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EPA Method 525.2 – Drinking Water SVOCs by GC/MS

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1. Scope and Application

1.1. This is a general purpose method for the identification and measurement of organic compounds in finished drinking water or source water. The method is applicable to organic compounds that are partitioned from the water sample using a C18 organic phase that is chemically bonded to Teflon disks and sufficiently volatile and thermally stable for gas chromatography.

1.2. The target list includes:

Compound	CAS Number
Di(2-ethylhexyl)adipate	103-23-1
Di(2-ethylhexyl)phthalate	117-81-7
Hexachlorocyclopentadiene	77-47-4

1.3. Restricted Procedure

1.3.1. 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.

2.2. Primary Source – target chemical standards that are purchased from a vendor and used to make up the various concentration levels for an instrument calibration curve, matrix spike mixes, and surrogate mixes.

2.3. Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the calibration curve using the primary source standards. The ICV is run a level equal to that of a Laboratory Control Sample (LCS) or that of a point on the calibration curve. The ICV is prepared from a manufacturer other than that of the primary source, or from a different lot number if from the same manufacturer.

3. Interferences

3.1. Possible contaminant sources are reagents, liquid-solid extraction disk apparatus, drying column, and turbo-vap glassware. Analyses of laboratory reagent blanks provide information about the presence of contaminants, most frequently in the form of phthalates.

3.2. Carry over contamination may occur when a sample containing low concentrations of target semi-volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of target or non-target organic compounds. During sample spiking during extraction prep spiking syringes should be rinsed as needed to prevent carry over between the 1 liter bottle spiking.

4. Safety

4.1. Refer to Laboratory Safety/Chemical Hygiene Plan and Fire Safety Plan.

4.2. Methanol is used during the extraction, store the 4-liter bottle in the flammable storage cabinet, keep squeeze bottles inside the hood. If a Methanol spill occurs, activated carbon (large yellow bucket) should be used to soak up the spill and prevent fumes from building up in the room.

4.3. Keep solvent squeeze bottles inside the hood.

4.4. When neutralizing 1L samples wear lab coats, gloves, and safety goggles.

4.5. Store the neutralizing NaOH solution separate from any acid storage.

4.6. Wear safety googles during extraction in the extraction room, all sample bottles contain water at pH <2.

5. Apparatus and Equipment

5.1. Drying column, 1” x 12”

5.2. Class A volumetric flasks

5.3. Factory certified glass syringes between 10 µl and 1000 µl are used.

5.4. 10µL auto-pipette (calibrated every 6 months and checked before each use).

5.5. A 6 position manifold vacuum system connected to house vacuum via a 10 liter Büchner jar. The jar is used to collect the sample water for later pH adjustment before disposal.

5.6. 2ml amber GC/MS autosampler vials with Teflon-lined screw caps.

5.7. pH indicator strips, pH range 0 -6, catalogue #9586 from EM Science

5.8. C18 extraction disks (JT Baker, catalog # 8055-07) or an equivalent is used during filtration and elution of the extract.

5.9. HP-5MS 15 m x 0.25 x 0.25 µm film.

5.10. 0.5 mm inner diameter 5 m deactivated guard column.
5.11. Gas chromatograph and mass spectrometer and auto-sampler with a computer data system
5.12.1. GC/MS Systems: *GCMS05 5975C* and *GCMS06 5973*
5.12.2. Gas chromatograph set points are as follows:

Table 5.12.2.1. – GC Parameters

Parameter	Setting GCMS05 5975C	Setting GCMS06 5973
Injection Mode	On Column	On Column
Injection Volume	1 µl	1 µl
Inlet Temp	Oven Track	Oven Track
MSD Transfer Line	280°C	280°C
Oven Equilibration Time	1.5 min	1.5 min
Oven Initial Temp/Hold Time	55°C/1.0 min	55°C/1.0 min
Oven Level 1: Rate, Final Temp, Hold Time	30°C/min, 280°C, 0.0 min	30°C/min, 280°C, 0.0 min
Oven Level 2: Rate, Final Temp, Hold Time	80°C/min, 310°C, 2.25 min	80°C/min, 310°C, 2.25 min
Total Run Time	11.125 min	11.125 min
Column Flow	2ml/min Constant Flow	2ml/min Constant Flow

5.12.3. Operating parameters for GCMS05 5975C and GCMS06 5973 mass selective detectors:

Table 5.12.3.1 – Mass Spectrometer Operating Parameters

Parameter	Setting
Tune File	Dftpp.u
Acquisition Mode	Scan
EM Mode	Relative
Low Mass	45

Table 5.12.3.1 – Mass Spectrometer Operating Parameters	
Parameter	**Setting**
High Mass	450
Threshold	150
Sample #	1 A/D Samples 2

5.13 Chemstation Enviroquant by Agilent is the data software system for acquiring, storing, reducing, and outputting mass spectral data and reports.

6. Reagents and Standards

6.1. Anhydrous sodium sulfate (baked at 425° C ± 25° C for 4 hours)
6.2. House Helium carrier gas, Agilent final filter installed just before GC gas inlet
6.3. 1-Liter amber glass sample bottles with Teflon-lined screw caps, amber to prevent PAH light sensitive from photo-oxidizing or decomposing. These bottles are prepared from a supplier with 50mg of Sodium Sulfite
6.4. Solvents (High Purity Pesticide Quality Reagents)
6.4.1. Methylene chloride
6.4.2. Ethyl acetate
6.4.3. Methanol
6.4.4. Reagent-grade water that has been treated in a water purification system
6.4.5. Glass vial containing 5ml 1:1 HCl mix, prepared and purchased from a supplier
6.4.6. 50% Sodium Hydroxide solution (to neutralize sample water before disposal)
6.5 Anhydrous sodium sulfate
6.6 Silanized glass wool
6.7 Calibration Standards
6.7.1 *Calibration Standard Component/Mixtures Purchased*
6.7.1.1 Internal Standard and Surrogate Fortification Mix, 500 µg/ml vial or equivalent, contains Acenaphthene-d10, Chrysene-d12 and Surrogates 1,3-Dimethyl-2-Nitrobenezene, Pyrene-d10, and Triphenyl phosphate. Purchased from vendor.
6.7.1.2 Fortification Standard, p-Terphenyl-d14, 500 µg/ml vial or equivalent. Purchased from vendor.
6.7.1.3 Di(2-ethylhexyl)adipate,100 µg/ml vial or equivalent, purchased from vendor.
6.7.1.4 Di(2-ethylhexyl)phthalate, 100 µg/ml vial or equivalent, purchased from vendor.
6.7.1.5 Hexachlorocyclopentadiene, 100 µg/ml vial or equivalent, purchased from vendor.
6.7.1.6 100ug/ml standard purchased as a custom mixture, contains Di(2-ethylhexyl)adipate, Di(2-ethylhexyl)phthalate, Hexachlorocyclopentadiene.

