done, turn MS switch on and pump down. Any electrical work on the GC must be performed with the power switch turned off.

5 Apparatus and Equipment

5.1 Supplies and Equipment

5.1.1 Class A Volumetric flasks: 25 mL, 50 mL and 100 mL 250ml and 500 mL

5.1.2 Gas tight syringes: 10µl; 25µl; 50µl; 100µl; 250µl; 500µl; 1000µl; and 5ml. The Luer-Lok is used on 5ml syringes for direct injection into the purging vessel.

5.1.3 Refrigerator to store samples and standards, capable of maintaining a temperature of 6°C or below.

5.1.4 Freezer to store standards capable of maintaining a temperature of <10°C.

5.1.5 40 mL borosilicate amber vials certified cleaned and preserved with 3mg Sodium Thiosulfate.

5.1.6 An analytical balance capable of weighing to the nearest 0.0001 gram (g).

5.1.7 0.3ml, 1ml, 2.5ml micro-reaction glass vial equipped with a syringe valve and a mininert seal septa.

5.2 Purge and Trap System

5.2.1 The sparging vessel is specifically designed for purging a 5ml sample volume. A glass frit is installed at the base of the sample chamber with a diameter of <3mm at the origin. Larger sparging vessels are not allowed

5.2.2 Two EST Evolution Purge and Traps are used for each 524.3 THM GC/MS system. A 5ml sample loop in the Centurion autosampler is used to transfer sample to each Evolution. The sample is purged with Helium bubbles for 11 minutes onto the trap. When the GC is ready for the sample the Evolution will

heat the trap and open a valve to transfer the trapped VOC compounds from the trap to the GC column. The set points for the purge and trap instrument are listed in table 5.2.2

Table 5.2.2.1 EST Evolution Parameters

Parameter	Setting
Purge Time	11 min
GC Start Option	Desorb
Desorb Time	1 min
Bake Time	6 min
Sample Fill Volume	5 ml
Purge Flow Rate	40ml/min
Purge Temperature	Ambient

5.2.3 The use of two purge and trap concentrators on one GC/MS system requires separate internal standards for each concentrator sample path, separate calibration methods, and the use of a unique marker compound (Fluorobenzene) to specifically identify the sample results from Concentrator #2 as different from the Concentrator #1. Fluorobenzene has no recovery limits or retention time limits, it is simply used as a marker in the TIC chromatogram to identify Concentrator #2.

5.2.4 The trap used is a Supelco -Purge Trap K- VOCARB 3000.

5.2.5 An EST Centurion autosampler with a refrigerated sample tray is used to automate the sample analysis procedure. The autosampler is capable of maintaining samples at 10°C or lower. Do not alter tray temp after the initial calibration as it may change analyte purging efficiencies. The Centurion has its own software with mouse/keyboard to enter and control data acquisition and the vial sequence.

5.2.6 The Centurion has a fixed loop sample size of 5.0 ml.

5.2.7 The Centurion has an adjustable Internal Standard injection size, for 524.3 analyses the injection size is set to 5µL.

5.3 Gas Chromatograph Mass Spectrometer System

5.3.1 A high speed Windows 10 computer system is used as the GC/MS controller. The computer is used for data collection, storage, and post analysis data manipulation and auto transfer of results to the LIMS system. The GC/MS controller software is Agilent Masshunter/Chemstation.

5.3.2 This software is required to auto-integrate the ion abundance of specific target ions using specified retention time windows that are set using the initial calibration curve compounds.

5.3.3 The software allows construction of linear or second order regression calibration curves and calculation of concentrations using the internal standard technique. For low level compound detection below the curve (for QC Blanks use for MDL studies) the origin is used for curve fit.

5.3.4 The GC is capable of temp programming and is equipped with a split/splitless injector and electronic flow controller compatible with P&T analysis.

5.3.5 A Gas Chromatograph is used to separate the THM compounds that desorb from the trap, the set points for the GC are listed in table 5.3.5.

Table 5.3.5.1 GC Parameters	
Parameter	**Setting GCMS 06 5973 and GCMS 10 5975**
GC Inlet	
Inlet	200°C
Split Mode	SPLIT
Column Flow	1.0 ml/min
Split Ratio	20:1 for GCMS06 5973 30:1 for GCMS10 5975
GC Oven	
Initial	50°C hold 1.0 min
Ramp	8°C/min to 35°C
Final	20°C/min to 210°C Hold 0.4 min

5.3.6 The GC column is a fused silica capillary column DB-624 20m x 0.180mm x 1µm. The column is capable of resolving the method analytes such that a unique quantitation ion is available for each analyte. The vacuum pump capacity is sufficient to allow direct feed of the column to the ion source.

5.3.7 Mass spectrometers, models 5973 and 5975 are in use. Parameters for the MS system are listed in table 5.3.7.

Table 5.3.7.1 Mass Spectrometer Parameters		
Parameter	**GCMS 06 5973**	**GCMS 10 5975**
Acquisition Mode	Scan	Scan
Low Mass	35	35
High Mass	260	260
Threshold	200	200
Sampling	3	3
Scans/sec	3.18	3.18

5.3.8 The MS is capable of electron ionization at a nominal energy of 70 electron volts and operated in positive ion mode.

5.4 Instrument Maintenance

5.4.1 Red instrument maintenance logbook contains a front section of 7 items that must be checked on a daily basis for proper functioning of the instrument.

5.4.2 (1)-In manual tune on GC instrument, scan for possible leaks. Make sure water, oxygen, and baseline remain low and at acceptable control levels.

5.4.3 (2)-Check glycol/water solution in chiller for ice formation. Add new 50/50 mixture in as needed.

5.4.4 (3)-Check autosampler rinse reservoir for water level, turn pressure off and refill as needed.

5.4.5 (4)-Check tray temp must be <10C.

5.4.6 (5)-Check oil level on rough pump, use flashlight to see oil level, add if needed.

5.4.7 (6)-Run 2 instrument equilibration samples to clean system and stabilize

instrument and check for gross contamination.

5.4.8 (7)-Dump the Centurion drain collection containers.

5.4.9 The rear section of the red logbook contains Red-Tagged instrument repairs that required taking the instrument out of service.

5.4.10 Rough pump oil is changed every 6 months during PM.

6 Reagents

6.1 All sample vials, reagents, and solvents are logged into reagent logbook and standards into standard prep.

6.2 All standards are logged into the standards prep logbook.

6.3 Stock standard solutions are purchased in mixtures from commercial suppliers (i.e Absolute or Ultra Scientific). Certificates of analysis are required for all standards and must be filed in the 524.3 standard logbook. Each ampule is given a standard number when opened and given a 1 month expiration date. Unopened liquids are stored at the manufacturer's requirements. Standards prepared and placed into the autosampler standard vials are valid for 6 months.

6.4 Helium carrier gas – Ultra High Purity (building manifold system).

6.5 DI water used has a final carbon filter before use in preparation of all Method Blanks and CCCs and Curve and ICV standards.

6.6 Reagent grade Methanol is used in general laboratory cleanup of glassware and autosampler valves.

6.7 Purge-and-trap grade Methanol is used in all standards preparations.

6.8 All opened/daily use working standard and opened stock solutions are stored in a freezer <10°C in the VOC room. All standards must be warmed to room temperature before opening or use.

