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Purgeable Organic Compounds Analysis - EPA Method 524.2

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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 EPD Laboratory does not use the results of this SOP for VOC LIMS method $524V to regulate THMS, the four trihalomethane disinfection by-products. High levels of THMs encountered that fall above the calibration curve will be flagged as "E" (estimated amount). Also, results for any THM with failing QC, either in the calibration curve or the CCV, LCS/LCSD, or Precision, will be flagged as "E" (estimated amount). The 524.2 target list includes the following:

1.1.1

Compound	CAS Number
Dichlorodifluoromethane	75-71-8
Chloroethene	75-01-4
Chloromethane	74-87-3
Bromomethane	74-83-9
Chloroethane	75-00-3
Trichlorofluoromethane	75-69-4
1,1-Dichloroethene	75-35-4
Methylene Chloride	75-09-2
trans-1,2-Dichloroethene	156-60-5
1,1-Dichloroethane	75-34-3
2,2-Dichloropropane	590-20-7
cis-1,2-Dichloroethene	156-59-2
Bromochloromethane	74-97-5
Chloroform	67-66-3
1,1,1-Trichloroethane	71-55-6
1,1-Dichloropropene	563-58-6

Carbon Tetrachloride	56-23-5
Benzene	71-43-2
1,2-Dichloroethane	107-06-2
Trichloroethene	79-01-6
1,2-Dichloropropane	78-87-5
Dibromomethane	74-95-3
Bromodichloromethane	75-27-4
cis-1,3-Dichloropropene	10061-01-5
Toluene	108-88-3
trans-1,3-Dichloropropene	10061-02-6
1,1,2-Trichloroethane	79-00-5
Tetrachloroethene	127-18-4
1,3-Dichloropropane	142-28-9
Dibromochloromethane	124-48-1
1,2-Dibromoethane	106-93-4-
Chlorobenzene	108-90-7
1,1,1,2-Tetrachloroethane	630-20-6
Ethylbenzene	100-41-4
o,m&p-Xylene	95-47-6,108-38-3,106-42-3
Styrene	100-42-5
Bromoform	75-25-2
Isopropylbenzene	98-82-8
1,1,2,2-Tetrachloroethane	79-34-5
Bromobenzene	108-86-1
1,2,3-Trichloropropane	96-18-4
n-Propylbenzene	103-65-1
2-Chlorotoluene	95-49-8
1,3,5-Trimethylbenzene	108-67-8
4-Chlorotoluene	106-43-4
tert-Butylbenzene	98-06-6
1,2,4-Trimethylbenzene	95-63-6
sec-Butylbenzene	135-98-8
4-Isopropyltoluene	99-87-6
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
n-Butylbenzene	104-51-8
1,2-Dibromo-3-chloropropane	96-12-8
1,2,4-Trichlorobenzene	120-82-1
Hexachlorobutadiene	87-68-3
Naphthalene	91-20-3
1,2,3-Trichlorobenzene	87-61-6
2-Methoxy-2 methyl-propane	1634-04-4

1.2 Restricted Procedure

1.2.1 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 Analyst Proficiency 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.

2 Definitions

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

2.2 Primary Source (PS) – A standard that is used to make up the primary calibration points of a curve.

2.3 Second Source (SS) – A standard made from another manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV)- An ICV is a second source standard that is used to verify the correctness of the primary sources calibration curve. The ICV is run a level equal to that of a Laboratory Control Sample (LCS) or that of a point on the calibration curve.

3 Interferences

3.1.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

3.1.2 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. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel, copper, or PEEK.

3.1.3 Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination and should be assessed before standards are prepared in the methanol.

4 Safety

4.1 Refer to Laboratory Safety/Chemical Hygiene Plan and Fire Safety Plan. (SOP reference 13.8)

5 Apparatus and Equipment

5.1 An EST Centurion autosampler is used to automate the sample analysis procedure. The Centurion has its own software with mouse/keyboard to enter and control data acquisition and the vial sequence.

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

5.1.2 The Centurion has an adjustable Internal Standard injection size, for 524.2 analyses the injection size is set to 5µL.

5.2 A high speed Pentium based computer system is used as the GC/MS controller. The computer is used for data collection, storage, and post analysis data manipulation. The GC/MS controller software is Agilent Chemstation.

5.4 An EST Evolution Purge and Trap is used for 524.2 VOC samples. A 5ml sample transferred to the Evolution using the Centurion. 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 5.4.1

5.4.1 The trap used is a Supelco -Purge Trap K- VOCARB 3000 (or equivalent.).

Table 5.4.1 EST Evolution Parameters

Parameter	Setting
Purge Time	11 min
GC Start Option	Desorb
Desorb Time	4 min
Bake Time	8 min
Sample Fill Volume	5 ml
Purge Flow Rate	40ml/min
Purge Temperature	Ambient

5.5 A Gas Chromatograph is used to separate the VOCs that desorb from the the trap, the set points for the GC are listed in table 5.5.1.

Table 5.5.1 GC Parameters

	Setting GCMS 14 5975	Setting GCMS 11 5977
Parameter		
GC Inlet		
Inlet	200°C	200°C
Split Mode	SPLIT	SPLIT
Column Flow	1.0 ml/min	1.0ml/min
Split Ratio	20:1	20:1
GC Oven		
Initial	40°C hold 1.5 min	40°C hold 1.5 min
Ramp	8°C/min to 110°C	8°C/min to 110°C
Final	20°C/min to 210°C Hold 0 min	20°C/min to 210°C Hold 0 min

5.6 Fused silica capillary column DB-624, RTX-624, or equivalent.

5.7 Mass spectrometers, there are two of them, a model 5975 and a model 5977. Parameters for the MS system are listed in table 5.7.1.

Table 5.7.1 – Mass Spectrometer Parameters		
Parameter	**Setting GCMS 14 5975**	**Setting GCMS 11 5977**
Acquisition Mode	Scan	Scan
Low Mass	35	35
High Mass	260	260
Threshold	200	200
Sampling	3	3
Scans/sec	3.18	3.18

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

5.9 Gas tight syringes: 10 µl; 25 µl; 50 µl; 100µl; 250µl; 500µl; 1000µl

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

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

5.12 40 mL borosilicate vials certified cleaned and preserved with 0.5 mL of 1:1 hydrochloric acid solution.