6.8 *Calibration Curve*

6.8.1 The 0.2µg/L curve point standard mixture is prepared in a 5ml vial using the 3 compound custom mix and adding the internal standard and Terphenyl-d14 fortification standard. 5 aliquots of approximately 1ml are transferred into a 1ml autosampler vials, stored at -10° C.

Table 6.8.1.1 – 525.2 Calibration Curve Level 0.2ug/L				
Aliquot to Add				
Custom Mix 3 compounds@100 µg/ml Di(2-ethylhexyl) adipate Di(2-ethylhexyl) phthalate Hexachlorocyclopentadiene (ul)	Internal and Surrogate @500 µg/ml (µl)	Fortification Standard @500 µg/ml (µl)	Ethyl Acetate (µl)	**Final Concentration 5ml Volume**
10	50	50	4,890	0.2 µg/L

Final volume of calibration standards in Ethyl Acetate	5.0 ml
Total volume of standard aliquots	0.110 ml
Total volume of Ethyl Acetate added	4.890 ml

6.8.2 The 1.0µg/L curve point standard mixture is prepared in a 5ml vial using the 3 compound custom mix and adding the internal standard and Terphenyl-d14 fortification standard. 5 aliquots of approximately 1ml are transferred into a 1ml autosampler vials, stored at -10° C.

Table 6.8.2.1 – 525.2 Calibration Curve Level 1.0ug/L				
Aliquot to Add				
Custom Mix 3 compounds@100 µg/ml Di(2-ethylhexyl) adipate Di(2-ethylhexyl) phthalate Hexachlorocyclopentadiene	Internal and Surrogate @500 µg/ml (µl)	Fortification Standard @500 µg/ml (µl)	Ethyl Acetate (µl)	**Final Concentration 5ml Final Volume**
50	50	50	4,850	1.0 µg/L

(*ug/L*) units based on 1L of sample extracted

Final volume of calibration standards in Ethyl Acetate	5.0 ml
Total volume of standard aliquots	0.15 ml
Total volume of Ethyl Acetate added	4.85 ml

6.8.3 The 6.0µg/L curve point standard mixture is prepared in a 5ml vial using the 3 compound custom mix and adding the internal standard and Terphenyl-d14 fortification standard. 5 aliquots of approximately 1ml are transferred into a 1ml autosampler vials, stored at -10° C

Table 6.8.3.1 – 525.2 Calibration Curve Level 6.0ug/L				
Aliquot to Add				
Custom Mix 3 compounds@100 µg/ml Di(2-ethylhexyl) adipate Di(2-ethylhexyl) phthalate Hexachlorocyclopentadiene	Internal and Surrogate @500 µg/ml (µl)	Fortification Standard @500 µg/ml (µl)	Ethyl Acetate (µl)	**Final Concentration 5ml Final Volume**
300	50	50	4,600	6.0 µg/L

(*ug/L*) units based on 1L of sample extracted

Final volume of calibration standards in Ethyl Acetate	5.0 ml
Total volume of standard aliquots	0.40 ml
Total volume of Ethyl Acetate added	4.60 ml

6.8.4 The 4.0µg/L 8.0µg/L and 10.0µg/L curve point standard mixtures are prepared directly into 1ml autosampler vials as follows and stored at -10° C

Table 6.8.4.1 – 525.2 Calibration Curve Levels 4.0, 8.0, 10.0 ug/L				
Aliquot to Add				
Custom Mix 3 compounds@100 µg/ml Di(2-ethylhexyl) adipate Di(2-ethylhexyl) phthalate Hexachlorocyclopentadiene	Internal and Surrogate @500 µg/ml (µl)	Fortification Standard @500 µg/ml (µl)	Ethyl Acetate (µl)	**Final Concentration 1ml Final Volume**
40	10	10	940	4.0 µg/L
80	10	10	900	8.0 µg/L
100	10	10	880	10.0 µg/L

(*ug/L*) units based on 1L of sample extracted

6.9 GC/MS DFTPP Mass Spec Tune Check Solution

6.9.1 Prepared in a 1ml auto sampler vial and stored at -10° C.

Table 6.9.1.1 – 525.2 5.0 µg/L DFTPP Tune Solution			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
DFTPP	500 µg/ml	10µL	5.0 µg/mL

Final volume of calibration standards in Methylene Chloride	1.0 ml
Total volume of standard aliquots	0.01 ml
Total volume of Methylene Chloride added	0.99 ml

6.10 Breakdown Check Solution

6.10.1 In a 1ml auto sampler vial prepare the solution

6.10.2 Store the solution at -10° C

Table 6.10.2.1 – 525.2 5.0 µg/L Breakdown Check Solution			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Endrin	100 µg/ml	50µL	5.0 µg/mL
P,P'-DDT	100 µg/ml	50µL	5.0 µg/mL

Final volume of calibration standards in Methylene Chloride	1.0 ml
Total volume of standard aliquots	0.1 ml
Total volume of Methylene Chloride added	0.9 ml

6.11 GC Column Performance Check Solution

6.11.1 In a 1ml auto sampler vial prepare the solution then store the solution at -10° C

Table 6.11.1.1 – 525.2 5.0 µg/L GC Column Performance Check Solution			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Anthracene/Phenanthrene	100 µg/ml	60µL	6.0 µg/mL

Final volume of calibration standards in Ethyl Acetate	1.0 ml
Total volume of standard aliquots	0.06 ml
Total volume of Ethyl Acetate added	0.94 ml

6.12 Initial Calibration Verification Standard (Second Source) Solution

6.12.1 The ICV is prepared at the same level and with the same ratio of components as the 6.0 µg/ml calibration standard, but using second source target analytes which can be from a different vendor, or the same vendor but a different lot number or separate individual vials.

6.12.2 Individual vials are purchased that each contain Di(2-ethylhexyl)adipate, Di(2-ethylhexyl)phthalate, and Hexachlorocyclopentadiene, at 100 µg/ml each, or equivalent in methanol. The ICV is prepared as follows in a 1ml auto sampler vial and is stored at -10° C.