6.8.1 Standards can be transferred to micro-reaction glass vials with mininert caps and stored at ≤ -10C. The stored standard vials expire in one month.

6.9 Internal Standards are purchased at 2500ug/ml, the Surrogate Fortification mix is at 2500µg/ml. Fluorobenze is purchased at 2000ug/ml and added to the Centurion vial #2 to be used for Concentrator #2 as a unique chromatogram identifier.

6.9.1 The concentration of the stock solution is based on the Centurion autosampler which injects a 5µl volume of the .05µg/µL internal standard/surrogate solution into each 5ml sample. The final concentration of the internal and surrogate standards in the 5ml sparge vessel is 50µg/L.

6.9.2 All QC vials and curve vials and field sample vials will be spiked with the same concentration of Int Std and Surg.

6.9.3 The Internal Standards with Surrogates stock mix solution is prepared as indicated in table 6.9.3.1 for Concentrator #1 and table 6.9.3.2 for Concentrator #2.

Table 6.9.3.1 – Internal Standard and Surrogate for Concentrator #1
Centurion Vial #1

Compound	Initial Concentration	Aliquot	Final Concentration
Internal Std Mix 1,4-Difluorobenzene Chlorobenzene-d5	2500µg/ml	100µL	.05µg/µL
Surrogate Std Mix Methyl-t-butyl-ether 4-Bromofluorobenzene	2500µg/ml	100µL	.05µg/µL

Final Volume in Methanol	5.0 ml
Total Volume of Standard Aliquots	0.200 ml
Total Volume of Purge/Trap Grade Methanol added	4.800 ml

Table 6.9.3.2 – Internal Standard and Surrogate for Concentrator #2 Centurion Vial #2

Compound	Initial Concentration	Aliquot	Final Concentration
Fluorobenzene	2000µg/ml	125µL	.05µg/µL
Internal Std Mix 1,4-Difluorobenzene Chlorobenzene-d5	2500µg/ml	100µL	.05µg/µL
Surrogate Std Mix Methyl-t-butyl-ether 4-Bromofluorobenzene	2500µg/ml	100µL	.05µg/µL

Final Volume of Methanol	5.0 ml
Total Volume of Standard Aliquots	0.325 ml
Total Volume of Purge/Trap Grade Methanol added	4.675 ml

6.10 The THM stock standard solutions are purchased at 2000µg/ml and used to prepare the Primary Dilution Standards (PDS). Opened stock standard vials expire after 1 month.

6.10.1 For calibration curves and CCC, and MDL the PDS is prepared at 0.05µg/µl and at 0.5µg/µl. The diluting solvent is purge/trap grade Methanol and the diluted standards are stored in mininert vials with septum valves and expire 30 days after the stock standard vial was opened.

6.10.2 See Table 6.10.2.1 for the 0.05µg/µl PDS and Table 6.10.2.2 for the 0.5µg/µl PDS.

Table 6.10.2.1 – 0.05µg/µL THM Primary Dilution Standard			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Dibromochloromethane	2000µg/ml	250µL	0.05µg/µL
Dichlorobromomethane	2000µg/ml		
Bromoform	2000µg/ml		
Chloroform	2000µg/ml		

Final Volume of Liquid Standard Solution in Methanol	10.0 mL
Total Volume of Standard Aliquot	0.250 mL
Total Volume of Purge/Trap Grade Methanol added	9.75 mL

Table 6.10.2.2 – 0.5µg/µL THM Primary Dilution Standard			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Dibromochloromethane	2000µg/ml	1250µL	0.5µg/µL
Dichlorobromomethane	2000µg/ml		
Bromoform	2000µg/ml		
Chloroform	2000µg/ml		

Final Volume of Liquid Standard Solution in Methanol	5.0 mL
Total Volume of Standard Aliquot	1.250mL
Total Volume of Purge/Trap Grade Methanol added	3.75 mL

6.10.3 THM PDS for auto-spike Matrix Spike/Matrix SpikeDup

6.10.3.1 Prepare primary dilution standard using Table 6.10.3.1.1, this PDS is used to fill vial #3 on the Centurion. Vial #3 is used to spike the matrix spike LFSM and matrix spike duplicate LFSMD samples automatically.

Table 6.10.3.1.1 – 0.01µg/µL THM Primary Dilution Standard			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**

Dibromochloromethane	2000µg/ml	100µL	0.01µg/µL
Dichlorobromomethane	2000µg/ml		
Bromoform	2000µg/ml		
Chloroform	2000µg/ml		

Final Volume of Liquid Standard Solution in Methanol	20.0 mL
Total Volume of Standard Aliquot	0.1mL
Total Volume of Purge/Trap Grade Methanol added	19.9 mL

6.10.3.2 The amount added is adjustable in the Centurion, a separate matrix spike method is created in the Centurion software that allows for different spike amounts based on the volume added by the Centurion.

6.10.3.3 The amounts that are spiked are adjusted to allow for a 10, 20, 50, and 80 µg/L spike, based on the 5ml sample loop in the Centurion.

6.10.3.4 Example of Centurion auto-spiked for Matrix Spike Sample @10µg/L

5.0µL of 0.01µg/µL Spike mix in .005L sample loop= 10µg/L

6.11 Calibration Curve Standard Vial Preparation

6.11.1 The 0.05 µg/µl and the 0.5 µg/µl analyte primary dilution standards are used to prepare the 7 different concentrations for a curve.

Table 6.11.1.1 524.3 THM Calibration Curve using PDS Standards

Primary Dilution Std 0.05µg/µl	Primary Dilution Std 0.5µg/µl	DI Water Volume	Volumetric Flask Volume	Final Concentration
5 µL		249.995 ml	250 ml	1 µg/L
20 µL		99.980 ml	100 ml	10 µg/L
	5 µL	99.995 ml	100 ml	25 µg/L
	10 µL	99.990 ml	100 ml	50 µg/L
	15 µL	99.985 ml	100 ml	75 µg/L
	20 µL	99.980 ml	100 ml	100 µg/L
	25 µL	99.975 ml	100 ml	125 µg/L

6.12 BFB tune check is used from the IntStd/surrogate analyte primary dilution standards in the Centurion vial.

7 Sample Collection

7.1 Water samples for THMs are collected in a 40ml amber glass vial with septum top

containing 3.0mg of Sodium Thiosulfate. Per EPA Method 524.3 if sampling only for THMs the vial may be preserved with Sodium Thiosulfate. Do not add Ascorbic or Maleic acid when employing this reservation option.

7.2 When collecting sample allow the water system to flow for 3-5 minutes and fill sample vials to just overflowing but take care not to flush out rapidly dissolving preservatives. All samples must be cooled to <10°C (not frozen).

7.2.1 Any vials received at the laboratory >10°C are voided and must be resampled.

7.3 Holding time for preserved samples in the lab is 14 days.

7.4 Samples at the lab must be stored at <6°C, not frozen.

7.5 Review sampling form (COC) to identify residual chlorine check in mg/L

7.5.1 If the residual chlorine is <5mg/L, the 3mg of sodium thiosulfate in the 40ml bottle is sufficient to neutralize all the residual chlorine in the sample.

7.5.2 If the collector reports >5mg/L of residual Chlorine, then resample, call the system to find out why the level is so high before sending new sample vials out.