6 Reagents

6.1 All reagents are logged into reagent logbook.

6.2 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 QC standard logbook. Each ampule is given a standard number when opened, gases are given a 1 week expiration date, liquids are given a 1 month expiration date. Unopened gases and liquids are stored at manufacturer's requirements.

6.3 Helium carrier gas – Ultra High Purity (supplied by building manifold system).

6.4 Organic free reagent water is used in preparation of all blank and standard analysis.

6.5 An Ascorbic Acid water solution reagent is prepared and used in all blanks and standards as an equivalent of the dechlorinating solution used in field sample collection. L-(+)-Ascorbic Acid powder is added to reagent water to prepare a concentration at 600 mg/L.

6.5.1 The Ascorbic Acid water solution reagent amber glass bottle is stored at 0-4°C.

6.6 Organic residue 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 are stored in a refrigerator at 0-4°C in the VOC room. All standards must be warmed to room temperature before opening or use.

6.9 The 524 Internal Standard/Surrogate Fortification Mix is purchased at a concentration of 2000ug/ml for each component (or equivalent). The preparation of the stock solution and subsequent dilution is based on the Centurion autosampler which injects a 5µl volume of the internal standard

solution into each sample. Using the standard 5ml sample size, the concentration of the internal standard that is purged is 5µg/L.

6.9.1 Internal Standard stock solution prepared as indicated in table 6.9.1.

Table 6.9.1 – 524.2 Internal Standard Stock Preparation			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Fluorobenzene	2000µg/ml	625µl	25µg/ml
4-Bromofluorobenzene	2000µg/ml		25µg/ml
1,2-Dichlorobenzene-d4	2000µg/ml		25µg/ml

Final Volume of Internal Standard/Surrogate Spike Solution in Methanol	50.0 ml
Total Volume of Standard Aliquot	0.625 ml
Total Volume of Purge/Trap Grade Methanol added	49.375 ml

6.9.2 The internal standard stock solution is diluted using a 5ml volumetric flask and then transferred to the internal standard vial in the Centurion autosampler, see table 6.9.2.1.

Table 6.9.2.1 – 524.2 Internal Standard dilution for Centurion			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Fluorobenzene	25µg/ml	1.0ml	5µg/ml
4-Bromofluorobenzene	25µg/ml		5µg/ml
1,2-Dichlorobenzene-d4	25µg/ml		5µg/ml

Final Volume of Internal Standard/Surrogate Spike Solution in Methanol	5.0 ml
Total Volume of Standard Aliquot	1.0 ml
Total Volume of Purge/Trap Grade Methanol added	4.0 ml

6.10 LCS Spiking Standard: 500µl of each vendor stock mix (1 mix for gases, 2 mixes for liquids) at 2000µg/ml(or equivalent). Gases are prepared in a 50ml volumetric flask containing purge/trap grade Methanol then stored in a miniert vials. Liquids

are prepared in a separate 50ml volumetric flask containing purge/trap grade Methanol then stored in a miniert vials. Final concentration is 0.02µg/ml for each component.

Table 6.10.1 – Gas Stock Standard in Methanol			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Dichlorodifluoromethane	2000µg/ml	500µl	0.02µg/µl
Chloroethene	2000µg/ml		0.02µg/µl
Chloromethane	2000µg/ml		0.02µg/µl
Bromomethane	2000µg/ml		0.02µg/µl
Chloroethane	2000µg/ml		0.02µg/µl

Final Volume of Gas Standard Solution in Methanol	50.0 ml
Total Volume of Standard Aliquot	.5 ml
Total Volume of Purge/Trap Grade Methanol added	48.5 ml

Table 6.10.2 – Liquid Stock Standard in Methanol				
Standard Vial Mix	**Compound**	**Initial Concentration**	**Aliquot**	**Final Concentration**
Liquid Mix #1	Trichlorofluoromethane	2000µg/ml	500µl	0.02µg/µl
	1,1-Dichloroethene	2000µg/ml		0.02µg/µl
	Methylene chloride	2000µg/ml		0.02µg/µl
	trans-1,2-Dichloroethene	2000µg/ml		0.02µg/µl
	1,1-Dichloroethane	2000µg/ml		0.02µg/µl
	2,2-Dichloropropane	2000µg/ml		0.02µg/µl
	cis-1,2-Dichloroethene	2000µg/ml		0.02µg/µl
	Bromochloromethane	2000µg/ml		0.02µg/µl
	Chloroform	2000µg/ml		0.02µg/µl
	1,1,1-Trichloroethane	2000µg/ml		0.02µg/µl
	1,1-Dichloropropene	2000µg/ml		0.02µg/µl
	Carbon tetrachloride	2000µg/ml		0.02µg/µl
	Benzene	2000µg/ml		0.02µg/µl
	1,2-Dichloroethane	2000µg/ml		0.02µg/µl
	Trichloroethene	2000µg/ml		0.02µg/µl
	1,2-Dichloropropane	2000µg/ml		0.02µg/µl
	Dibromomethane	2000µg/ml		0.02µg/µl
	Bromodichloromethane	2000µg/ml		0.02µg/µl
	cis-1,3-Dichloropropene	2000µg/ml		0.02µg/µl
	Toluene	2000µg/ml		0.02µg/µl
Liquid Mix	trans-1,3-	2000µg/ml		0.02µg/µl

