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Determination of Chlorinated Herbicide Acids - EPA Method 515.4

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1 Scope and Application

1.1 A 40mL volume of sample is adjusted to pH ≥ 12 with 4 N sodium hydroxide solution and allowed to sit for one hour at room temperature to hydrolyze derivatives. Following hydrolysis, a wash step using a hexane: MTBE mixture is performed as a sample cleanup and to remove Dacthal. The aqueous sample is then acidified with sulfuric acid to a pH < 1 and extracted with 4mL of methyl tert-butyl ether (MTBE). The chlorinated acids that have been partitioned into the MTBE are then converted to methyl esters by derivatization with diazomethane. The target esters are separated and identified by capillary column gas chromatography using an electron capture detector (GC/ECD). Analytes are quantified using a procedural standard calibration technique with an internal standard. Calibration standards are derivatized and taken through the sample extraction procedure.

1.2 This method is restricted to analysts who have completed the requirements of the initial demonstration SOP. See reference 13.2.

1.2.1 Method 515.4 requires ±20% recovery and 20% RSD for initial demonstrations. See Reference 13.1, Section 9.2

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control definitions.

2.2 Refer to GA EPD Laboratory SOP - Organics Data Validation, SOP 1-052, online revision.

3 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that may lead to discrete artifacts and/or elevated baselines in the chromatograms.

3.2 Glassware must be scrupulously cleaned with hot water and detergent followed by de-ionized water then rinsed with methanol followed by acetone.

3.3 The use of high purity reagents and solvents is absolutely necessary to minimize interference problems.

3.4 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes.

3.5 Matrix interferences may be caused by containments that are co-extracted from the sample.

3.6 All samples, standards, and extracts must be protected from light by using amber vials or wrapping clear sample bottles or vials with aluminum foil. A dark refrigerator is also appropriate.

3.7 Interferences by phthalates esters can pose a major problem in pesticide analysis when using an electron capture detector (ECD). These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates that are easily extracted or leached during laboratory operation. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive purification of reagents and glassware may be required to eliminate background phthalate contamination.

4 Safety

4.1 Refer to Georgia EPD Laboratory Chemical Hygiene Plan, online revision.

5 Apparatus and Equipment

5.1 Sample containers– Amber glass bottles, approximately 60mL, fitted with a PTFE (polytetrafluoroethylene) lined screw caps.

5.2 Extraction Vial – 60mL clear glass vials with PTFE lined screw caps

5.3 Auto-sampler vials - 2.0mL vials with screw or crimp cap and a PTFE faced seal.

5.4 Standard Solution Storage Containers – 10-20 mL amber glass vials with PTFE lined screw caps.

5.5 Clear vials – 7mL glass, disposable, with PTFE lined screw caps for extract and drying and derivation.

5.6 Wide range pH paper or strips. 0-14

5.7 Pipets: Pasteur, disposable glass

5.8 Pipettes – Class A, 2.0 mL and 4.0 mL glass, or adjustable volume dispensers.

5.9 Volumetric flasks – Class A, suggested sizes 5mL, 10mL, and 100mL.

5.10 Micro-syringes – Various sizes

5.11 Balance – Analytical, capable of weighing to the nearest 0.0001g.

5.12 Diazomethane generator. Refer to Reference 13.11.

5.13 Gas Chromatograph:

5.13.1 Capillary GC (Perkin Elmer Gas Chromatograph XL or better or equivalent), the gas chromatograph must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column split/splitless injector.

5.13.2 Electron Capture Detector

5.13.3 Column #1: 30m, 0.53mm, ID RTX-1701 or equivalent

5.13.4 Column #2: 30m, 0.53mm, ID DB-5 or equivalent

5.14 Detergent: Steris Lablenz or equivalent

5.15 10mL, 50mL Graduated Cylinders, Class A
5.16 1-10mL Dispensette bottle top dispenser

6 Reagents and Standards

6.1 Reagent Water – Purified water which does not contain any measureable quantities of target analytes or interfering compounds for each compound of interest. (Deionized, HPLC, Milli-Q water or equivalent. Milli-Q water has a resistivity of 18 [MΩ·cm] or greater at 25°C and a TOC of 50µg/L or less).