7.6 No trip blanks or field reagent blanks required for THM only analysis.

7.7 Each vial is examined for headspace. If both vials for the same sample have excess headspace the sample is voided and must be resampled.

7.8 All samples should have a duplicate vial. For QC requirements 10% of samples mailed will have 8 vials.

7.9 A THM/HAA Chain of Custody sampling sheet and instructions are sent with all samples.

8 Calibration

8.1 BFB Tune Verification of the mass spectrometer must be done after major instrument modification or maintenance is performed and before any calibration curve. The Bromofluorobenzene (BFB) in the Centurion Int Std vial is used.

8.1.2 A laboratory Method Blank(LRB) is analyzed and used for tune verification. If the mass spectrum of BFB does not meet the criteria in Table 8.1.3.1, the MS must be re-tuned to meet all tune criteria. Daily BFB tune verification is not required.

8.1.3 Tune acceptance criteria:

Table 8.1.3.1 – Mass Spectrometer Tune Criteria

Mass (M/Z)	Relative Abundance Criteria
95	base peak, 100 percent relative abundance
96	5.0 to 9.0 percent of m/z 95
173	less than 2.0 percent of m/z 174
174	>50.0 percent of m/z 95
175	5.0 to 9.0 percent of m/z 174
176	>95.0 but < 101.0 percent of m/z 174
177	5.0 to 9.0 percent of m/z 176

8.1.4 The average of the entire peak across, an average spectrum using three of the

highest points, or one scan of the apex of the peak may be used for BFB tune criteria.

8.1.5 If the tune fails, the instrument must be red-tagged. Usually cleaning the source will restore tune. After cleaning select ***BFB tune***. The software profile scan should find the PFTBA mass peaks (69, 219, 502) with sharp narrow peaks and proceed with adjusting source voltages. After the tune is finished, save and overwrite the BFB.U file. Keep the printout copy of the tune file in a folder to verify mass and abundance and voltages of the MS in case the BFB.U file is deleted. It is necessary to document the maintenance performed in the instrument log.

8.1.6 Check for air leaks before running the GC to high temperatures

8.1.6.1 Check for air or water leaks daily and after major maintenance, go to manual tune then scan the range 10m/z to 50m/z. Look for 18, 28, 32, and 44 ions. Excessive m/z 28 and 32 indicates an air leak that ***must*** be repaired before any further instrument action is taken.

8.2 GC conditions

8.2.1 Initially for method development establish optimal column performance to optimize GC operating conditions, such as split ratio and temperature ramps. For the split ratio make sure there is a balance between the transfer of enough method analytes to achieve the MRL and the need to reduce water transfer from the purge and trap concentrator.

8.2.2 The split ratio affects peak area. Sufficient resolution and symmetrical peak profiles with minimal tailing for these analytes must be achieved to enable accurate and precise integration.

8.2.3 A minimum of six scans across each peak is specified for full scan conditions.

8.2.4 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time. The relative intensities of the characteristic ions agree within 20% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 100% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 80% and 120%.)

8.2.5 Cleaning a dirty ion source will increase sensitivity, tune voltage above 1500 or failed BFB will indicate a dirty source or a failing multiplier.

8.2.6 Molecular ions present in the reference spectrum should be present in the sample spectrum. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

8.3 Calibration Curve

8.3.1 Calibration must be performed using peak areas and the internal standard technique.

8.3.2 The qualitative marker compound Fluorobenzene is added to all samples in concentrator #2 using Centurion vial #2 to uniquely identify the sample path and ensure samples are matched to the proper calibration and QC results.

8.3.3 Prepare a set of seven calibration standards for both concentrators as described earlier. The MRL at 1µg/L is the lowest concentration on the curve.

8.3.4 Field samples must be quantified using a curve that spans the same concentration range used to collect the IDC.

8.3.5 Prepare and run at least two instrument equilibration water samples to clean and stabilize instrument prior to analyzing tune blank and the standards.

8.3.6 If the chromatography is poor (i.e. unusually broad peaks, excessive tailing), corrective action must be taken before the remainder of the curve standards can be analyzed.

8.3.7 The system software must be able to autofind all THM analytes using mass spectra and retention time compensation without manual integration at the curve mid-point.

8.3.8 All surrogates are calibrated using average of RF and all target compounds are calibrated RSD linear or inverse concentration quadratic regression curve, forcing the curve through the origin is not recommended. However, origin is forced for method analytes (e.g., lab contaminants). Since the LRB is used for continuous MDL study based on EPA method, update rule for MDLs.

8.3.9 The lowest calibration point at the MRL must calculate to be within ±50% of their true spiked value. All other calibration points must calculate to be within ±30% of their true spiked value. If these criteria are not met, corrective action is recommended such as reanalyzing the calibration standards or performing instrument maintenance.

8.3.10 Use a Laboratory reagent blank after the high calibration standard during the instrument IDC to test for carryover, there must be no target compounds present at > ½ the MRL(0.5µg/L) . If carryover is present then the cause must be identified and eliminated through a long bake time or more rinses.

8.3.11 The GC/MS instrument curve fit can use inverse concentration weighted and quadratic curves through or not through the origin.

8.3.12 When establishing the calibration curve, the 50µg/L calibration standards are used as the qualifier ions, and the ion response ratios are replaced.

8.4 *Initial Calibration Verification*

8.4.1 Following the initial calibration curve, an alternate sourced THM standard is analyzed as a Second Source or Initial Calibration Verification (ICV) standard at 50 µg/L.

8.4.2 The ICV compounds must be ±30% from the expected value as calculated using the newly calibration curve.

8.4.3 The ICV report sheet is filed with the initial calibration curve file.

8.4.4 The analyst must analyze the ICV at least quarterly and during initial calibration.

8.4.5 If the accuracy for any analyte fails the recovery criterion, check the standard preparation process, stock standard sources, and the purity of neat materials used to prepare the stock standards to locate and correct the problem

8.5 *Performance Based Method*

8.5.1 This is a performance based method meaning there is not a calibration curve fit criteria. A quadratic regression calibration curve may be constructed from the response factors. If the fit is not close to a linear fit the analyst may have difficulty meeting ongoing QC criteria.

9 Quality Control

9.1 Each QC parameter and performance criteria must be met to satisfy EPA quality objectives. Compliance with the requirements of the Initial Demonstration Capability (IDC) is demonstrated for each analyte reported in full scan MS.

9.2 The Ga EPD Lab follows the Purge and Trap Parameter Limits listed in Method 524.3, listed in Table 9.2.1, that do not require additional method validation.

Table 9.2.1 Method 524.3 Minimum and Maximum Limits for P/T

Parameter	Minimum	Maximum
Sample temp	Ambient	40C
Purge flow rate	40ml/min	80ml/min
Purge volume	360ml	520ml
Desorb time	1 min	2 min
Purge volume + dry purge volume	360ml	720ml

9.3. Initial Demonstration of Capability

9.3.1 The analyst must meet the calibration requirements by creating a calibration curve for both concentrators. Analyst must also successfully perform IDC for each concentrator system prior to analyzing any field samples.