Table 6.10.2 – Liquid Stock Standard in Methanol				
Standard Vial Mix	**Compound**	**Initial Concentration**	**Aliquot**	**Final Concentration**
#1	Dichloropropene			
	1,1,2-Trichloroethane	2000µg/ml		0.02µg/µl
	Tetrachloroethene	2000µg/ml		0.02µg/µl
	1,3-Dichloropropane	2000µg/ml		0.02µg/µl
	Dibromochloromethane	2000µg/ml		0.02µg/µl
	1,2-Dibromoethane	2000µg/ml		0.02µg/µl
	Chlorobenzene	2000µg/ml		0.02µg/µl
	1,1,1,2-Tetrachloroethane	2000µg/ml		0.02µg/µl
	Ethylbenzene	2000µg/ml		0.02µg/µl
	o,m& p-xylene	2000µg/ml		0.02µg/µl
	Styrene	2000µg/ml		0.02µg/µl
	Bromoform	2000µg/ml		0.02µg/µl
	Isopropylbenzene	2000µg/ml		0.02µg/µl
	1,1,2,2-Tetrachloroethane	2000µg/ml		0.02µg/µl
	Bromobenzene	2000µg/ml		0.02µg/µl
	1,2,3-Trichloropropane	2000µg/ml		0.02µg/µl
	2-Chlorotoluene	2000µg/ml		0.02µg/µl
	4-Chlorotoluene	2000µg/ml		0.02µg/µl
	tert-Butylbenzene	2000µg/ml		0.02µg/µl
	1,3,5-Trimethylbenzene	2000µg/ml		0.02µg/µl
	1,2,4-Trimethylbenzene	2000µg/ml		0.02µg/µl
	4-Isopropyltoluene	2000µg/ml		0.02µg/µl
	1,2-Dichlorobenzene	2000µg/ml		0.02µg/µl
	1,3-Dichlorobenzene	2000µg/ml		0.02µg/µl
	1,4-Dichlorobenzene	2000µg/ml		0.02µg/µl
	1,2-Dibromo-3-chloropropane	2000µg/ml		0.02µg/µl
	1,2,4-Trichlorobenzene	2000µg/ml		0.02µg/µl
	Hexachlorobutadiene	2000µg/ml		0.02µg/µl
	Naphthalene	2000µg/ml		0.02µg/µl
	1,2,3-Trichlorobenzene	2000µg/ml		0.02µg/µl
	n-Butylbenzene	2000µg/ml		0.02µg/µl
	n-Propylbenzene	2000µg/ml		0.02µg/µl
	sec-Butylbenzene	2000µg/ml		0.02µg/µl
Liquid Mix #2	2-Methoxy-2-methyl-propane (MTBE)	2000µg/ml	500µl	0.02µg/µl

Final Volume of Gas Standard Solution in Methanol	50.0 ml

Total Volume of Standard Aliquot	1.0 ml
Total Volume of Purge/Trap Grade Methanol added	49.0 ml

6.11 Calibration Standards:

6.11.1 The 0.02 µg/µl LCS stock solution is used to prepare the 4 different concentration mixes for a curve.

Table 6.11.1 – 524.2 Calibration Curve

LCS Stock Solution 0.02µg/µl (20µg/ml)	Ascorbic Acid Solution Volume	Volumetric Flask Volume	Final Concentration
Aliquot	Aliquot		
.002 ml	99.998 ml	100 ml	(.0004 µg/ml) 0.4 µg/L
.005 ml	49.995 ml	50 ml	(.002 µg/ml) 2.0 µg/L
.0125 ml	49.9875 ml	50 ml	(.005 µg/ml) 5.0 µg/L*
.025 ml	49.975 ml	50 ml	(.01 µg/ml) 10.0 µg/L

*Equivalent to CCV

6.12 Initial Calibration Verification (ICV) Standard: The ICV is prepared at the same level as the CCV and with the same ratio of components as the 5.0ug/L calibration standard, but using second source VOC target analytes.

6.12.1 Use a different supplier, or a different lot number if a different supplier is not available.

6.12.2 95% of all analytes must be within ±30% of the expected value.

6.13 GC/MS Tune Performance Check Solution

6.13.1 The 25ng of Bromofluorobenzene which is a surrogate auto-added as part of the internal standard/surrogate mixture by the autosampler is used for the tune performance check during the initial analysis of a purged method blank.

7 Sample Collection

7.1 Each entry point to sample is sent two empty 40ml acidified vials, along with one empty 125ml amber glass bottle with 75mg of Ascorbic Acid.

7.2 Water samples for volatile organic compounds are initially collected in a 125ml amber glass bottle containing 75mg of Ascorbic Acid (a dechlorinating agent). After shaking to dissolve the ascorbic acid, the contents of the bottle are split between two-40ml glass vials, each containing 0.5ml 1:1 HCl (preservative). All samples must be cooled to <4°C (not frozen). Holding time for preserved samples is 14 days.

7.2.1 A residual chlorine check is done in the field by the collector, before sample collection. The collector records the numerical value for residual chlorine in mg/L on the sampling form.

7.2.2 If the residual chlorine measured by the collector is less than 5mg/L, the 75mg of Ascorbic Acid in the 125ml bottle is sufficient to neutralize all the residual

chlorine in the sample.

7.2.3 If the collector reports >5mg/L of residual Chlorine, then the sample must be voided and new sample recollected.

7.3 Quarterly, Annual, and 3-Year sample lists of the scheduled samples are sent to the laboratory from the State's drinking water program and labels are printed in-house. A VOC COC sampling sheet and instructions are sent with all samples.

7.4 A laboratory-prepared travel blank is prepared for each system and placed in the shipping cooler, filtered deionized water is used to fill a 125ml Ascorbic Acid-spiked amber bottle which is then used to fill 40ml acidified vials.

7.5 Any vials received at the laboratory above 6°C are voided and must be resampled.

7.6 Each vial is examined for headspace. If present and the bubble is larger than the size of a small pea, that vial is discarded. If both vials for the same sample have excess headspace the sample is voided and must be resampled.

7.7 The sample vials are placed in the sample refrigerator and stored at 0°C-6°C (Not Frozen) along with the travel blank.

8 Calibration

8.1 Initial BFB Tune Verification

8.1.1 The auto sampler purges a 40ml vial of the Ascorbic Acid solution water blank and injects 1µl of the 524 internal standard/surrogate solution. The resulting 25 ng of BFB is used by the mass spectrometer software to determine if tune criteria in Table 8.1.1.1 is met.