Table 6.12.2.1 – 525.2 ICV (second source)						
Aliquot to Add						
Di(2-ethylhexyl) adipate @100 µg/ml (µL)	Di(2-ethylhexyl) phthalate @100 µg/ml (µL)	Hexachlorocyclop entadiene @100 µg/ml (µL)	Internal and Surrogate @500 µg/ml (µl)	Fortification Solution @500 µg/ml (µl)	Ethyl Acetate (µl)	**Final Concentration 1ml Final Volume**
60	60	60	10	10	800	6.0 µg/L

6.13 QC LCS/LCSD/MS/MSD Spiking Solution

6.13.1 Purchased from vendor, a custom mixture or equivalent containing Di(2-ethylhexyl)adipate, Di(2-ethylhexyl) phthalate, and Hexachlorocyclopentadiene, each at 100 µg/ml in methanol, and used directly from the vial without further dilution for QC spiking, stored at 4°C.

6.14 MDL Spiking Solution

6.14.1 Prepare MDL spike mix using the individual component vials used for the second source, ICV standard, dilute in 5ml Methanol, stored at 4°C.

Table 6.14.1.1 – 525.2 MDL Spiking Solution			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Hexachlorocyclopentadiene	100 µg/ml	200µL	4 µg/ml
Di(2-ethylhexyl)adipate	100 µg/ml	1000µL	20 µg/ml
Di(2-ethylhexyl) phthalate	100 µg/ml	1000µL	20 µg/ml

Final volume of calibration standards in Methanol	5.0 ml
Total volume of standard aliquots	2.2 ml
Total volume of Methanol added	2.8 ml

7 Sample Collection

7.1 Water samples for 525 semivolatile organic compounds are collected in a 1-liter amber glass bottle containing 50 mg of sodium sulfite to dechlorinate the sample. After water sample collection in the bottle, it is shaken and 5 ml of 1:1 HCl is then poured into the bottle for preservation. All sample bottles must be cooled to 4° C after sample collection. Two bottles are required for each sampling location. Four from one sampling location in the batch sent out are sent and used for the matrix spike, matrix spike duplicate. Holding time for preserved samples is 14 days from the collection date. Holding time of final 1ml extraction for instrument analysis is 30 days from the extraction date.

7.2 For 525 SOC samples the batch of coolers picked up by the collectors from the lab in their vehicle and taken to the field is defined as the batch. This batch of coolers contains 2 travel blank bottles and the MS/MSD bottles. Any samples for recollection that are sent out individually, and not as part of a batch of coolers being picked up need a travel blank for that sample.

8 Calibration

8.1 Mass Spectrometer Tune Verification must be performed initially.

8.1.1 Inject 1 ul of the DFTPP Tune Performance Check Solution and verify that the resulting mass ion fragmentation pattern meets the criteria in Table 8.1.1. 1 below using the DFTPP data analysis method:

Table 8.1.1.1 – Mass Spectrometer Tune Fragmentation Criteria

Mass (M/z)	Relative Abundance Criteria
51	10-80% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	10-80% of mass 198
197	<2% of mass 198
198	Base Peak
199	5-9% of mass 198
275	10-60% of mass 198
365	>1% of mass 198
441	Present and < mass 443

Table 8.1.1.1 – Mass Spectrometer Tune Fragmentation Criteria	
Mass (M/z)	**Relative Abundance Criteria**
442	>50% of mass 198
443	15-24% of mass 442

8.1.2 A single scan of the peak or the entire peak may be averaged and used for DFTPP fragmentation evaluation, the evaluation can be automatic or manual.
8.1.3 Print the manual tune evaluation (the automatic evolution will auto-print)
8.1.4 Should the tune fragmentation parameters not be met, re-inject the DFTPP, if it still fails then maintenance must be performed which is usually the cleaning of the mass spectrometer's ion source.

8.2 GC Column performance check

8.2.1 Inject and analyze 1 µl of the GC Column Performance Solution.
8.2.2 Load the datafile on the screen and quantitate the datafile using the DFTPP method.
8.2.3 Go into "Q-Edit" and find the quantitation ions m/z 178 for Anthracene and Phenanthrene which will be plotted on the screen. There must be a baseline separation between the two peaks for the GC Column Performance to pass. Print the screen displaying the 2 peaks separated by a baseline.
8.2.4 While still in "Q-Edit" find the quantitation ion m/z 228 for Benzo(a)anthracene and Chrysene which will be plotted on the screen. Use the Chemstation software (left top tab, "Evaluate Resolution") to determine the height of the peaks and the valley between the two peaks. The software will auto-calculate a Peak/Valley ratio. This ratio must be ≥75%. Print the screen.
8.2.5 If there is no baseline separation between Anthracene and Phenanthrene, then the GC column/inlet requires maintenance.
8.2.6 If the Peak/Valley ratio is <75% for Benzo(a)anthracene and Chrysene then the GC column/inlet requires maintenance.

8.3 Endrin and p,p'-DDT breakdown must be evaluated

8.3.1 Inject and analyze 1 µl of the breakdown solution containing Endrin and p,p'-DDT
8.3.2 Load the datafile on the screen and use the DFTPP method to integrates the DDT, Endrin, and their breakdown products. On the Chemstation top menu tab choose "Quant", then "Q-Edit" to review the peaks integrated. All the areas and integration retention times used for the calculation should be checked to make sure they are correct and not duplicated.
8.3.3 From the method top toolbar select Custom Reports and select the template file "EDbreakdown.CRT" for the *GCMS05 5975C* and "525test.CRT" for the *GCMS06 5973*. The report will perform the calculations for the percent breakdown report using the peak areas and print automatically.
8.3.4 Also print the data file quantitation report as a "summary" report; it will contain the total ion chromatogram peaks and areas and retention times for the Endrin and p,p'-DDT and their breakdown compounds.
8.3.5 If the custom report has the breakdown of either Endrin or p,p'-DDT exceeding 20% then maintenance on the GC inlet must be performed

8.3.6 After inlet maintenance re-inject Endrin and p,p'-DDT solution to determine if the breakdown is ≤ 20%.

8.3.7 If the breakdown is >20%, the GC column and inlet require maintenance.

8.4 Initial Calibration Curve

8.4.1 After all the above listed performance checks pass, the 6 µg/L mid-level standard is run. The data analysis software must auto-identify 99% of the compounds. If the software cannot do this, the instrument, analysis method, or data analysis program must be inspected and the problem resolved.

8.4.2 After the 6µg/L standard is analyzed and passes the 99%, the remaining calibration curve standards can be injected in order from low to high concentration.