6.2 Methyl tert-Butyl Ether (MTBE) – High purity, demonstrated to be free from analytes and interferences (HPLC grade or better).

6.3 Acetone – High purity, demonstrated to be free from analytes and interferences (HPLC grade or better).

6.4 Carbitol (Diethylene Glycol Monoethyl Ether) – High purity, demonstrated to be free from analytes and interferences (HPLC grade or better).

6.5 Hexane:MTBE (90:10, v/v) Wash Solvent - High purity, demonstrated to be free from analytes and interferences (HPLC grade or better).

6.6 Hexane - High purity, demonstrated to be free from analytes and interferences (HPLC grade or better).

6.7 Sodium Sulfate, $NaSO_4$ – Suitable for Pesticide Residue Analysis, granular, anhydrous. (Fisher Brand or equivalent): sodium sulfate is baked at 400°C for four hours.

6.8 Acidified Sodium Sulfate:

6.8.1 Acidify by slurrying 100g sodium sulfate with enough ethyl ether to just cover the solid. Add 0.5mL of concentrated sulfuric acid drop wise while mixing thoroughly. Remove the ether under vacuum. Mix 1g of the resulting solid with 5mL of reagent water and measure the pH of the mixture. The pH must be at/or below pH of 4. If the pH is above 4, add a few drops of sulfuric acid and mix thoroughly. Repeat until the pH is at or below 4. Store in an oven at 100º C to keep the reagent dry.

6.9 Copper II Sulfate Pentahydrate, $CUSO_4$-$5H_2O$ – ACS reagent grade or better.

6.10 4N Sodium Hydroxide Solution

6.10.1 Dissolve 16g of sodium hydroxide (NaOH) pellets (ACS grade or equivalent) in reagent water and dilute to 100mL final volume. (If available, a commercially prepared, reagent grade 4N NaOH solution may be used to achieve a pH greater than 12 for the extraction.)

6.11 Potassium Hydroxide solution (37% w/v) "Take out" needed for other type generator

6.11.1 Dissolve 12g of potassium hydroxide (KOH) pellets (ACS grade or equivalent) in reagent water and dilute to 20mL final volume.

6.12 Sodium Sulfite, Na_2SO_3 – Reagent grade or equivalent, used as a de-chlorinating agent in this method.

6.13 Sulfuric Acid – Concentrated, ACS reagent grade.

6.14 Silica gel – ACS reagent grade, 35-60 mesh.

6.15 Diazomethane – In house solution used for the methylation of herbicide extracts. Refer section 13.11 or SOP 1-043 Rev. 2 or later

6.16 Stock Standard Solutions: **All standards that are made for the 515.4 analysis are to have a 6 month expiration date from the opening of the vendor stock ampule. (A**

vendor mix may also be used. If it is used, start from section 6.15.2 with the final concentration. All vendor stocks are in the acid form.)

6.16.1 Primary Stock #1 Solution: 1.00-10.0µg/mL is made up from a vendor stock of a pre-made mix solution.

Table 6.16.1.1 – 515.4 Primary Stock #1 Solution in Methanol (1st Dilution)			
Compound Name	**Stock Concentration (µg/mL)**	**Aliquot (mL)**	**Final Concentration (µg/mL)**
Dalapon	100	1.00	10.0
Dicamba	50		5.00
2,4-D	100		10.0
PCP	10		1.00
Silvex	25		2.50
Dinoseb	100		10.0
Picloram	50		5.00
Total Volume of Standard Aliquots		1.00 mL	
Addition of Methanol to Standard Aliquots		9.00 mL	
Final Volume of Spiking Stock Standard in Acetone		10mL	

6.16.2 Spiking Stock Solution: 1.0-10.0µg/mL is made up from Primary stock #1 at 10.0-100µg/mL.

Table 6.16.2.1 – 515.4 Spiking Stock Solution in Methanol (2nd Dilution)			
Compound	**Initial Concentration (µg/mL)**	**Aliquot (mL)**	**Final Concentration (µg/mL)**
Dalapon	10.0	1.0	1.00
Dicamba	5.00		0.500
2,4-D	10.0		1.00
PCP	1.00		0.100
Silvex	2.50		0.250
Dinoseb	10.0		1.00
Picloram	5.00		0.500
Total volume of Standard Aliquot		1.00 mL	
Addition of Methanol to Standard aliquots		9.00 mL	
Final Volume of Spiking Stock Solution in Methanol		10.0 mL	