9.3.2 Analyst must also demonstrate instrument low system background using a LRB prior to any other IDC sample analysis.

9.3.2.1 For the LRB, all method analytes must be <½ of the Minimum Reporting Level (MRL) and demonstrate that possible interferences from reagents and glassware do not prevent the identification and quantitation of method analytes.

9.3.3 Analyst must test for instrument system carryover after running the 125µg/L standard highest calibration point by running an LRB immediately after the highest calibration curve sample. All method analytes must be <½ of the Minimum Reporting Level (MRL)

9.3.4 Analyst must demonstrate precision using 7 replicate LFBs fortified at 50µg/L concentration.

9.3.4.1 Documentation for 7 replicates is on Admin Forms, a controlled document on the network S:\ drive, file is "IDC Folder for 7 replicates for Office 2010 524.3"

9.3.4.2 The percent relative standard deviation must be ≤20%RPD and the mean recovery must be ±20% of the true spiked value.

9.3.5 MDL Study

9.4 MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The actual MDL varies depending on the individual instrument and matrix.

9.4.1 The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound. For new instruments or major replacement parts the MDL must be determined before results are reported. MDL studies must be performed on a yearly basis and before the MDL for the instrument expires.

9.4.2 There are two ways to perform the MDL. The first way is with 7 MDL spiked samples at the lowest point of the calibration curve and also 7 LRB blanks over 3 separate days, at a minimum 2 MDL samples and 2 blanks must be run on any single analysis day. In the second preferred way the MDL spiked sample at the lowest point of the curve is run as a continuous format with each batch of 20 samples..

9.4.3 For the 7 sample MDL study, it is performed by preparing 7 spiked vials, MDL Spike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDL Blank. These 7 sets of spiked and blank vial "pairs" are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials will be prepared and analyzed, 7 spikes and 7 blanks. The 7 sample MDL and MDL Blank forms are a controlled document and located on the S:/ drive under Admin Forms. "MDL Table for Office 2010-MDLblanks" and "MDL Table for Office 2010-MDLspiked"

9.4.3.1 PIR (Prediction Interval of Results) for MDL Confirmation of 7 replicates

9.4.3.2 Calculate the mean (*Mean*) and standard deviation (*S*) for the MDL replicates. Determine the Half Range for the Prediction Interval of Results (*HRPIR*) using the equation : $HRPIR = 3.963S$

9.4.3.3 *Confirm that the Upper and Lower limits for the Prediction Interval of Results (PIR = Mean + HRPIR) meet the upper and lower recovery limits as shown below.*

The Upper PIR Limit must be ≤150% recovery.

$$\frac{Mean + HR_{PIR}}{FortifiedConcentration} \times 100 \leq 150\%$$

The Lower PIR Limit must be ≥50% recovery.

$$\frac{Mean - HR_{PIR}}{FortifiedConcentration} \times 100 \geq 50\%$$

9.4.3.4 The MDL is validated if both the Upper and Lower PIR Limits meet the criteria described above. If these criteria are not met, the MDL has been set too low and must be confirmed again at a higher concentration.

9.4.4 For the continuous format, MDLs are performed where one vial is spiked as an MDL Spike at the lowest point of the calibration curve. One MDL spike is analyzed with every batch of 20 samples along with the method blank vial which is used as the MDL Blank.

9.4.4.1 The results of the MDL Blank will be entered into Labworks using the Method Blank test code, $B_THM524. The MDLSpike result will be entered using the $MLTHM524. The MDL Spiked Amount will be entered into the test code $MATHM524. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-THM524. .

9.5 Sequence QC for a sample batch

9.5.1 IF the initial low level MRL CCC fails QC then re-run the CCC again. If the re-run fails a second time, instrument maintenance may needed to restore performance and meet QC. If the CCC failures persist, maintenance such as bake cycles for both the purge and trap concentrator and the GC/MS, clipping the GC column, replacing the concentrator trap, and cleaning the MS source may be

required. Because of the volatile nature of the method analytes, Primary Dilution Standards have limited shelf life of 30 days. Prepare fresh PDS and repeat the CCC. Following major maintenance, the analyst may have to run a new initial calibration curve.

9.5.2 If any CCC after 10 or 20 samples fail, the samples bracketed by the most previous valid CCC must be re-run. Perform instrument maintenance and find the problem. It is advisable to also run additional CCCs after samples #5 and #15 to void losing an entire batch of samples due to instrument error or matrix problems that adversely affect the P/T or the GC column.

9.5.3 The general setup for the order of a sequence of QC and samples is to have 2 instrument equilibration samples which are LRB water samples, then the MRL/CCC/MDL sample, then the LRB/Method Blank, then 10 samples, then a mid-level CCC, then 10 more samples, then a high-level CCC as a closing CCC for the batch.

9.5.4 Use the correct concentrator method in Chemstation to evaluate all QC and to quantitate the samples.

9.5.4.1 The LRB cannot have any detect >1/2 the MRL.

9.5.4.2 The initial MRL CCC must have targets at ±50% of the spiked value.

9.5.4.3 The mid-level and high-level closing CCC must have target at ±30% of the spiked value.

9.5.4.4 The Internal standard response in any chromatographic run must not deviate from the response in the most recent CCC by more than ±30% and must not deviate by more than ±50% from the average area measured during initial calibration.

9.5.6 Due to the possibility of batch failures, a mid-point or closing high-point CCC can be added as an additional guard against losing an entire batch. The samples that run after a passing CCC will still fail if the mid-pint or closing CCC fail, but the entire batch will not be lost. Positions #5 and #15 in a batch of 20 are a “backkup” CCC to not lose the entire batch.

9.6 Ongoing QC Requirements

9.6.1 These ongoing QC procedures must be followed when processing and analyzing field samples.

9.6.2 Run a calibration curve using the internal standard calibration technique to generate the optimal curve fit. Use at least 7 standard concentrations. Validate the calibration curve by calculating the concentration of each analyte to get new curve using method regression equation.

9.6.2.1 Using the just created calibration curve, the curve points are re-quanted and the lowest level standard must be within ±50% of the true value. All other points must be within ±30% of the true value.

9.6.2.2 If the re-quant criteria in cannot be met, in this case corrective action is recommended such as reanalyzing the calibration standards or performing instrument maintenance.

9.6.2.3 An ICV/Second Source at 50µg/L must be run with each calibration curve and be at ±30% of the spiked value.

9.6.3 Analyze a mid-level ICV second source at least quarterly if the calibration curve is still valid from one quarter into the next annual quarter.

9.6.4 Run one LRB with each Analysis Batch, it is run after the lowest level CCC. All target analytes must be <½ the Minimum Reporting Level (MRL). Subtracting LRB values from sample results is not permitted.

9.6.5 THM only analysis does are not require running multiple LRBs until system

meets the LRB acceptance criteria if a sample has target analytes that exceed the calibration range.