8.4.3 After the curve has run all levels are quantitated and all compound peaks are reviewed for correct identification and retention time and peak shape, each level is used to re-calibrate each calibration level in the data analysis software by uploading the datafile result into the correct curve level in the software.

8.4.4 The software will calculate the response factors (RF) for each analyte using the internal standard with the closest retention time to the analyte.

8.4.5 The software will calculate the mean response factor, $\overline{(RF)}$ of the response factors for each compound.

8.4.6 The software will calculate the percent relative standard deviation (%RSD) for each compound using the $\overline{(RF)}$ and standard deviation, σn-1. If any compound has a %RSD of > 30%, it may be necessary to take action to improve GC/MS performance or use a linear calibration fit with a correlation coefficient (r) of ≥ 0.995. Print the report sheet

8.4.6.1 If any compound has a %RSD>30% or a correlation coefficient (r^2) of < 0.995, it may be necessary to take action to improve GC/MS performance.

8.4.7. Immediately following initial calibration, a second source standard or Initial Calibration Verification (ICV) standard of equivalent concentration to the 6.0 µg/ml initial calibration standard is analyzed.

8.4.7.1. 90% of the ICV compounds with a %RSD fit must have a percent difference calculated in the same way a CCV %Drift is calculated and be of less than ± 30% from the expected value. If more than 10% 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. A linear fit compound must have a calculated amount of ± 30% of the nominal value.

8.5. Upon completion of the initial calibration and verification, the internal standard recovery method that uses p-Terphenyl-d14 must be updated.

8.5.1. From the initial calibration curve levels, determine the calibration level point with the highest p-Terphenyl-d14 peak area.

8.5.2. Load this highest value data file into the data analysis software and open the internal standard recovery method

8.5.3. Use the software to quantitate the p-Terphenyl-d14 and the internal standards.

8.5.4. Use the software to update the internal standard recovery method, it is a 1 point only calibration curve fit, print the %RSD report sheet.

8.5.5. Due to variances in concentration of the purchased p-Terphenyl-d14 vials, the ISR method may need to be updated to reflect these variations. A 1 ml auto sampler vial is prepared using the new p-Terphenyl-d14 and Internal Standard spike mix used for extractions. The vial is analyzed and the results are used to

update the internal standard recovery method. Print the new %RSD report and place it in the calibration curve file as a record.

8.5.6. All the QC samples, information, datafiles, and RSD reports used to create the calibration curve are gathered into one file folder and the date of the method written on the file folder and stored in a file cabinet for all 525 calibration curves.

8.6. Continuing Calibration Verification

8.6.1. Prior to the analysis of samples and at the beginning of each 12-hour shift, the instrument calibration must be verified. All of the following must be performed using the same instrumental conditions used for the initial calibration.

8.6.2. Inject and analyze the DFTPP tune standard, Performance Check solutions, and Breakdown Check solutions as described.

8.6.3. If the performance checks pass, inject a 0.2 µg/ml, and a 1.0 µg/ml calibration standard (see reference "Drinking Water Certification" manual) for inspection of each component at the 525.2 reporting limits. Because no criteria are given for this standard, the criteria recommended by various EPA auditors are adopted and each compound must pass at ±50% of nominal value.

8.6.3.1. Check the compound with the lowest area/height response for the quant ion. If this area/height is less than 3 times the noise (i.e. signal to noise ratio of > 3), remedial action should be taken to improve instrument response.

8.6.3.2. Calculate the %Drift for the low level standard.

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

8.6.4. A 6.0 µg/ml Continuing Calibration Verification standard (CCV; same as the 6.0 µg/ml calibration standard) is injected to check system response.

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

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

8.6.4.3. Calculate the %Drift for the CCV.

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

8.6.4.5. The CCV absolute area of both internal standards and surrogates 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.

8.6.4.6. 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.

8.6.5. A closing CCV is analyzed at the end of the batch sequence at a 6.0µg/ml level. The internal standard areas and surrogate areas of the calibration check must be 50-150% of the initial curve (the method also allows the option of 70-130% if using the areas of the most recent CCV). All targets and surrogate compounds must have a calculated amount that is within 70-130% of the true value

8.6.5.1. If the closing CCV fails one surrogate low recovery and the other surrogates

pass or are high recovery, the closing CCV can be valid.

8.6.5.2 If any or all target compounds fail high recovery and they were not detected in any samples of the batch then closing CCV is valid. However, if any target compound fails low recovery the column must be cut and baked and the closing CCV run again. If the target compound still fails low recovery then corrective action on the instrument is required and all the samples run before the closing CCV must be re-analyzed.

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 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 is 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. The preferred continuous format MDL study is performed where one vial per batch 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, $B_525H. The MDLSpike result will be entered using the $ML525H. The MDL Spiked Amount will be entered into the test code $MA525H. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-525H. Analyze the same extraction batch's MDL and MDL-Blank on the second instrument to upload into Labworks.

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

9.3. ICN, Initial capability demonstration of the analyst's ability to produce acceptable recovery, accuracy, and precision the following operation must be performed for each matrix before an analyst can sample run analysis. Results must meet limits listed in Appendix A. A blind sample is also prepared. This includes an MDL study of 7 spiked MDL samples and 7 Blank samples over 3 (skipped) days.

9.3.1. Analysts must also perform a Continuing Demonstration (CDF) twice a year to prove the analyst's ability to produce acceptable recovery, accuracy, and precision for each matrix. Results must meet limits listed in Appendix A.

9.3.2. Samples prepared and analyzed for IDCs and CDCs should be spiked so that the same concentration as the midpoint of the curve, 6.0 µg/ml.

9.4. Control chart limit defaults for analyte and surrogate recovery, and precision are based on Method 525.2 initial control limits.

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

9.4.2. Surrogate control carts are based on sample analysis control charts.

9.4.3. LCS/LCSD precision and recovery limits are developed from control charts.

9.4.4. MS/MSD precision and recovery limits have control charts generated, however they will be assigned the same values as the LCS/LCSD control chart limits.

9.4.5. LCS/LCSD pairs must be analyzed at a rate of 1 per batch of up to 20 samples.

9.4.6 Matrix Spike pairs (MS/MSD) are analyzed at a frequency of 5% of all samples analyzed over time or one MS/MSD pair for each batch of up to 20 samples.