6.16.3 ICV Stock #1 Solution: 100-1000µg/mL is made up from a vendor stock of a pre-made mix solution. **NOTE:** ICV vendor stocks may not have the same concentration as the primary vendor stocks. (All ICV vendor stocks are in the acid form.) It may be necessary to skip this step and move to the ICV Spiking Solution seen in section 6.16.4 if primary vendor stock is a different concentration from listed in table 6.16.4.1

Table 6.16.3.1 – 515.4 ICV Stock Solution #1 in Methanol (1st Dilution)			
Compound Name	**Stock Concentration (µg/mL)**	**Aliquot (mL)**	**Final Concentration (µg/mL)**
Dalapon	1000	1.00	100
Dicamba	500		50
2,4-D	1000		100
PCP	100		10
Silvex	250		25
Dinoseb	1000		100
Picloram	500		50
Total Volume of Standard Aliquots		1.0mL	
Addition of Methanol to Standard Aliquots		9.0mL	
Final Volume of ICV Stock Solution #1 in Acetone		10mL	

6.16.4 ICV Stock #2 Solution: 1.00-10.0µg/mL made up from vendor stock of a pre-made mix solution. **NOTE**: This standard will be made in one 10 mL volumetric flask.

Table 6.16.4.1 – 515.4 ICV Stock Solution #2 in Methanol (2nd Dilution)			
Compound Name	**Stock Concentration (µg/mL)**	**Aliquot (mL)**	**Final Concentration (µg/mL)**
Dalapon	100	1.00	10.0
Dicamba	50		5.00
2,4-D	100		10.0
PCP	10		1.00
Silvex	25		2.50
Dinoseb	100		10.0
Picloram	50		5.00
Total Volume of Standard Aliquots		1.00 mL	
Addition of Methanol to Standard Aliquots		9.00 mL	
Final Volume of ICV Stock Solution #2 in Methanol		10mL	

6.16.5 ICV Spiking Stock Solution: 1.0-10.0µg/mL is made up from ICV stock #2 at 10.0-100µg/mL.

Table 6.16.5.1 – 515.4 ICV Spiking Stock Solution in Methanol (2nd Dilution)

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Dalapon	10.0	1.0	1.00
Dicamba	5.00		0.500
2,4-D	10.0		1.00
PCP	1.00		0.100
Silvex	2.50		0.250
Dinoseb	10.0		1.00
Picloram	5.00		0.500
Total volume of Standard Aliquot		1.0mL	
Addition of Methanol to Standard aliquots		9.0mL	
Final Volume of ICV Spiking Stock Solution in Methanol		10.0mL	

6.16.6 Surrogate Spiking solution #1. 100µg/mL made up from vendor stock at 1000 µg/mL. (Surrogate is in the acid form)

Table 6.16.6.1 – 515.4 Surrogate Spiking Stock #1 Solution in Methanol (1st Dilution)

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS: Di-chloroacetic acid (DCAA)	1000	1.00	100
Total volume of Standard Aliquot		1.00 mL	
Addition of Methanol to Standard aliquots		9.00 mL	
Final Volume of Surrogate Spiking Solution #1		10.0 mL	

6.16.7 Surrogate Spiking solution #2. 10µg/mL made up from vendor stock at 100 µg/mL.

Table 6.16.7.1 – 515.4 Surrogate Spiking Solution in Methanol (2nd Dilution)

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS: Di-chloroacetic acid (DCAA)	100	1.00	10.0
Total volume of Standard Aliquot		1.00 mL	
Addition of Methanol to Standard aliquots		9.00 mL	
Final Volume of Surrogate Spiking Solution #2		10.0 mL	