9.6.6 Results for field samples that are not bracketed by acceptable CCCs are invalid.

9.6.7 Internal standards and surrogates are added to all QC standards and samples.

9.6.7.1 Peak area counts for each IS must be within ±30% of the area in the most recent CCC, and ±50% of the average peak area in the initial calibration. If IS fails for CCC bracket, samples must be reanalyzed

9.6.7.2 To evaluate Int Std areas from the most recent CCC use "QA Check Report" after updating the recent CCC to the Int Std area in Chemstation Continuing Calibration. The most recent CCC must be updated in Chemstation for the following 10 samples in the sequence to be evaluated for Int Std areas. ***Be careful to not use the MRL/LCS/MDL/CCC Int Std areas to evaluate samples #11-#20 run after the mid-level CCC (the mid-level CCC must be used)

9.6.7.3 To evaluate Int Std area from the curve, quant the sample and evaluate file as Continuing Calibration. (make sure Initial Calibration Option is checked)

9.6.7 Surrogate recovery must be in the range of 70% to 130% recovery.

9.6.7.1 When surrogate recovery from a field sample, blank, or QC sample is less than 70% or greater than 130% check: 1) calculations to locate possible errors, 2) the integrity of the surrogate analyte solution and the fortification technique, 3) contamination, and 4) instrument calibration. Correct the problem and reanalyze the second backup sample vial in a subsequent batch. If it meets the surrogate criteria use the field duplicate backup sample data. If it does not the data cannot be reported, resample the WSID entry point.

9.6.8 Analyze a LFSM/LFSMD per Analysis Batch. Fortify the LFSM/D at a concentration in which the method analytes will not exceed the calibration range.

9.6.8.1 Run the unspiked field sample to determine matrix spike concentrations to use.

9.6.8.2 For analytes fortified at the MRL (1.0), the recoveries must be within ±50% of the true value. Recoveries for all other spike levels must be within ±30% of the true value.

9.6.8.3 For LFSM/Dup, the relative percent differences must be ≤30% or ≤50% if concentration at the MRL.

9.6.8.4 If the recovery or precision for any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs, the precision results and/or recovery results and the unspiked sample must have a corrective action comment with "matrix suspect".

9.6.8.5 The analyst must prepare at least one MS/MSD for each batch via syringe or autosampler. If there is not enough sample for MS/MSD, then generate a corrective action for the batch.

9.7 Dilutions

9.7.1 If the initial analysis of the method analytes in a sample or in a dilution is over the calibration curve, prepare a dilution that will satisfy ongoing criteria and fall within calibration range.

9.7.2 Dilutions must be made in class A volumetric flasks. Select the volumetric flask that will allow for the necessary dilution. The 50mL flask is mostly use but for samples that require higher dilution may use another volumetric flask.

9.7.3 If a dilution was run, prepare a dilution sheet. Use S drive;GCMSLAB;FORMS; 524.3THM; "THMDILUTION FORM"

9.7.4 If the dilution was prepared and run in the same batch, then a <D> is placed in the Qualifier Field in Labworks, and the MRL is raised by the dilution factor. If the

dilution was run on a different day, then flag with <D> and add comment of QC passing on the day the dilution was analyzed. See Comment SOP for detailed wording to use.

9.8 All QC and field sample data is Q-Edited using Chemstation to verify peak integration, compound identity against known standard's mass ion ratios, and peak retention time against known standards retention times.

9.8.1 The experience of the analyst is very important to review all data points, QC and field sample unknowns. Detailed reports are printed for review on paper.

9.8.2 Any questions of QC target or sample identification of target compounds is discussed with the supervisor.

9.8.3 Any QC failures are immediately discussed with a supervisor.

9.8.4 All QC data from a batch of samples is organized into a folder, one folder for each batch for each concentrator.

9.8.5 Each batch of 20 samples will have a QA/QC report generated from S:\MarkN. 2 copies are printed, they list all the batch QC in one report for review by the EPD Lab QA Officer.

9.8.6 Each COC for each sample will be checked and verified in Labworks as having the correct collection date, time, collector name, WSID number, Entry Point number, date and time of sample submittal to the

10 Procedure of GC/MS Analysis of Samples

10.1 Samples

Refer to Section 7. Do not put samples on the chilled autosampler until the analytical batch sequence is ready to begin.

10.2 Perform an Air and Water check using Manual Tune

10.2.1 Scan for Water (18), Oxygen (32) and Nitrogen (28) and Carbon Dioxide (44). If Oxygen and Nitrogen are high, look for leaks using Methanol. Check for leaks after replacing traps or GC column or GC inlet repairs.

***DO NOT HEAT THE OVEN UNTIL THE LEAK IS LOCATED AND FIXED ***

10.3 Perform daily routine checks in the red logbook beside each instrument. Verify the temperature of autosampler during the IDC and in daily routine.

10.3.1 The GC/MS operating conditions have been established from IDC and MDL studies, do not modify any GC or MS operating or scanning conditions.

10.3.1 The P&T parameters have been established during the IDC and MDL studies, do not modify any Purge/Trap or Autosampler conditions.

10.4 Evaluate the BFB in the blank, only after major instrument maintenance or before a new calibration curve.

10.4.1 If the BFB fails after 3 attempts, red-tag the instrument and begin to perform system repair.

10.4.2 Daily BFB analysis is not required…. only before initial calibration and after major GC/MS maintenance.

10.5 Sequences are saved on the Agilent software the analysis calendar date as the datafile name (YearMonthDay) i.e. 210516.

10.5.1 Data files follow this format: 210401C1-V1-BLK1

10.5.1.1C1 is concentrator #1 (C2 is concentrator #2)

10.5.1.2V1 is sequence position on the Centurion.
10.5.1.3BLK1- sample name
10.5.1.4MRL1- for the initial low level MRL/CCC/LCS/MDL
10.5.1.5AKXXXXX- sample name, sample
10.5.1.6AKXXXXX"–MS, or -MSD add MS or MSD for matrix spike and spike duplicate
10.5.2 The datafile in the sequence must have correct Centurion sequence position number V1 is #1 vial for Concentrator #1.
10.5.2.1V52 is #1 vial for Concentrator #2.
10.5.3 The same sample run on both concentrators would have the same name, only a different concentrator and different vial number: For example, the first two equilibration blanks should be labeled "210401C1-V1-EQBK1" and "210401C2-V52-EQBK1".
10.5.3 Sample comment field on the detailed sequence printout must have sample name and for QC, its identification and the concentration. All QC need a brief description. For example, for the Method Blank which is ran after the MRL/CCC/MDL/LCS, the sequence the comment must have "Method Blank" or "LRB" written for that sample.
10.5.4 All samples and all QC and each days runs, used or not, are printed out and saved in the sequence logbook. For a batch the detailed and summary printout of the sequence is saved to put in the logbook (each page/batch is numbered sequentially) and for the batch folder (same page number). On the Agilent main instrument control screen, at the top command line type "fullorshortseq" in the white search box then click green arrow. Options are to print brief or full sequence, both are printed.
10.5.5 In comment section of the sequence setup, the top margin information, it must also list IntStd/Surr lot number used, 40ml vial reagent number number used, and instrument number used in the analysis of the samples for future traceability. The instrument operator analyst will enter their initials in the analyst box.
10.6 To start any sequence at the beginning of the shift/day/24hr batch..the purge and trap concentrators and autosampler need to run 2 equilibration blank samples
10.6.1 In the sequence, name them "EQBK1" and "EQBK2"
10.6.2 The equilibration blanks are prepared by with carbon filtered DI water samples and 524.3 preservatives to clean and stabilize instrument before running the MRL (Initial CCV/MDL/LCS) from a calibration curve or batch sequence.
10.6.3 Bake and rinse cycles are programmed to ensure removal of contaminants that may have collected in the system overnight or while the instrument sat unused.
10.7 Next analyze the MRL as the Initial Calibration Verification (LFB) the name is "MRL1", it is used also as the LCS, CCC, and MDL.
10.7.1 Verify that the calibration curve is still valid by evaluating the 1.0µg/L THM sample as being 50-150% true value, the IntStd must be ±50% of the curve and Surrogates must be 70-130% of the true value.
10.8 Next analyze the Instrument Method Blank (LRB)- In sequence, name as "BLK1". This sample is also used as the MDL-Blank.
10.8.1 The method is very specific, the the LRB is run as an instrument method blank using DI water and is run after the MRL/CCC sample.
10.8.2 Check the blank for background peaks, the baseline should be flat without a lot of noise peaks.
10.8.3 For the LRB to valid, all THMs should be at a level of <0.5µg/L (1/2 the MRL)

and the IntStd must be ±50% of the curve and ±50% of the LFB/CCC and the Surrogates must be 70-130% of the true value