9.5 A sample batch is defined as up to 20 field samples that are extracted during one work shift. In each batch, an extracted method blank, laboratory control spike (LCS), laboratory control spike duplicate (LCSD), matrix spike (MS), matrix spike duplicate (MSD), and an MDL sample are included.

9.6 Sample extracts are stored in a refrigerator ≤4° C. The refrigerator is labeled for sample extracts only. Extracts must be protected from light. A separate refrigerator must be used to store the standard stocks and prepared standards.

9.7 Stock standard solutions are purchased in mixtures from commercial suppliers. Certificates of analysis are required for all purchased standards and must be filed in the 525 standards logbook. Each ampule is given a standard number when opened and stored at 4º C in the 525 refrigerator. Warm the standards to room temperature before use. Opened vials are valid for 6 months.

9.8 All standard mixtures that are prepared from 2 or more vials of standard are assigned an expiration date of 6 months from the preparation date. This date will be written on the standard mix vial.

9.9 All printed paperwork is saved for 10 years.

9.10 All sequences are printed brief and detailed for the batch folder; the brief format is also saved in a sequence logbook.

9.11 All calibration curve related paperwork is printed and saved in a file folder and stored in a file cabinet drawer with the curve name written on the top tab.

9.12 All QC that is part of the batch is stored in the sample batch file folder, this includes DFTPP tune, CCV, Method Blank, MDL analysis, sequence pages, Int Std Area reports, sample reports, dilution pages, extraction sheets, sample preparation sheets, etc.

9.13 The GC/MS system must meet DFTPP criteria every 12 hour shift.

9.14 20 field samples max per QC batch, does not include QC samples.

9.15 If 20 sample analysis batch runs over 12 hrs, a new DFTPP must be analyzed to extend 12 hrs.

9.16 Initial Calibration of the 7 point curve must meet method QC criteria

9.17 The software will calculate a percent Relative Standard Deviation for each compound. This percent Relative Standard Deviation (%RSD) should be less than 30% for each compound.

9.18 For any target compound if the %RSD greater than 30% then a linear regression curve fit may be used.

9.19 If a Linear fit is used, must be $r \geq 0.995$.

9.20 System Performance Checks must pass before instrument calibration or sample analysis, this includes peak baseline separation, peak/valley ratios, and breakdown being within method limits.

9.21 ICV, second source verification of the instrument with each new curve built. The percent deviation should be ± 30% for all performance compounds, or ± 30% of the true value for linear fit compounds.

9.22 An initial CCV is run daily, 20 samples max in the batch for each 12 hour shift (run after DFTPP). A closing CCV is also run after the samples in the batch are analyzed.

9.23 In the CCV all compounds must have a percent deviation of ±30% from the initial cuve, or ± 30% of the true value for linear fit compounds.

9.24 If any compound fails low (<30% deviation), cut the column and bake and re-run the CCV. However if the source of the failure cannot be identified and the CCV deviation still fails low, a new calibration curve must be generated.

9.25 CCV compounds should have a deviation of <30%. It is permissible to have compounds fail high (>30% deviation, or +30% of the true value for linear fit compounds) if there are no hits for these compounds in any samples of the batch. On a closing CCV it is permissible to have one surrogate fail low if the other surrogates pass QC.

9.26 Internal standard and surrogate areas for the CCV must be between 50 - 150% of the areas of the internal standards in the mid-point standard of the most recent initial calibration analysis. The method also allows the option of 70-130% of the area if using the most recent CCV.

9.27 Surrogate limits are set through annual control charting.

9.28 A Method Blank is required to run on the instrument system for each analysis batch. The purpose of a blank is to verify that the instrument and all reagents associated with an anlysis are free from contamination (no compounds > reporting limits).

9.29 A water Method Blanks is 1L of reagent water, in an amber bottle like the samples, with preservatives.

9.30 Laboratory Control Spike, LCS (Laboratory Fortified Blank) and Laboratory Control Spike Duplicates (LCSD, consist of 6µg/L standard (all 525 target compounds are included) that are extracted and analyzed sequentially at the beginning of each sample batch (after the CCV). The recoveries and precisions of these compounds must meet quality control limits listed in Appendix A.

9.31 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) are utilized to determine quality control limits that are affected by sample matrix interference. The spike compounds are all 525 target compounds at a concentration of 6µg/L. The recovery and precision of these compounds should meet quality control limits listed in Appendix A.

9.32 Charting for 525 LCS/LCSD, Surrogates, and MS/MSD for upper and lower control limits are performed twice per year. The Appendix A control limits are updated only annually. These upper and lower control limits are based on a maximum of 500 data points, 48 months of data may be used if less than 20 points are available.

9.33 The low recovery control limit for any compound cannot be less than the method specified limit of 70%, and the highest low value is 85%.

9.34 The high recovery control limit for any compound cannot be less than 115%, and the highest value is the method specified 130%.

9.35 The internal standard recovery method is set to the method limit, both internal standards must have a recovery >70%. If a QC sample, Method Blank or LCS fails, the batch fails and must be re-extracted.

9.36 The precision for LCS/LCSD must meet Appendix A limits. A failure in LCS/LCSD precision will not fail the batch if the compound is not detected in any samples of the batch, and if the LCS is within recovery limits.

9.37 The method states a MS/MSD precision failure only to have a corrective action due to possible matrix interference.

9.38 The pH of a 1L field preserved sample, upon being received at the GC/MS lab must have the pH tested and be <2 for the sample to be valid for extraction.

9.38.1 Approximately 5 ml of a sample is poured into a clean dry vial. A pH test strip is dipped into the vial and the wet pH strip compared to the color chart. If the pH value is <2, then check off the "pH<2" pH receiving sheet.

9.38.2 The pH result, analyst, date, and the lot number of the test strip are all recorded on the 525H pH receiving sheet. The sheet is placed in the analysis batch when analysis is completed.

9.39 Each lot of 1ml autosampler vials is filled with 1,000µl (1.0 gm) of water on an analytical balance to verify the 1ml volume mark on the vial, this is recorded on a vial report sheet and stored in the extraction logbook.

10 Procedure

10.1 Remove the sample bottles and standard vials from cold storage; allow to equilibrate to room temperature.

10.2 The sample bottle tracking number is recorded on the extraction sheet.

10.2.1 The manifold position of the Method Blank, LCS, LCSD, MS, MSD and MDL are recorded on the extraction sheet, positions of each must rotate with each batch.

10.2.2 The TurboVap position of the Method Blank, LCS, LCSD, MS, MSD, and MDL are recorded on the extraction sheet, positions of each must rotate with each batch.