6.16.8 Internal Standard Spiking solution. 250 µg/mL made up from vendor stock at 1000µg/mL.

Table 6.16.8.1 – 515.4 Internal Standard Spiking Stock #1 Solution in Acetone			
Compound	**Initial Concentration (µg/mL)**	**Aliquot (mL)**	**Final Concentration (µg/mL)**
IS: 4,4'-dibromooctafluoro-byphenyl (DBOFBP)	1000	2.50	250
Total volume of Standard Aliquot		2.50 mL	
Addition of MtBE to Standard aliquots		7.50 mL	
Final Volume of Internal Standard Spiking Stock #1		10.0mL	

Table 6.16.8.2 – 515.4 Internal Standard Spiking Stock #2 Solution in Acetone			
Compound	**Initial Concentration (µg/mL)**	**Aliquot (mL)**	**Final Concentration (µg/mL)**
IS: 4,4'-dibromooctafluoro-byphenyl (DBOFBP)	250	1.00	25.0
Total volume of Standard Aliquot		1.00 mL	
Addition of MtBE to Standard aliquots		9.00 mL	
Final Volume of Internal Standard Spiking Stock #2		10.0 mL	

Table 6.16.8.3 – 515.4 Internal Standard Spiking Stock #3 Solution in Acetone			
Compound	**Initial Concentration (µg/mL)**	**Aliquot (mL)**	**Final Concentration (µg/mL)**
IS: 4,4'-dibromooctafluoro-byphenyl (DBOFBP)	25.0	1.00	2.50
Total volume of Standard Aliquot		1.00 mL	
Addition of MtBE to Standard aliquots		9.00 mL	
Final Volume of Internal Standard Spiking Stock #3		10.0 mL	

6.16.8.1 The addition of 1 mL of the primary dilution standard (2.5 µg/mL) to 99-mL MtBE results in a final internal standard concentration of 0.025 µg/mL.

6.16.9 MDL: The Spiking Stock Solution in Sec. 6.16.2 is used for the MDL spike. The MDL is spiked at a volume of 8µL of the Spiking Stock Solution that is equal to the same concentrations as Level 1 on the calibration curve. See Table 8.1.1, Level 1.

Table 6.16.9.1 – 515.4 MDL Level in MtBE			
Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Dalapon	1.00	0.008	0.00200
Dicamba	0.500		0.00100
2,4-D	1.00		0.00200
PCP	0.100		0.000200
Silvex	0.250		0.000500
Dinoseb	1.00		0.00200
Picloram	0.500		0.00100
Final Volume of extracted MDL in MtBE w/ DBOFBP		4 mL	

7 Sample Collection

7.1 Drinking water samples for EPA Method 515.4 are collected in pre-certified 60mL amber glass bottles (to shield from light) with Teflon lined screw caps and preserved with 3 mg sodium sulfite. The 3 mg of Sodium sulfite is sufficient to neutralize up to 5mg/L (ppm) residual chlorine.

7.2 A residual chlorine check is done in the field by the collector. The collector writes down the numerical value for residual chlorine in ppm on the sampling form.

7.3 The shipping and receiving staff log in the samples and enter the information for residual chlorine in the DNR_LAB Labworks field. The analyst prints a backlog to determine samples to be analyzed.

7.4 The backlog report contains the residual chlorine concentration determined by the collector. If the residual chlorine measured by the collector is less than 22 ppm, the 3mg of Sodium sulfite in the vial was sufficient to neutralize all of the residual chlorine in the sample.

7.4.1 If the collector reports 5ppm or more residual chlorine, the sample must be recollected.

7.5 Samples are cooled to 0-6º C or below (not frozen) after sample collection. Three vials are to be collected for every sample. Samples must be extracted within 14 days of collection and the extracted samples must be analyzed within 21 days. Extract vials should remain stored at 0º C or below.

8 Calibration

8.1 Calibration Standards

8.1.1 Calibration Standards, CCCs, and ICVs are prepared in the same manner as LCS samples and carried through the entire procedure (see section 10.4). This results in standards being in the methyl ester form in the final extract. Concentrations are calculated based on the acid forms of the compounds for all standards, QC samples and standards.