10.8.4 If the blank fails, rerun another blank, then try to bake out the column, check for leaks, run more blanks to clean the system.

10.9 Load autosampler tray with field samples if LFB/CCC and LRB pass QC limits.

10.9.1 If all QC requirements are met for LFB and LRB then samples can be analyzed.

10.9.2 Remove samples from refrigerator and place on autosampler tray, the tray is chilled to keep samples at <10°C.

10.9.3 Total field sample numbers is 20 per batch. QC sample vials are not included in the 20. Analyze a mid- level CCC after every 10 field samples and a high-level CCC after sample 20. The 20 samples must run within the 24 hour clock of the MRL.

10.10 The batch must include a Matrix Spike LFSM and Matrix Spike Duplicate LFSMD. Field sample kits are shipped at 10% frequency with 4 vials to allow for LFSM and LFSMD analysis.

10.10.1 Fortify two of the 4 vials to be used as the LFSM and LFSMD. The amount spiked will be determined by the amount detected in the non-spiked sample vial, the spike should not exceed the upper limit of the curve, 125µg/L. Select a spiking concentration that is greater than or equal to the native background concentration. Rotate through low, medium, and high calibration concentrations when selecting a fortifying concentration.

10.10.2 For manual LFSM and LFMD spiking add the appropriate concentration amount by puncturing the septa of each vial with a syringe. Allow time for the compounds to disperse homogeneously within the sample, about 3 hours. The typical volume of a "40-mL" vial in use at the lab has been measured to exactly 43mL.

10.10.3 For automatic LFSM and FLMD the spiking is done by the Centurion autosampler using the third vial standard addition module. The amount spiked can vary from 10µg/L to 80 µg/L depending upon the amount detected in the non-spiked sample.

10.10.4 Matrix Spike and Matrix Spike Duplicate recoveries ±50% of true value for concentrations at the MRL and ±30% of true value at all other concentrations.

10.10.5 Precision between the LFSM and LFSMD must be ≤30% for all concentration levels > MRL. Precision for concentration at the MRL level must be ≤50% RPD.

10.11 If a field sample target compound is over the curve limit of 125µg/L then perform a dilution. Transfer the appropriate amount of sample from an unused collected duplicate sample vial into a volumetric flask then fill to mark with DI water. Pour the diluted sample into a clean 40 ml amber THM vial that contains preservative.

10.12 No trip blank is required for THM only sample analysis

10.13 A complete batch of 20 field samples analyzed on the instrument within a 24hr clock will include an initial MRL/LCS/CCC/MDL, next the LRB, LFSM and LFSMD must be included, a mid-level CCC after 10 samples and a high-level CCC after 20 samples.

10.13.1 The QC samples are not included in the count of 20 field samples in a batch.

10.13.2 For a new batch of 20 samples that will analyzed on the instrument after a previous batch analyzed on the instrument, all the QC listed in 10.13 must be repeated.

10.14 Mid-level CCC at 50µg/L after 10 field samples must be ±30% of true value and high-level CCC at 100µg/L after 20 field samples must be ±30% of true value.

10.15 THMs except at the MRL (50-150%) must be 70-130% true value

10.16 The IntStd for samples must be 70-130% of recent CCC and 50-150% of the initial calibration curve,

10.17 To set retention time windows each instrument had its own operating efficiencies that can influence each analyte's retention time. Establish an appropriate retention time window for each analyte using the know standards in the calibration curve, usually the 50µg/L midpoint is used to set retention times.

10.17.1 The retention time window will be set using Chemstation in the program "Easy ID", the peak will be centered in the window time, with the beginning and ending of the window set to the extracted ion peak beginning of the ion peak and ending of the ion peak.

10.18 Each datafile will be reviewed using Chemstation QEDIT to identify target peaks using the predetermined retention time and mass spectrums.

10.18.1 Each target analyte is identified and confirmed as a positive detect by comparison of its retention time with that of the corresponding analyte peak in a recent initial calibration standard and the reference mass spectrum.

10.18.2 The Quant Report from Chemstation will give a Q-Value percentage match of the mass spectrum ion ratios of the unknown to the known mass spectrum ions.

10.18.3 In general, all mass ions that are present above 30 percent relative abundance in the mass spectrum of the user-generated database must be present in the mass spectrum of the sample component and must agree within an absolute 20 percent of the relative abundance in the reference spectrum. The molecular ion is of special importance and should be evaluated even if they are below 30 percent relative abundance.

10.18.4 The Chemstation software can also use the Wiley library to help identify peaks that are difficult to positively identify.

10.19 The final decision of target compound reporting based upon the retention time windows and matching the reference mass spectrum is always based upon the experience of the analyst who is reviewing the data file.

10.20 Chemstation software calculates analyte concentrations. Report values that fall between the MRL and the highest calibration standard.

10.20.1 The analyst must not extrapolate beyond the established calibration range. If the sample exceeds the range of the initial calibration curve, refer to section 9 explaining dilutions. Inject the diluted sample. Incorporate the dilution factor into final concentration calculations. The resulting data must be flagged in Labworks with a <D>, and the reported MRLs must be adjusted using the dilution factor.

10.20.2 All results for samples and QC are auto-transferred to Labworks; in Labworks samples are reported with 2 sig figs; QC is 3 sig figs

10.21 Test codes in Labworks to auto-upload results.

Table 10.21.1 Labworks Test Codes for THM via EPA 524.3

Data Element	Labworks Test Code
Sample Results	$THM524
Method Blank (LRB)	$B_THM524
Matrix Spike LFSM % Recovery	$R_THM524
Matrix Spike LFSMD %Recovery	$RDTHM524
Matrix Spike/MSDup Precision (%RPD)	$P_THM524
Matrix Spiked Amount	$A_THM524
Matrix Spike LFSM Result	$S_THM524

Matrix Spike Duplicate LFMSD Result	$D_THM524
LCS/LFB/MRL Result	$LSTHM524
LCS/LFB at MRL Spiked Amount	$LATHM524
LCS/LFB at MRL %Recovery	$LRTHM524
MDL Result	$MLTHM524
MDL Spiked Amount	$MATHM524
Final Validation by GC/MS Lab	GCMS_VAL
MDL Instrument used	Instr-THM524
Receiving Login Code for THM/HAA	#DBP
QA/QC THM524 Batching Code	#Q$THM524

10.21.1 Any QC result in Labworks that flags RED means a criteria limit has been violated. Labworks determines the actual pass/fail criteria.The GC/MS manager must be notified via email and a corrective action initiated. If the QC failure is severe enough, the sample or entire batch will be voided and re-run or re-collected.