10.2.3 If the sample pH was not < 2 and the second bottle failed then the sample must be voided and be resampled.

10.3 Mark with a marker all field sample bottles (after pH test) to indicate the sample volume in the bottle prior to proceeding with spiking and extraction.

10.4 Each extraction batch should include the following QC 1L bottles: Method Blank, LCS, LCSD, MS, MSD, Trip Blank, and MDL.

10.4.1 For the Method Blank, LCS, LCSD, and MDL amber 1 L bottles are prepared and should contain 1 L of reagent grade water, the Sodium Sulfite, the 1:1 HCl.

10.4.2 On the extraction sheet record all reagents (HCl, Sodium Sulfite, etc) used.

10.5 To all bottles in the batch add 5 ml of trace analysis grade Methanol.

10.6 Rinse the syringes used with MeCl2, the LCS, LCSD, MS, MSD are each spiked with 60 µl of the QC Spiking Solution (525.2 target compounds) for a concentration of 6µg/L.

10.6.1 The MDL is spiked with 50uL of the MDL spike solution

10.6.2 10 ul of the Internal Standard/Surrogate standard is spiked into all the bottles of the batch. The final concentration of the Internal Standards and Surrogates is 5 µg/L.

10.7 Cap and shake each sample and QC bottle to thoroughly mix.

10.8 Samples are extracted utilizing a manifold vacuum system and C18 disks assembled on a Teflon or glass filtration apparatus.

10.8.1 Using labeling tape, mark each extraction positon with the QC name or sample login ID number of the batch.

10.8.2 NOTE: If using the Speedisk disk filter, the filter's manufacturing production leaves Phthalate residues on the disk that MUST be rinsed and removed to reduce false positives. Rinse the filtration apparatus reservoir with the 15ml MeCl2. Draw half of the solution through the disk and close the vacuum, wait for 2 minute and then pull the remaining solution through the disk until dry using the vacuum. If using a 3M style disk filter, this step is not necessary.

10.8.3 Follow method procedures and clean the C18 disk by adding 5 ml of the 50/50 Ethyl Acetate/Methylene Chloride. Draw half of the solution through the disk and close the vacuum, wait for 2 minute and then pull the remaining solution through the disk until dry using the vacuum.

10.8.4 Condition the C18 disk by adding 5 ml of trace analysis Methanol to the filter and carefully pull some methanol through the filter, allow the Methanol to sit for 1 minute on the disk. It is very important from this point on to **NOT** allow the disk to go dry as this will decrease analyte recovery. There must always be Methanol or reagent water or sample water on the disk keeping it wet.

10.8.5 After 1 minute, rinse the disk with 5 ml of reagent water, remember it is important not to allow the disk to dry. Repeat with 5 more ml of reagent water.

10.8.6 Extract the sample bottle by inverting the bottle onto the extraction disk apparatus. Apply only a partial vacuum by opening the valve a slight amount

10.8.7 If using the Speedisk, 1 liter should pass through the filter apparatus in 40 min for good recovery. If using the 3M style extraction disk and glass apparatus, 1hr will provide good recovery. With either disk, 15-30 minutes to pull the 1 liter bottle will result in poor recoveries.

10.9 After the sample has finished filtering, open the vacuum valve to full and allow the disk to dry for 10 minutes.To collect the target compounds trapped on the dry C18 disk place a 40ml vial to be used as a collection tube into the extraction manifold, above the valve and below the disk.

10.9.1 Add 5 ml of Ethyl Acetate to the now empty 1L liter sample bottle and rinse the inside walls. Transfer the bottle rinse to the appropriate filter apparatus; pass a small amount through the disk which will drip into the collection tube, allow the Ethyl Acetate to sit on filter for 1 minute, then pull remaining solvent through using a partially opened vacuum valve into the collection tube.

10.9.2 Repeat the step above using 5 ml of Methylene Chloride.

10.9.3 Using a pipette rinse the inside of the filter housing on the manifold with 3 ml of 50/50 Ethyl Acetate/Methylene Chloride. Pull a partial amount through the disk and allow the remainder to sit on the disk for 1 minute, then apply partial vacuum and pull through into collection tube. Repeat this with a second aliquot rinse.

10.10 Remove the collector tube. If time does not allow for continuing the extraction procedures, cap and store the 40ml vial collection tubes in a dark 4º C refrigerator.

10.11 Pass the 40ml collection tube extract through a drying tube to remove any water.

10.11.1 If extracts were refrigerated allow them to come to room temperature.

10.11.2 Prepare (12in long x 1in diameter) tubes plugged with a small amount of silanized glass wool and 5-7 gm of sodium sulfate (about 1 inch high in tube).

10.11.3 Rinse the prepared collection tube with 3 ml of 50/50 Ethyl Acetate/Methylene Chloride, collect into a labeled waste jar.

10.11.4 Pour the 40ml collection vial extract through the drying tube and collect in a 50 ml TurboVap concentrator tube.

10.11.5 Add ml of 50/50 Ethyl Acetate/Methylene Chloride into the 40ml collection vial, cap, and shake well. Pour the 40ml vial solvent rinse through the drying tube. Repeat with a second rinse. Be care to not overfill the Turbovap concentrator tube.

10.12 Concentrate the extract in the Turbovap tube in a Turbovap set to 38ºC and at 7 psi Nitrogen to start, as the volume drops raise the pressure to a maximum of 13-14 psi. Concentrate to a final volume of less than 1 ml but do not concentrate the extract to less than 0.5 ml or poor recoveries will result.

10.12.1 A 1ml auto sampler vial (batch lot number volume must be verified) is used to collect the sample. Use a pasteur pipette to rinse the tube walls then transfer the extract from the TurboVap tube to the vial. Use Ethyl Acetate and add to the tube as needed and transfer to the autosampler vial to bring the total volume to 1ml.

10.12.2 To each 1ml autosampler vial with extract add 10 µl of p-Terphenyl-d14 using a glass Hamilton 10µL syringe and then shake the vial well to mix.

10.12.3 The 1ml auto sampler extract vials are stored at < 4°C and protected from light. Extracts are valid for analysis for 30 days after date of extraction.

10.13 After the extraction is completed the 1L sample bottles are filled to the marked line (from the beginning of the extraction procedure) and the sample volume measured in a Class A 1000ml graduated cylinder and recorded on the extraction sheet.

10.14 Analyze the 1ml vials on the GC/MS system after passing all required QC.

10.14.1 If extracts were refrigerated after concentration, remove them from the refrigerator and allow equilibration to room temperature.