Table 8.1.1.1 – Mass Spectrometer Tune Criteria

Mass (M/Z)	Relative Abundance Criteria
50	15.0 to 40.0 percent of m/e 95
75	30.0 to 80.0 percent of m/e 95
95	base peak, 100 percent relative abundance
96	5.0 to 9.0 percent of m/e 95
173	less than 2.0 percent of m/e 174
174	>50.0 percent of m/e 95
175	5.0 to 9.0 percent of m/e 174
176	>95.0 but < 101.0 percent of m/e 174
177	5.0 to 9.0 percent of m/e 176

8.1.2 The resulting BFB mass spectra peak must meet all of the criteria in method 524.2 using straightforward background subtraction.

8.1.3 The entire peak may be averaged and used for BFB tune criteria, or one scan may be used.

8.1.4 The Mass Spectrometer BFB automatic tune parameter file is saved to BFB.U, and the printout saved.

8.1.5 Alternatively, 25ng of BFB may be directly injected into the GC via the inlet port.

8.2 Calibration Curve

8.2.1 The 5µg/L mid-level 524 standard is run before the remainder of the curve

standards are analyzed.

8.2.1.1 The graphical plot of each target peak shape should be symmetrical with minimal tailing. 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.

8.2.1.2 The system software must be able to autofind 99% of the 5µg/L mid-level initial standard target compounds using mass spectra and retention time compensation without manual integration. If fewer than 99% are properly identified then corrective action must be taken before the remainder of the curve standards can be analyzed.

8.2.2 After the 4 calibration levels have run on the instrument, Q-Edit each data file to be sure each peak has been integrated correctly and upload each data file into the concentration level it represents.

8.2.3 *Internal Standard Average Response Factor*

8.2.3.1 Calculate the response factors (RF) for each analyte using the internal standard with the closest retention time to the analyte per the calculation in section 11.3.

8.2.3.2 Calculate the mean response factor, $\overline{RF}$ (calculation 11.3.2) of the response factors.

8.2.3.3 Calculate the percent relative standard deviation (%RSD) for each compound using the $\overline{RF}$ (see 11.2.3) and standard deviation, σ_{n-1} (see 11.3.2). IF any compound has a %RSD of > 20% it may be necessary to improve GC/MS performance or alter the range to obtain an acceptable %RSD.

8.2.3.4 A four level curve is prepared with the lowest concentration level being below the method detection limit. Per Method, only a 3 point curve is required for a factor of 20, and a curve of 0.4, 2.0, and 5.0 µg/L may be used, therefore the 10µg/L level may be dropped from the calibration should the detector not be linear in the 5-10µg/L range. Should any other level fail criteria the cause of the failure should be determined and the system recalibrated.

8.2.4 *Linear Internal Standard*

8.2.4.1 A linear calibration curve may be constructed from the response factors calculated in section 8.2.3.1. If any compound has a correlation coefficient (r) of <0.995, it may be necessary to take action to improve GC/MS performance or alter the range to obtain an acceptable correlation coefficient.

8.2.5 *Initial Calibration Verification*

8.2.5.1 Following the initial calibration curve, an alternate source standard or Initial Calibration Verification (ICV) standard of equivalent concentration to the 5.0 µg/L initial calibration standard is analyzed.

8.2.5.2 95% of the ICV compounds must have a percent difference (%DIFF), calculated in the same way a CCV %Drift is calculated (see 11.3.3) of less than ±30% from the expected value as calculated using the new calibration. If more than 5% of the compounds have a %DIFF of more than ±30%, it may be necessary to take action to improve GC/MS performance followed by recalibration of the instrument.

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

8.3 Continuing Calibration Verification

8.3.1 Initial Curve is verified at the beginning and ending of every 12 hour shift by analyzing a full 524 standard at a concentration of 5.0 µg/L, the CCV is also used as the LCS for 524.2.

8.3.2 Analyze the BFB tune standard as described in section 8.1.

8.3.3 A 5.0µg/L Continuing Calibration Verification standard (CCV: same as the 5.0 µg/L calibration standard) is injected to check system response, once a week a different concentration level of the curve is used.

8.3.4 If the CCV fails the criteria below, a second injection may be attempted before corrective actions are required.

8.3.5 Inspect the surrogates and internal standards of the CCV. Each surrogate or internal standard must have a minimum response of at least 50% of the average area response of the initial calibration.

8.3.6 Calculate the %Drift (see 11.3.3) for the CCV.

8.3.7 The CCV must have a %Drift of not more than ±30% from the expected value. If the %Drift of any compound (THMs may be excluded, but flagged as estimated) exceeds ±30%, remedial action should be taken to improve the GC/MS performance. Any or all of the instrument maintenance, new standards, or recalibration may be required.

8.3.8 The CCV absolute area of internal standards must be within 50% of the area measured during initial calibration. In the case of a loss of response exceeding 50%, maintenance should be performed and the instrument may require new standards, recalibration, or both.

8.3.9 The Chemstation software must auto-find 99% of the target compounds using mass spectra and retention time compensation without manual integration. If fewer than 99% are properly identified corrective action must be taken before samples can be analyzed.

8.3.10 Column performance should be demonstrated by symmetrical peak shape and minimal tailing. If the chromatography is poor (i.e. unusually broad peaks, excessive tailing), corrective action must be taken before samples can be analyzed.

8.3.11 In the event of high analyte response in a CCV (>30%Drift), a sequence may be considered to be valid if there are no analytes detected above the reporting limits for any field samples analyzed in that sequence. In this case, corrective action is still required after the sequence has finished.

8.3.12 The CCV is used to update the Retention Time Method. All samples of the batch are quantitated using this Retention Time Method to verify all sample detects are within 0.1min of the CCV.

8.4 A 0.4µg/L calibration standard is also analyzed before any field samples to verify responses for each regulated compound. The criteria is ± 50% of the expected value.

8.4.1 If the %Drift of the low level standard is more than ±50%, remedial action should be taken to improve instrument response.