10.22 Chemstation will generate a QA Check report for time clock check (<24hr), and for the Internal Standard area using the most recent CCC.

10.22.1 Load most recent CCC

10.22.2 Save the ISTD responses, then click "show IS responses to screen" to confirm

10.22.3 Select QA Check and select MRL/CCC/MDL file as the tune file, then select all samples after the most recent CCC that was updated to process.

10.22.4 Any files that fail 24hr clock or fail +/-30% Int Std will flag with a "*".

10.23 Chemstation will auto-create an RR file to auto-upload into Labworks and save a copy to the "G" drive under the instrument name being used.

10.23.1 To manually generate RR, go to Chemstation Tools, select generate RR file using current results.

10.24 All THM data files and methods from the computer must be backed up at least once per year to DVD.

10.25 Check Lists exist for Calibration Curves and Batches, the are located in the S drive ; GCMSLAB; FORMS; 524THM; "524.3 BATCHCHKLIST" and "524.3 CURVECHKLIST"

11.0 Calculations

11.1 General Notations

n = Number of values

i = The i^{th} value of n values

11.2 Response Factor Calculations

11.2.1 *Response Factors*

Response Factors

$$\text{Response Factor (RF)} = \frac{A_X * Q_{is}}{A_{is} * Q_X}$$

Where:

A_X = integrated abundance (area of the peak) of the analyte quant ion
A_{is} = integrated abundance (area of the peak) of the int std quant ion
Q_{is} = quantity of analyte injected in µg
Q_X = quantity of internal standard injected in µg

11.2.3 *Mean Response Factor* $\overline{RF}$

11.2.3.1 The mean of the response factors for the initial calibration is calculated as follows:

$$\overline{RF} = \sum_{i=1}^{n} RF_i$$

11.2.3.2 Where:

RF_i = Individual response factors

11.2.4 *Relative Response Factor (RRF)*

11.2.4.1 The relative response factors (RRF) of each target compound is calculated relative to the appropriate internal standard (usually the internal standard nearest in retention time) as follows:

$$RRF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

11.2.4.2 Where:

RRF = Relative response factor
A_x = Area of the primary ion for the compound to be measured
A_{is} = Area of the primary ion for the internal standard
C_{is} = Concentration of internal standard spiking mixture, µg/L
C_x = Concentration of the compound in the calibration standard, µg/L

11.2.5 *Mean Relative Response Factor (*$\overline{RRF}$*)*

11.2.5.1 Calculate the mean relative response factor ($\overline{RRF}$) for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{x_i}{n}$$

11.2.5.2Where

$\overline{RRF}$ = Mean relative response factor
X_i = Relative response factor (RRF) of the compound

11.2.6 *Mean Area Response* $(\overline{Y})$ *for Internal Standard*

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

11.2.6.1 Where:

$\overline{Y}$ = Mean area IS
Y_i = Area response of primary quant ion IS of each initial cal level

11.3. Statistical Calculations

11.3.1. *Standard Deviation* (δ_{n-1})

11.3.1.1.Calculate the sample (n-1) standard deviation:

$$\delta_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(RRF_i - \overline{RRF})^2}{n-1}}$$

11.3.1.2Where:

δ_{n-1} = Std deviation (n-1) of initial RRFs (per compound)
RRF_i = RRF at a concentration level i

$\overline{RRF}$ = Mean relative response factor
n = Number of values

11.3.2 *Percent Relative Standard Deviation (%RSD)*

$$\%\text{RSD} = \frac{\delta_{n-1}}{\overline{\text{RRF}}} * 100$$

11.3.2.1 Where:

%RSD	=	Percent relative standard deviation
δ_{n-1}	=	Std deviation (n-1) of initial RRFs (per compound)
$\overline{\text{RRF}}$	=	Mean relative response factor (per compound)

11.3.3 *Percent Drift (%Drift)*

11.3.3.1 Calculate the percent difference in the RRF of the daily RRF (24 hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%\text{Drift} = \frac{\text{RRF}_c - \overline{\text{RRF}_i}}{\overline{\text{RRF}_i}} * 100$$

11.3.3.2 Where:

%Drift	=	Percent drift of standard responses
RRF_c	=	RRF of the compound in the CCV
$\overline{\text{RRF}_i}$	=	Mean RRF of the compound in the initial calibration

11.4 Retention Time Calculations

11.4.1 *Relative Retention Times (RRT)*

$$\text{RRT} = \frac{\text{RT}_c}{\text{RT}_{is}}$$

11.4.1.1 Where:

RRT	=	Relative retention time of the target compound
RT_c	=	Retention time of the target compound
RT_{is}	=	Retention time of the internal standard

11.4.2 *Mean Relative Retention Time* $\overline{\text{RRT}}$

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

11.4.2.1 Where:

$\overline{RRT}$	=	Mean RRT of the target compound for the initial cal
RRT	=	Relative retention time of the target compound
n	=	Number of values

11.4.3 *Mean Retention Time of the Internal Standard ($\overline{RT_{is}}$)*

$$\overline{RT_{IS}} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

11.4.3.1 Where:

$\overline{RT_{IS}}$	=	Mean retention time for the IS
RT_i	=	Retention time for the IS for each initial calibration level

11.5 Quality Assurance Calculations

11.5.1 *Relative Percent Difference (%RPD) Between Replicate Results*

11.5.1.1 A measure of ***precision*** is the absolute value of the relative difference between replicate measurement of the same sample (sample and duplicate, LCS and LCSD or MS and MSD) expressed as a percentage as follows:

$$\%RPD = \frac{|x_1 - X_2|}{\bar{x}} * 100$$

11.5.1.2 Where:

x_1	=	First measured value
x_2	=	Second measured value
$\bar{x}$	=	Average of the two values

11.5.2 *Percent Spike Recovery for LCS/LFB at MRL) (%R)*

11.5.2.1 A measure of ***accuracy*** is the ratio of an observed value to that expected in a spiked laboratory control sample expressed as a percentage (observed and expected values are calculated as "True Values" based on amount spiked and the size of the sample spiked before any extractions or dilutions):

$$\%R = \frac{R_{Observed}}{R_{Expected}} * 100$$

11.5.2.2. Where:

$R_{Observed}$ = True value of an analyte observed in the sample

$R_{Expected}$ = Expected value of an analyte based on the amount spiked

11.5.3 *Percent Spike Recovery for MS/MSD (%R)*

11.5.3.1 A measure of accuracy is the ratio of an observed value to that expected in a spiked field sample expressed as a percentage (see "True Values" comment in section 11.6.2.1.):

$$\%R = \frac{R_{Expected} - R_{Observed}}{R_{Expected}} * 100$$

11.5.3.2. Where:

$R_{Observed}$ = True value of an analyte observed in the sample

$R_{Expected}$ = Expected value of an analyte based on the amount spiked

11.6 Sample Concentration Calculation

$$C_x = \frac{A_x * C_{is} * DF}{A_{is} * RRF}$$

11.6.1 Where:

C_x = Compound concentration, µg/L
A_x = Area of the characteristic ion of the compound
A_{is} = Area of the characteristic ion of the associated IS
C_{is} = Concentration of the IS spiking mixture, µg/L
RRF = Relative response factor (see 11.2.4.)
DF = Dilution factor

11.6.2. NOTE: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis.

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard

Operating Procedures (SOP reference 13.4)

12.2 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. In addition, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, see the publications of the American Chemical Society's Laboratory Environment, Health & Safety Task Force on the Internet at http://membership.acs.org/c/ccs/publications.htm. Additional waste management information can be found in "Laboratory Waste Minimization and Pollution Prevention," Copyright © 1996 Battelle Seattle Research Center, which can be located at http://www.p2pays.org/ref/01/text/00779/ch05.htm.