10.14.2 Inject a 1µl aliquot on the GC/MS system under the same conditions used for the initial curve and continuing calibration evaluation.

10.14.3 Any target detected peaks must be positively identified by comparison of its mass spectrum (after background subtraction) to a stored reference spectrum. The GC retention time of the sample component should be within 5 sec of the retention

time observed for that same compound in the most recently analyzed continuing calibration check standard.

10.14.4 If a sample has a possible analyte detect but is not within the 5 second window, re-analyze the sample. If the second analysis is not within the 5 second window then extract and analyze the second bottle sample to determine if the findings of the original sample confirm or do not confirm.

10.14.5 Generally, all ions that are above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component. They should also agree within ± 20% or have good visual comparison that agrees with the saved reference mass spectrum.

10.14.6 For any target compounds above the calibration curve, a dilution must be performed. Due to the 525 method procedure of adding internal standard before extraction, a dilution of a sample will require adding the appropriate amount of internal standard to the dilution volume to bring the internal standard back to its original amount. A dilution log sheet is filled out and placed in the batch folder.

10.14.7 Dilution Example: If performing a 2X dilution, 500µL of sample and 500µL of Ethyl Acetate are placed into a 1ml auto sampler vial. Since half the internal standard was lost in the dilution, 5µL of pure internal standard must be added to the dilution vial to bring the internal standard concentration back to 5µg/L.

10.14.8 p-Terphenyl-d14 is used as an indicator of overall extraction efficiency. Recoveries of the 525 data analysis internal standard compounds are monitored using this p-terphenyl-d14 spike as the internal standard in the Internal Standard Recovery Data Analysis Method. This recovery method has only 3 compounds, the p-Terphenyl-d14 as the internal standard, and the two 525 internal standards used to quantitate all targets in the 525 data analysis method.

10.14.9 Recoveries of the 2 internal standards in the internal standard recovery method must be ≥ 70%. Any internal standards that fail must be re-analyzed, if the internal standard still fails < 70% the sample must be re-extracted.

10.15 At the end of every sample analysis sequence a closing CCV is analyzed at 6.0µg/ml. The internal standard area must be 50-150% of the initial curve. All targets and surrogate compounds must be within 30 %RSD, or if linear fit have a calculated amount that is within 70-130% of the true value.

10.15.1 After analysis of all the samples they are batched in LIMS, the EPD uses Labworks.

10.15.2 In Labworks batch 525 regulated samples using "#Q$525H".

10.15.3 A computer with the Labworks program is used to auto upload the analysis results directly into Labworks by mapping via the network the analysis results from the analytical instrument.

10.15.4 Data results are entered as follows:

Table 10.15.4.1 - LIMS Test Codes

Data Element	Labworks Test Code
Sample Results	$525H
Extracted Blank	$B_525H
LCS	$LS525H
LCSD	$LD525H
LCS Recovery	$LR525H
LCSD Recovery	$L2525H
LCS/LCSD Precision	$LP525H

Table 10.15.4.1 - LIMS Test Codes	
Data Element	**Labworks Test Code**
Matrix Spike	$S_525H
Matrix Spike Duplicate	$D_525H
Matrix Spike Recovery	$R_525H
Matrix Spike Duplicate Recovery	$RD525H
Matrix Spike/Matrix Spike Duplicate Precision	$P_525H
MDL Analysis Results	$ML525H
MDL Analysis Instrument Used	INSTR-525H
Amount of LCS/LCSD Spike	$LA525H
Amount of Matrix/Matrix Duplicate Spike	$A_525H
Amount of MDL Spike	$MA525H

10.15.5 Any QC that flags red in Labworks must have a corrective action generated to address the QC failure.

10.15.6 After all analytical data is entered into Labworks, a QC\QC batch report is generated. Any flagged QC data must have a corrective action printed at the bottom of the page.

10.15.7 The Trip Blank sample is usually selected to load the results for the MDL and MDL Blank analyzed on the 2nd instrument. The MDL and MDL and Instr-525H test codes must be added to upload results into Labworks.

11 Calculations

11.1 General Notations

n = Number of values.

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

11.2 Breakdown

11.2.1 *DDT Breakdown*

$$\%p,p' - \text{DDT Breakdown} = \frac{\left(\text{Area}_{4,4'-\text{DDE}} + \text{Area}_{4,4'-\text{DDD}}\right) * 100}{\text{Area}_{4,4'-\text{DDE}} + \text{Area}_{4,4'-\text{DDD}} + \text{Area}_{4,4'-\text{DDT}}}$$

11.2.1.1 Where:

$\text{Area}_{4,4'\text{-DDE}}$ = Area under the peak for 4,4'-DDE

$\text{Area}_{4,4'\text{-DDD}}$ = Area under the peak for 4,4'-DDD

$\text{Area}_{4,4'\text{-DDT}}$ = Area under the peak for 4,4'-DDT

11.2.2 *Endrin Breakdown*

$$\%\text{Endrin Breakdown} = \frac{\left(\text{Area}_{\text{Endrin Aldehyde}} + \text{Area}_{\text{Endrin Ketone}}\right) * 100}{\text{Area}_{\text{Endrin Aldehyde}} + \text{Area}_{\text{Endrin Ketone}} + \text{Area}_{\text{Endrin}}}$$

11.2.2.1 Where:

$\text{Area}_{\text{Endrin Aldehyde}}$ = Area under the peak for Endrin Aldehyde

$\text{Area}_{\text{Endrin Ketone}}$ = Area under the peak for Endrin Ketone

$\text{Area}_{\text{Endrin}}$ = Area under the peak for Endrin

11.3 Response Factor Calculations

11.3.1 *Response Factors*

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

11.3.1.1 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

11.3.2 *Mean Response Factor ($\overline{RF}$)*

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

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

11.3.2.2 Where:

RF_i = Individual response factors

11.3.3 *Relative Response Factor (RRF)*

11.3.3.1 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:

$$RRF = \frac{A_X * C_{is}}{A_{is} * C_X}$$

11.3.3.2 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} = Conc. of internal standard spiking mixture, µg/L

C_X = Conc. of the compound in the calibration standard, µg/L

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

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

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

11.3.4.2 Where:

$\overline{RRF}$ = Mean relative response factor

X_i = Relative response factor (RRF) of the compound

11.3.5 *Mean Area Response $\left(\overline{Y}\right)$ for Internal Standard*

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

11.3.5.1 Where:

$\overline{Y}$ = Mean area response of IS

Y_i = Area response of primary quant ion IS of each initial cal level

11.4 Statistical Calculations

11.4.1 *Standard Deviation (δ_{n-1})*

11.4.1.1 Calculate the sample (n-1) standard deviation:

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

11.4.1.2 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

11.4.2 *Percent Relative Standard Deviation (%RSD)*

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

11.4.2.1 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)