9 Quality Control

9. Quality Control

9.1 Refer to Table 14.1. 1. for the Reporting Limits (RL), Appendix A, Table A.1. for Quality assurance criteria and Table 14.1.2. for Quality Control (QC) procedures associated with this method.

9.2 *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.

9.2.1 The actual MDL varies depending on instrument and matrix.

9.2.2 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.

9.2.3 The Method Detection Limit Study for all analytes must be performed initially on a new instrument and performed after major instrument repairs or changes to procedures. There are two ways to perform the MDL. The first is with 7 samples and 7 blanks over 3 separate days. The second preferred way the MDL is run as a continuous format.

9.2.4 The The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. 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 are prepared, 7 spiked and 7 blank.

9.2.5 A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.2.6 The results of the MDLBlank will be entered into Labworks using the Method Blank test code, $FB524V. The MDLSpike result will be entered using the $ML524V. The MDL Spiked Amount will be entered into the test code $MA524V. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-524V.

9.2.7 MDL study must be performed on a yearly basis and before the MDL for the instrument expires.

9.3 Refer to SOP reference 13.2. for training and certification procedures.

9.3.1 LCS/LCSD samples prepared and analyzed for IDCs and CDCs should be spiked so that the extract concentration is the same as the concentration of the 5.0 µg/ml point of the calibration curve.

9.3.2 IDC recovery and precision criteria are the same as the default limits listed in SOP section 9.5.5.

9.3.3 CDC recovery and precision criteria are the same as the current limits established by control charting.

9.4 A Closing CCV is analyzed at the end of the analytical batch sequence within the 12 hour shift at the 5.0µg/L or 10µg/L level. The internal standard area of the calibration check must be 50-150% of the initial curve. All targets and surrogates must have a calculated amount that is within 70-130% of the true value. THMs may be excluded, but will be flagged as estimated.

9.4.1 If the closing CCV fails criteria, a second injection may be attempted before corrective actions are required and the samples in the batch re-analyzed.

9.5 Control Limits

9.5.1 Refer to SOP reference 13.3. for control charting procedures.

9.5.2 Default method control limits for analyte and surrogate recoveries for LCS are based on EPA Method 524.2 initial control limits, see SOP reference 13.1. These limits are adjusted through the use of control charts, per method 524.2 section 9.3.5. Precision limit defaults are set by the EPD Laboratory.

9.5.3 In-house limits based on control charts may never exceed the default limits.

9.5.4 LCS and LCSD recovery limits and surrogate recovery limits are developed from control charts. By default the EPD Laboratory sets static LCS/LCSD precision control limits at <20 %RPD.

9.5.5 The default control limits from EPA 524.2 are 70-130% for LCS recoveries. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by the method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.5.6 By default, if an MS/MSD is analyzed per special request by a sample collector, the precision and recovery limits will be the same as LCS/LCSD charted limits per EPA Method 524.2. See SOP reference 13.1.

9.5.7 The default control limits for surrogates from EPA Method 524.2 are 70-130% recovery. These limits are adjusted annually using of control charts.

9.5.7.1 Method default limits table is to assist in defining control limits established with control charts and are not used as batch acceptance criteria.

Table 9.5.7.1. – Method Default Limits Criteria for EPA 524.2

QC Type	Analytes	Default LCL % Recovery	Default UCL % Recovery	Precision %RPD
LCS/LCSD	Dichlorodifluoromethane	70	130	20
	Chloroethene	70	130	20
	Chloromethane	70	130	20
	Bromomethane	70	130	20
	Chloroethane	70	130	20
	Trichlorofluoromethane	70	130	20
	1,1-Dichloroethene	70	130	20
	Methylene chloride	70	130	20
	trans-1,2-Dichloroethene	70	130	20
	1,1-Dichloroethane	70	130	20
	2,2-Dichloropropane	70	130	20
	cis-1,2-Dichloroethene	70	130	20
	Bromochloromethane	70	130	20
	Chloroform	70	130	20
	1,1,1-Trichloroethane	70	130	20
	1,1-Dichloropropene	70	130	20
	Carbon tetrachloride	70	130	20
	Benzene	70	130	20
	1,2-Dichloroethane	70	130	20
	Trichloroethene	70	130	20
	1,2-Dichloropropane	70	130	20
	Dibromomethane	70	130	20
	Bromodichloromethane	70	130	20
	cis-1,3-Dichloropropene	70	130	20
	Toluene	70	130	20
	trans-1,3-Dichloropropene	70	130	20
LCS/LCSD	1,1,2-Trichloroethane	70	130	20

Table 9.5.7.1. – Method Default Limits Criteria for EPA 524.2				
QC Type	**Analytes**	**Default LCL % Recovery**	**Default UCL % Recovery**	**Precision %RPD**
	Tetrachloroethene	70	130	20
	1,3-Dichloropropane	70	130	20
	Dibromochloromethane	70	130	20
	1,2-Dibromoethane	70	130	20
	Chlorobenzene	70	130	20
	1,1,1,2-Tetrachloroethane	70	130	20
	Ethylbenzene	70	130	20
	o,m& p-xylene	70	130	20
	Styrene	70	130	20
	Bromoform	70	130	20
	Isopropylbenzene	70	130	20
	1,1,2,2-Tetrachloroethane	70	130	20
	Bromobenzene	70	130	20
	1,2,3-Trichloropropane	70	130	20
	2-Chlorotoluene	70	130	20
	4-Chlorotoluene	70	130	20
	tert-Butylbenzene	70	130	20
	1,3,5-Trimethylbenzene	70	130	20
	1,2,4-Trimethylbenzene	70	130	20
	4-Isopropyltoluene	70	130	20
	1,2-Dichlorobenzene	70	130	20
	1,3-Dichlorobenzene	70	130	20
	1,4-Dichlorobenzene	70	130	20
	1,2-Dibromo-3-chloropropane	70	130	20
	1,2,4-Trichlorobenzene	70	130	20
	Hexachlorobutadiene	70	130	20
	Naphthalene	70	130	20
	1,2,3-Trichlorobenzene	70	130	20
	2-Methoxy-2-methyl-propane	70	130	20
	n-Propylbenzene	70	130	20
	sec-Butylbenzene	70	130	20
	n-Butylbenzene	70	130	20

10 Procedure of GC/MS Analysis of Samples

10.1 Perform an Air and Water check using Manual Tune

10.1.2 Turn scan on, see if the peaks resemble a staircase, with 18, the water being the highest peak, Oxygen (32) and Nitrogen (28) and Carbon Dioxide (44) should be less.