8.1.2 The calibration curve consists of the calibration standards at the following concentrations (µg/mL): Please aliquot 8 µL of Spiking stock for Level 1, 50 µL of Spiking stock for Level 2, 100 µL of Spiking stock for Level 3, 200 µL of Spiking stock for Level 4, 300 µL of Spiking stock for Level 5, and 400 µL of Spiking stock

for Level 6 listed under each level to make the appropriate calibration level. Add 10 µL of surrogate spiking solution to each of the levels below.

Table 8.1.1 - Calibration Curve for Herbicides as acids **(concentration of table is in µg/mL) NOTE: Use Spiking Stock Solution in Sec. 6.16.2 for each individual level. Final concentration is in 4 mL of MtBE extract**						
Compound	**Level 1 (8µL)**	**Level 2 (50µL)**	**Level 3 (100 µL)**	**Level 4 (200µL)**	**Level 5 (300µL)**	**Level 6 (400 µL)**
Dalapon	0.00200	0.0125	0.0250	0.0500	0.0750	0.100
Dicamba	0.00100	0.00625	0.0125	0.0250	0.0375	0.0500
2,4 D	0.00200	0.0125	0.0250	0.0500	0.0750	0.100
PCP	0.000200	0.00125	0.00250	0.00500	0.00750	0.0100
Silvex	0.000500	0.003125	0.00625	0.0125	0.01875	0.0250
Dinoseb	0.00200	0.0125	0.0250	0.0500	0.0750	0.100
Picloram	0.00100	0.00625	0.0125	0.0250	0.0375	0.0500
DCAA - SS	0.025	0.025	0.025	0.025	0.025	0.025
DBOFBP - IS	0.025	0.025	0.025	0.025	0.025	0.025

Table 8.1.2 - Herbicide Calibration Curve Levels as acids (concentration of table is in µg/L) NOTE: Use Primary Stock #1 Solution in Sec. 6.16.1 for each individual level. Final volume is in 4 mL of MtBE extract							
Compound	**Level 1 (8µL)**	**Level 2 (50µL)**	**Level 3 (100 µL)**	**Level 4 (200µL)**	**Level 5 (300µL)**	**Level 6 (400 µL)**	**EPA MCL**
Dalapon	0.200	1.25	2.50	5.00	7.50	10.0	200
Dicamba	0.100	0.625	1.25	2.50	3.75	5.00	
2,4 D	0.200	1.25	2.50	5.00	7.50	10.0	70
PCP	0.0200	0.125	0.250	0.500	0.750	1.00	1
Silvex	0.0500	0.3125	0.625	1.25	1.875	2.50	50
Dinoseb	0.200	1.25	2.50	5.00	7.50	10.0	7
Picloram	0.100	0.625	1.25	2.50	3.75	5.00	500
DCAA - SS	25.0	25.0	25.0	25.0	25.0	25.0	
DBOFBP - IS	25.0	25.0	25.0	25.0	25.0	25.0	

8.2 Initial Calibration

8.2.1 A six point calibration is performed for all single peak components (see Table 8.1.2 for standard concentrations). The calibration system uses traceable certified standards. The calibration is an internal standard, procedural calibration.

8.2.2 The calibration is an internal standard calibration based on mean relative response factors (see Calculations 11.1 – 11.2) with a relative standard deviation (%RSD) of < 30% (see calculation 11.3) or a linear fit internal standard curve with a correlation coefficient (r^2) of ≥ 0.960 (or a coefficient of variation (r) ≥ 0.980).

8.3 First Order Linear Calibration using Least Squares Regression:

8.3.1 If linear regression is used, linearity through the origin cannot be assumed in a linear squares fit. The instrument responses versus the concentrations of the standards for the 6 points is determined using the instrument data analysis software and the regression will produce the slope and intercept terms for a linear equation. The regression calculation will generate a correlation coefficient (r) that is a measure of "goodness of fit" of the regression line to the data. A value of 1.0 is a perfect fit, 515.4 requires a correlation coefficient, $r^2 \geq 0.960$ or a coefficient of variation $r \geq 0.980$. See Calculations 11.4.

8.3.2 Alternatively, Second Order Quadratic Fit may be used with an acceptable correlation of coefficient of $r^2 \geq 0.960$ or a coefficient of variation $r \geq 0.980$. See Calculations 11.5.