11.4.3 *Percent Drift (%Drift)*

11.4.3.1 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:

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

11.4.3.2 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

11.5 Retention Time Calculations

11.5.1 *Relative Retention Times (RRT)*

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

11.5.1.1 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

11.5.2 *Mean Relative Retention Time ($\overline{RRT}$)*

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

11.5.2.1 Where:

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

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

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

11.5.3.1 Where:

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

11.6 Quality Assurance Calculations

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

11.6.1.1 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:

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

11.6.1.2 Where:

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

11.6.2 *Percent Spike Recovery for LCS/LCSD (%R)*

11.6.2.1 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):

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

11.6.2.2 Where:

$R_{Observed}$ = True value of an analyte observed in the sample
$R_{Expected}$ = Expected value of an analyte based on the amount spiked

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

11.6.3.1 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.):

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

11.6.3.2 Where:

$R_{Observed}$ = True value of an analyte observed in the sample
$R_{Expected}$ = Expected value of an analyte based on the amount spiked

11.7 Sample Concentration Calculation

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

11.7.1 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 11.3.3.)
DF = Dilution factor

11.7.2 **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 525.2. Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry; U.S. EPA Office of Research and Development: Cincinnati, OH, 1995, Revision 2.0

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 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, EPA/815-R-05-004, January 2005

13.6 GA EPD Laboratory SOP- Determination of Method Detection Limit, Method Detection Limit SOP 6-007, 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 525.2

Parameter/Method	Analyte	Matrix (Water)	
		RL	Unit
Semivolatiles /525.2	Di(2-ethylhexyl)adipate	1.3	µg/L
	Di(2-ethylhexyl)phthalate	1.3	µg/L
	Hexachlorocyclopentadiene	0.2	µg/L

Table 14.1. 2. Summary of Calibration and QC Procedures for Method 525.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
525.2	SVOCs	Six -point initial calibration for all analytes	Initial calibration prior to sample analysis	%RSD for all calibration analytes <30%. A linear curve may be used if correlation coefficient r ≥ 0.995.	Correct problem then repeat initial calibration	
		Second-source calibration verification(ICV)	Once per initial calibration using different lot number or vendor.	95 % of all analytes within ± 30% of expected value.	Correct problem then repeat initial calibration	
		Calibration verification	Daily, before sample analysis, valid for12 hours of analysis time for one QC batch of samples and at the close of each batch with closing CCV.	All calibration analytes within ±30% RSD of calibration curve. Linear fit calibration. Concentration at ±30% of true value. Internal Std and surrogate within 50% area of curve (or 70-130% of most recent CCV) and Int Std. within 30 seconds of previous CCV.	Initial CCV cut column and bake and re-run. If still fails correct the problem and run new curve. If only one surrogate fails low, CCV valid but create a Corrective Action. If target compounds > 30% positive RSD and not detected in batch create corrective action. If closing CCV fails <30% cut column and bake and re-run. If still fails reanalyze batch samples	
		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 Table A.1 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.		
		CDC – Continuing Demonstration of Capability	Twice a year per analyst, ability to generate acceptable accuracy and precision using four replicate analyzes of a QC check sample. Once per year for supervisor	All targets must meet Appendix A Table A.1 limits.	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Check of mass spectral ion intensities using DFTPP	Daily, before sample analysis, every 12 hours of analysis shift time .	Refer to DFTPP SOP criteria.	Retune instrument and verify DFTPP again	
		MDL study	Continuous with every batch 7 days (over 3 days non-sequential)	MDL must be less than reporting limits	Check calculations, redo MDL analysis and redo results.	
		Internal Standard	Immediately after data acquisition of every sample run.	Recovery for the internal standards must be ≥70% based on the fortification standard. Method Blank and LCS must pass for valid batch.	Inspect mass spectrometry or GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning, and need to build new calibration curve if needed.	

Table 14.1. 2. Summary of Calibration and QC Procedures for Method 525.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
525.2	SVOCs	Method Blank	One per analytical batch before any samples are run for the batch period. One Black per MDL if using 7 days study.	No analytes detected >RL. All surrogate and internal standard meet QC.	If no detects in the batch, note in corrective action. If positive detects in a sample, re-extract the sample in a new batch.	
		LCS and LCSD	One LCS and LCS duplicate per analytical batch	Refer to Appendix A Table A.1.	If <30% negative recovery, correct problem and re-extract the batch. If >30% positive recovery and analyte not detected in batch, note in corrective action.	If unable to re-analyze, flag with a "J"
		Surrogate spike	Every sample, spiked sample, standard, and method blank	Refer to Appendix A Table A.1.	If LCS is in control comment possible matrix problem note in corrective action. One surrogate may fail if other surrogates pass QC.	
		Matrix spike/ Spike Duplicate	Once per batch	Refer to Appendix A Table A.1.	If LCS is in control then method specifies to comment possible matrix problem and note in corrective action.	
		Retention time for compounds	Per analysis	Within 5 sec of daily CCV	Rerun samples	

Appendix A – Quality Assurance Criteria for Method EPA 525.2*

Table A.1 - Quality Assurance Criteria for EPA 525.2

QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
***LCS/LCSD MS/MSD**	Di(2-ethylhexyl)adipate	70	-	130	13.8
	Di(2-ethylhexyl)phthalate	75	-	126	26
	Hexachlorocyclopentadiene	70	-	123	13.6
***Surrogates**	1,3-Dimethyl-2-nitrobenzene	70	-	130	NA
	(1,3-Dimethyl-2-nitrobenzene as µg/L)	3.5	-	6.5	
	Pyrene-d10	82	-	115	
	(Pyrene-d10as µg/L)	4.12	-	5.75	
	Triphenyl Phosphate	76	-	130	
	(Triphenyl Phosphate as µg/L)	3.81	-	6.5	
****Internal Standards**	All Internal Standard	> 70% Recovery			NA

**LCS/LCSD recovery and precision limits, and surrogate recovery limits based on control charts of data collected from 1/1/2019 to 12/31/2020.*

***The Internal Standard recovery is relative to the Fortification Standard.*

Updates
Revised for online revision. Appendix A added.