10.2. Analyze an Instrument Blank

10.2.1 Run an instrument blank prepared using the organic free water Ascorbic Acid solution using the same method as will be used for samples that day.

10.2.2 Evaluate the BFB used in the blank, if it fails, attempt another blank and evaluate the tune. The passing BFB begins the 12hr shift clock for a batch.

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

10.2.4 Check the blank for any background, baseline should be flat without a lot of noise peaks, all target VOC's are not detected at a level of >0.5 µg/L.

10.2.5 The response and area of the internal standard and surrogates must fall within QC limits.

10.2.6 If the blank fails, and the system is contaminated with target VOC's try to rerun another blank, bake out the column, check for leaks, run more blanks.

10.3 Analyze the Continuing Calibration Verification

10.3.1 Prepare, analyze, and evaluate the CCV 524 std.

10.3.2 If all QC requirements are met then samples can be now analyzed.

10.4 Analysis of Samples

10.4.1 After the BFB, Blank, LCS, LCSD, and low level MRL have been completed and passed then samples are ready to be analyzed, total field sample numbers is 20 per batch, and the total number of samples must run in the 12 hour clock of the BFB.

10.4.2 Remove samples refrigerator and allow them to equilibrate to room temperature.

10.4.3 The sample sequence is filled in the Enviroquant sequence window and saved to that analysis calendar date as the datafile name.

10.4.4 A printout of the sequence is saved in the logbook.

10.4.4.1 The QC sample header must also list all standards and reagents used in the analysis of the samples on that page/batch for future traceability.

10.4.5 In each 12hr batch of samples, a travel blank from one of the samples is chosen at random and analyzed with the samples.

10.4.6 Samples are analyzed in the 12hr clock of the BFB. If more than 20 samples are analyzed in a batch (12hr clock) then there must be an additional BFB, Blank, LCS, LCSD, low level MRL, and closing CCV for the additional samples in a the new additional batch (of 20 samples or less).

10.5 pH all field samples after they are analyzed

10.5.1 Check pH using indicator strips for each sample vial after finishing the batch to assure the sample was preserved at pH< 2.

10.5.2 Remove the samples that ran overnight from the auto-sampler and measure and record the pH data in pH logbook.

10.5.3 If the pH >2 analyze the 2nd vial. If the second vial has a pH >2 begin a corrective action to resample the entry point.

10.6 Data Processing

10.6.1 After analysis of all the samples if the surrogates limits are met and internal standard recovery passes and time clock passes then the sample data is batched and results auto-uploaded in "Labworks".

Table 10.6.1.2 Data Elements by LIMS Test Code	
Data Element	**Labworks Test Code**
Sample Results	$524V
LCS	$LS524V
LCSD	$LD524V
Method Blank	$B_524V
LCS Recovery	$LR524V
LCSD Recovey	$L2524V
LCS/LCSD Precision	$LP524V
LCS Spike Amount	$LA_524V
Sample Trip Blank	$524TB
MDL Result	$ML524V
MDL Blank Amount	$FB524V
MDL Spike Amount	$MA524V
524V Instrument List for MDL	INSTR-524V

10.6.2 A sample batch sheet for up to 20 samples is generated and saved with each batch datafile package.
10.6.3 All results for samples and QC are uploaded to Labworks using RR results.
10.6.3.1 For RR uploading the analysis computer must be mapped to Labworks.
10.6.4 If a dilution was run on a sample prepare a dilution sheet.
10.6.5 Any Tentatively Identified (TIE) detect must have a concentration greater than the internal standard (5µg/L) to be reported.
10.6.6 Any target compound sample result in Labworks that appears in RED means a MCL limit has been violated. The GC/MS manager must be notified via email.
10.7 Instrument Maintenance
10.7.1 Red instrument maintenance logbook contains a front section of 5 items that must be checked on a daily basis for proper functioning of the instrument.
10.7.1.1 (1)-Check capillary column by CC response and performance, replace as needed.
10.7.1.2 (2)-Check trap performance by reviewing CC, replace as needed
10.7.1.3 (3)-Check ion source performance by surrogate recovery, clean as needed
10.7.1.4 (4)-Check gas line filter by reviewing blank, change as needed
10.7.1.5 (5)-Check rough pump oil, refill as needed.
10.7.2 The rear section of the red logbook contains Red-Tagged instrument repairs that required taking the instrument out of service.
10.8 Data Storage
10.8.1 All 524 data files and methods from the computer must be backed up at least once per year.
10.8.2 Copy the files to the network directory G:\GCMS\(instrument name) then burn these files up to a DVD.
10.9 Data Interpretation
10.9.1 Qualitative identification is achieved based on retention time of compounds from the 524 standards and comparison of sample mass spectra with reference spectra generated on the instrument under the same operating conditions from 524 standards.
10.9.4 The relative intensities of the mass spectra ions must agree within 20% of the

relative intensities of these ions in the reference spectra and/or visual inspection should agree. This is very reliant upon the experience of the analyst.