13 REFERENCES

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14. Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

14.1 Refer to Appendix A, Table A.1 for precision and accuracy criteria.

Table 14.1.1-Reporting Limits for EPA Method 524.3

		Matrix (Water)

Parameter/Method	Analyte	RL	Unit
VOC/524.3	Dibromochloromethane	1.0	µg/L
	Chloroform	1.0	µg/L
	Bromodichloromethane	1.0	µg/L
	Bromoform	1.0	µg/L

Table 14.1.2 Summary of Calibration and QC Procedures for Method 524.3

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
524.3	Volatile Organics	Seven(7) - point initial calibration for all analytes.	Initial calibration prior to sample analysis.	Lowest calibration point = MRL must calculate to be within ±50% of true value. All other calibration points must calculate to be within ±30% of true value.	Reanalyze the calibration standards or perform instrument maintenance	
		Second-source (ICV) calibration verification	Analyze mid-level (50µ/L) with every calibration curve. Quarterly if calibration curve is still valid	ICV must be within ±30% of true value.	Correct problem and run another 2nd Source. Recalibrate if necessary.	

Table 14.1.2 Summary of Calibration and QC Procedures for Method 524.3

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
		Continuing Calibration verification (CCC) Note: Initial CCC= LCS=MDL=MRL Mid-Level CCC High-Level CCC	Every batch of 20 samples. Initial MRL CCC then mid-level CCC after 1-10 samples then high-level CCC after 11-20 samples	MRL CCC must be within ±50% of the true value. All other CCC must be within ±30% of the true value. Results for field samples that are not bracketed by QC acceptable CCCs are invalid.	Acceptable QC method performance must be restored and bracketed samples re-run	
		Analyst IDC -7 replicates of LFBs fortified at midpoint of 50ug/L -Blind sample -MDL Study	Once per analyst	Precision for 7 replicates ≤20% RPD. Accuracy on 7 replicates ±20%. Blind ±20% of true value. MDL study must pass	Recalculate results; locate and fix problem with system and then rerun IDC for those analytes that did not meet criteria	
524.3	Volatile Organics	CDC – Continuing Demonstration of Capability – Refer to SOP 6-002 for criteria	Every six months after IDC for each analyst	See Appendix A, Table A.1	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Check of mass spectrometer tune calibration using mass spectral ion intensities of BFB	After a major instrument modification, maintenance is performed, or before calibration curve	Refer to criteria listed in Table 8.1.1.1	Run again. If BFB still fails, correct problem and run again. If necessary, retune instrument.	

Table 14.1.2 Summary of Calibration and QC Procedures for Method 524.3

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
		MDL Follow new EPA MDL Update Rule	MDL study at instrument install or after major repairs. 7 MDL and 7 LRB over 3 days. Update Rule: Run 1 MDL sample and 1 MDL-Blank every analysis batch.	MDL <MRL and MDL-Blank < MRL New instrument/Repairs: Upper PIR ≤ 150% Recovery Lower PIR ≥ 50% Recovery	Locate and fix problem. Re-Run MDL study.	
		Internal Standard	Add to all QC samples and field samples.	Int Std peak area counts for each IS must be within ±30% of the area in the most recent CCC, and ±50% of the average peak area in the initial calibration.	Inspect the instrument and correct the problem. If IS fails for a midpoint or final CCC, the bracketed samples must be reanalyzed. If a sample's IS area fails, reanalyze the sample.	
524.3	Volatile Organics	Method Blank (LRB)	One per analytical batch after the Initial CCC and before any field samples are run	All method analytes must be below ½ the MRL (<0.5µg/L)	Bake the trap, run rinse program 2 or 3 times, re-analyze method blank	
		MS/LFSM MSD/LFSMD/ (Recovery)	Analyze one set of LFSM/LFSMD per Analysis Batch of 20 samples.	Recovery must be within ±30% of the true value. 50% of the true value of analytes fortified at <2X of the MRL.	If CCCs in control, the recovery is judged matrix/suspect.	Comment unspiked sample as "matrix/suspect"
		MS/LFSM and MSD/LFSMD (Precision)	Analyze one set of LFSM/LFSMD per Analysis Batch of 20 samples.	The relative percent difference must be ≤30% (≤50% if concentration within 2x of MRL)	If CCCs in control, the precision is judged matrix/suspect.	Comment sample as "matrix/suspect"

Table 14.1.2 Summary of Calibration and QC Procedures for Method 524.3

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
		Surrogate analytes	Add to all standards and samples on every sample run.	Surrogate recovery must be in the range of 70% to 130% recovery	Correct the problem and reanalyze the field duplicate (FD). If FD fails, resample	
		THM analytes above calibration curve	None	All analytes < 125 µg/L.	Dilute the sample to be within calibration curve limits	Apply E if out of range and cannot be diluted.
		Target Retention time	At new instrument setup and after major instrument maintenance and after building calibration curve	Initial CCC compounds must be within established retention time windows	Reanalyze sample	If unable to reanalyze flag with "E"

Appendix A – Quality Assurance Criteria for Method EPA 524.3

Table A.1 - Quality Assurance Criteria for EPA 524.3

QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
*** CCV/LCS/MRL 1.0µg/L MS/LFSM MSD/LFSMD 1.0-2.0µg/L**	Dibromochloromethane	50	-	150	50
	Chloroform	50	-	150	50
	Bromodichloromethane	50	-	150	50
	Bromoform	50	-	150	30
***CCC Mid-level and High-level MS/LFSM MSD/LFSMD >2.0µg/L**	Dibromochloromethane	70	-	130	30
	Chloroform	70	-	130	30
	Bromodichloromethane	70	-	130	30
	Bromoform	70	-	130	30
***Surrogates**	Methyl-t-butyl-ether	70	-	130	NA
	(Methyl-t-butyl-ether as µg/L)	35 µg/L	-	65 µg/L	
	4-Bromofluorobenzene	70	-	130	

Table A.1 - Quality Assurance Criteria for EPA 524.3					
QC Type	**Analyte**	**Accuracy (%R) LCL**		**UCL**	**Precision (%RPD)**
	(4-Bromofluorobenzene as µg/L)	35 µg/L	-	65 µg/L	
***Internal Standards to Initial Curve**	1,4-Difluorobenzene	50	-	150	NA
	Chlorobenzene-d5	50	-	150	
***Internal Standards to most Recent CCV**	1,4-Difluorobenzene	70	-	130	NA
	Chlorobenzene-d5	70	-	130	