10.9.7 The isomers M/P Xylene are reported as a single result pair on the analytical instrument report.

10.9.12 The Wiley library is used to identify TIE compounds in the chromatogram.

11 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 internal standard injected in µg

Q_X = quantity of analyte 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:

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

11.3.1.2 Where:

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)*

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

11.3.2.1 Where:

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

$$\%Drift = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} * 100$$

11.3.3.2 Where:

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

11.4 Retention Time Calculations

11.4.1 *Relative Retention Times (RRT)*

$$RRT = \frac{RT_c}{RT_{is}}$$

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* $\overline{\text{RRT}}$

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

11.4.2.1 Where:

$\overline{\text{RRT}}$	=	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* ($\overline{RT_{is}}$)

$$\overline{\text{RT}_{\text{IS}}} = \sum_{i=1}^{n} \frac{\text{RT}_i}{n}$$

11.4.3.1 Where:

$\overline{\text{RT}_{\text{IS}}}$	=	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:

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

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/LCSD (%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)

13 References

13.1 Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; U.S. EPA Office of Research and Development: Cincinnati, OH, 1995, Revision 4.1

13.2 GA EPD Laboratory SOP's-Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.

13.3 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charting and Control Limits SOP, SOP 6-025, online revision.

13.4 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.5 Manual for the Certification of Laboratories Analyzing Drinking Water, EPS/815-R-05-004, January 2005.

13.6 GA EPD Laboratory SOP-Determination Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

13.7 GA EPD Laboratory Quality Assurance Plan, online revision.

13.8 GA EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

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 524.2

Parameter/Method	Analyte	Matrix (Water)	
		RL	Unit
Volatile Organics 524.2	Dichlorodifluoromethane	0.50	µg/L
	Chloroethene	0.50	µg/L
	Chloromethane	0.50	µg/L
	Bromomethane	0.50	µg/L
	Chloroethane	0.50	µg/L
	Trichlorofluoromethane	0.50	µg/L
	1,1-Dichloroethene	0.50	µg/L
	Methylene chloride	0.50	µg/L
	trans-1,2-Dichloroethene	0.50	µg/L
	1,1-Dichloroethane	0.50	µg/L
	2,2-Dichloropropane	0.50	µg/L

Table 14.1.1-Reporting Limits for EPA Method 524.2

Parameter/Method	Analyte	Matrix (Water)	
		RL	Unit
Volatile Organics 524.2	cis-1,2-Dichloroethene	0.50	µg/L
	Bromochloromethane	0.50	µg/L
	Chloroform	0.50	µg/L
	1,1,1-Trichloroethane	0.50	µg/L
	1,1-Dichloropropene	0.50	µg/L
	Carbon tetrachloride	0.50	µg/L
	Benzene	0.50	µg/L
	1,2-Dichloroethane	0.50	µg/L
	Trichloroethene	0.50	µg/L
	1,2-Dichloropropane	0.50	µg/L
	Dibromomethane	0.50	µg/L
	Bromodichloromethane	0.50	µg/L
	cis-1,3-Dichloropropene	0.50	µg/L
	Toluene	0.50	µg/L
	trans-1,3-Dichloropropene	0.50	µg/L
	1,1,2-Trichloroethane	0.50	µg/L
	Tetrachloroethene	0.50	µg/L
	1,3-Dichloropropane	0.50	µg/L
	Dibromochloromethane	0.50	µg/L
	1,2-Dibromoethane	0.50	µg/L
	Chlorobenzene	0.50	µg/L
	1,1,1,2-Tetrachloroethane	0.50	µg/L
	Ethylbenzene	0.50	µg/L
	o,m& p-xylene	0.50	µg/L
	Styrene	0.50	µg/L
	Bromoform	0.50	µg/L
	Isopropylbenzene	0.50	µg/L
	1,1,2,2-Tetrachloroethane	0.50	µg/L
	Bromobenzene	0.50	µg/L
	1,2,3-Trichloropropane	0.50	µg/L
	2-Chlorotoluene	0.50	µg/L
	4-Chlorotoluene	0.50	µg/L
	tert-Butylbenzene	0.50	µg/L
	1,3,5-Trimethylbenzene	0.50	µg/L
	1,2,4-Trimethylbenzene	0.50	µg/L
	4-Isopropyltoluene	0.50	µg/L
	1,2-Dichlorobenzene	0.50	µg/L
	1,3-Dichlorobenzene	0.50	µg/L
	1,4-Dichlorobenzene	0.50	µg/L
	1,2-Dibromo-3-chloropropane	0.50	µg/L
	1,2,4-Trichlorobenzene	0.50	µg/L

Table 14.1.1-Reporting Limits for EPA Method 524.2

Parameter/Method	Analyte	Matrix (Water)	
		RL	Unit
Volatile Organics 524.2	Hexachlorobutadiene	0.50	µg/L
	Naphthalene	0.50	µg/L
	1,2,3-Trichlorobenzene	0.50	µg/L
	2-Methoxy-2-methyl-propane	0.50	µg/L
	n-Propylbenzene	0.50	µg/L
	sec-Butylbenzene	0.50	µg/L
	n-Butylbenzene	0.50	µg/L

Table 14.1.2 Summary of Calibration and QC Procedures for Method 524.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
524.2	Volatile Organics	Four -point initial calibration for all analytes. Method allows a minimum of three points to calibrate a range of 20.	Initial calibration prior to sample analysis	% RSD for all calibration analytes ≤20%. Linear best fit calibration $r^2 \geq 0.990$ ($r \geq 0.995$). THM's may be excluded. Quadratic fit is not allowed.	Correct problem then repeat initial calibration. THMs may be excluded.	If THM is excluded flag as estimated.
		Second-source calibration verification	Once per four-point initial calibration or quarterly at a minimum.	95 % of all analytes within ±30% RSD of expected value.	Correct problem and run another 2nd Source. Recalibrate if necessary. THMs may be excluded.	If THM is excluded flag as estimated.
		Calibration verification	Daily, before sample analysis and at the close of each analytical batch.	All calibration analytes within ±30% RSD. Linear fit calib. conc. within ± 30%. THMs may be excluded	If <30% negative RSD, correct problem. If >30% positive RSD and analyte not detected in batch, note in corrective action.	If THM is excluded flag as estimated
		IDC – Initial Demonstration of Capability - Demonstrate ability to generate a calibration curve, plus acceptable accuracy and precision using four replicate analyzes of a CC check sample, plus a blind and a blank, plus perform an MDL study.	Once per analyst or for New Instrument	Recovery and Precision must meet Appendix A charting limits. A new instrument may use method default limits. New analyst or instrument must meet MDL requirement of being below reporting levels for all compounds.	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria.	
		CDC – Continuing Demonstration of Capability	Every six months after IDC for each analyst, 1 year for supervisor	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	

Table 14.1.2 Summary of Calibration and QC Procedures for Method 524.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
524.2	Volatile Organics	Check of mass spectral ion intensities using BFB	Daily, before sample analysis, starts 12 hours of analysis time batch.	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.	
		MDL study	MDL report and study is generated once per year, at the mid-year a check is generated. 1 MDL sample and 1 MDL blank is run with every batch If required, 7 MDLs and 7 Blanks may be analyzed over 3 separated days.	Theoretical detection limit must be less than less than the reporting limit.	Check calculations. Increase or decrease the spike as necessary. Re-Run MDL study.	
		Internal Standard	Immediately after or during data acquisition of calibration check standard, and on every sample run.	Internal standard retention times should not drift by more than 30 seconds from most recent calibration. Also, the ion area for the internal standards cannot change by more than 50% from the last PM.	Inspect the instrument and correct the problem. Any failed sample must be reanalyzed, however if the QC fails the entire batch must be reanalyzed.	
		Method Blank	One per analytical batch before any samples are run for the batch period.	No analytes detected >RL. THMs may be excluded.	Correct problem then reprep and analyze method blank	If unable to re-analyze, flag with a "B". If THM is excluded flag as estimated.
		LCS and LCSD recovery and precision	One LCS and LCS duplicate per analytical batch	Refer to Appendix A Table A.1	Correct problem and reanalyze LCS/LCSDup. THMs may be excluded. EPD Lab does not validate based on LCSD recovery	If unable to re-analyze, must flag with a "J". If a THM flag with "E".
		Surrogate spike	Every sample, spiked sample, standard, and method blank	Refer to Appendix A Table A.1	Correct problem then reanalyze sample	
		Estimated amount for analytes other than THM above calibration curve	None	All analytes < 10 µg/L. THMs may be excluded.	Sample must be diluted	Apply E to all analytes out of range that cannot be diluted.
		Target retention time	Per analysis	Target ion within 0.1 min of expected R.T.	Reanalyze sample. THMs may be excluded.	If THM is excluded flag as estimated.

Appendix A – Quality Assurance Criteria for Method EPA 524.2*

Table A.1 Quality Assurance Criteria for Method EPA 524.2			
		Accuracy (%R)	Precision
QC Type	Analyte	LCL UCL	(%RPD)
*LCS/LCSD	Dichlorodifluoromethane	71-130	20
	Vinyl Chloride	83-122	20
	Chloromethane	76-119	20
	Bromomethane	74-130	20
	Chloroethane	79-125	20
	Fluorotrichloromethane	84-128	20
	1,1-Dichloroethylene	85-119	20
	Dichloromethane	85-117	20
	trans-1,2-Dichloroethylene	85-116	20
	1,1-Dichloroethane	85-116	20
	2,2-Dichloropropane	77-126	20
	cis-1,2-Dichloroethylene	85-116	20
	Bromochloromethane	84-117	20
	Chloroform	85-117	20
	1,1,1-Trichloroethane	85-123	20
	1,1-Dichloropropene	85-120	20
	Carbon tetrachloride	85-127	20
	Benzene	85-115	20
	1,2-Dichloroethane	85-116	20
	Trichloroethylene	85-118	20
	1,2-Dichloropropane	85-116	20
	Dibromomethane	85-120	20
	Bromodichloromethane	85-123	20
	Cis-1,3-Dichloropropene	83-126	20
	Toluene	85-117	20
	trans-1,3-Dichloropropene	79-130	20
	1,1,2-Trichloroethane	85-119	20
	Tetrachloroethylene	85-123	20
	1,3-Dichloropropane	85-116	20
	Chlorodibromomethane	74-130	20
	1,2-Dibromoethane	85-120	20
	Chlorobenzene	85-117	20
	1,1,1,2-Tetrachloroethane	85-130	20
	Ethylbenzene	85-122	20
	Total Xylenes	85-123	20
	Styrene	85-124	20
	Bromoform	70-130	20
	Isopropylbenzene	85-124	20
	1,1,2,2-Tetrachloroethane	85-121	20
	Bromobenzene	85-120	20
	1,2,3-Trichloropropane	85-121	20
	n-Propylbenzene	85-125	20
	o-Chlorotoluene	85-122	20
	1,3,5-Trimethylbenzene	85-126	20
	p-Chlorotoluene	85-124	20
	Tert-Butylbenzene	85-126	20
	1,2,4-Trimethylbenzene	85-126	20
	sec-Butylbenzene	85-128	20
	p-Isopropyltoluene	85-128	20
	m-Dichlorobenzene	85-123	20
	p-Dichlorobenzene	85-122	20

Table A.1 Quality Assurance Criteria for Method EPA 524.2			
		Accuracy (%R)	Precision
QC Type	Analyte	LCL UCL	(%RPD)
***LCS/LCSD**	n-Butylbenzene	85-129	20
	o-Dichlorobenzene	85-120	20
	1,2-Dibromo-3-chloropropane	71-130	20
	1,2,4-Trichlorobenzene	83-124	20
	Hexachlorobutadiene	83-130	20
	Naphthalene	83-123	20
	1,2,3-Trichlorobenzene	84-124	20
	2-Methoxy-2-methyl-propane	84-116	20
*Surrogates	4-Bromoflurobenzene	77 - 115	NA
	4-Bromoflurobenzene (as ug/L)	3.83 - 5.75	
	1,2-Dichlorobenzene-d4	78 - 115	NA
	1,2-Dichlorobenzene-d4 (as ug/L)	3.90 - 5.75	

*LCS/LCSD recovery and surrogate recovery limits based on control charts of data collected from 01/01/2019 to 12/31/2020. Default limits for all method analytes and surrogates are 70 – 130%. Refer to EPA Method 524.2

Updates

Updated for online revision. Appendix A included.