8.3.3 It is optional to force or not to force the origin of the curve.

8.4 Calibration Verification

8.4.1 Second source calibration verification (ICV) must be analyzed after initial calibration and at least once per quarter, even if the system has not been recalibrated. All analytes must be within ± 30% Drift of the expected values. See Calculations 11.9.

8.5 Record Keeping

8.5.1 Documentation of an instrument calibration is reviewed for adherence to quality criteria and archived with the project records.

8.6 Daily Calibration Verification and Continuing Calibration:

8.6.1 A continuing calibration check standard (CCC) ensures the instrument target compound retention times and quantitation parameters meet method performance criteria. Preceding each analysis set, after every tenth sample analysis and after the final sample analysis, a calibration standard, alternating between a mid-level CCC and a high-level CCC, should be analyzed as a continuing calibration check to verify that instrument calibration accuracy does not exceed ± 30% Drift from the expected values. See calculation 11.9.

8.6.2 If a valid CCC cannot be achieved, then the instrument is considered to be out of calibration for the compounds in this method and the instrument must be recalibrated.

8.6.3 When the acceptance criteria for the continuing calibration verification (CCC) are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated, and accepted.

8.7 Daily Laboratory Performance Check (LPC)

8.7.1 A laboratory performance check (LPC) standard must be run at the beginning of every batch sequence. This standard must be at or below the RL and must have a percent recovery of 50-150%.

8.7.2 The LPC is equivalent to a Low CCC as specified in Table 14 of EPA Method 515.4, Rev. 1.0, 2000.

8.8 Daily Retention Time Update

8.8.1 Retention Times (RT) are updated once per 24 hour period when ran on a GC analyses are performed. The first CCC is processed using Totalchrom or an equivalent software. The new RT's are saved in a copy of the processing method used for analyzing this batch of samples. To the existing processing method an extension is added by using – Month-Day-Year. Then hard copies of the calibration parameters are added to the data package for that batch of samples. (**NOTE**: If an analytical sequence is stopped for any reason longer than a typical work shift a new retention time update is necessary for the next sequence.)

8.9 Retention Time Windows

8.9.1 Once per year or after major maintenance, retention time windows must be established. The width of the retention time windows for each analyte, surrogate, and internal standard is defined as ± 3 times the standard deviation of the mean absolute retention time established over the course of a day (24-hours) for all CCCs analyzed during that period. See Calculations 11.6.

8.10 Assessing the Internal Standard Response:

8.10.1 The response of the internal standard must be monitored for all samples and standards analyzed by this method. The internal standard response should not deviate from the mean internal standard response of the calibration curve standards by more than 50% on the quantitative column/detector. If the deviation is greater than 50% for this aliquot the sample is either re-extracted if within method hold times or recollected. A re-analyzed sample aliquot should be followed by a CCC to validate the calibration of the instrument. This method allows for a second re-injection of a previously run and validated CCC. If this CCC fails the IS acceptance criterion for quantitative column/detector, the instrument is considered to be out of calibration. A new calibration must be performed and validated before samples may be analyzed using this instrument.

8.11 Sample Concentration:

8.11.1 Sample results are expressed in µg/L.If an analyte response is calibrated by Mean Relative Response Factor, ($\overline{RRF}$)(see Calculations 11.2), the chromatographic software calculates the sample concentrations per calculations per calculation 11.10. Results are in µg/mL.

8.10.3 If an analyte response is calibrated by linear regression, the chromatographic software calculates the sample concentrations per calculation 11.11. Results are in µg/mL.

8.10.4 The sample concentration is calculated per Calculations 11.11.2.

8.10.5 If dilutions are required, see Calculations 11.11.3.

9 Quality Control

9.1 Refer to Table 14.1 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 A Method Detection Limit study is performed once per year. See Reference 13.6.

9.2.1 A Method Detection Limit study for all analytes must be performed initially, after major instrument repairs or changes to extraction procedures. MDL studies performed for these purposes can be done by the extraction and analysis of 7 samples and 7 blanks over 3 separate days.

9.2.2 The 7 MDL sample study is performed by extracting 7 spiked MDL samples, MDL_{Spike}, spiked at the lowest point of the curve and extracted along with 7 blank MDL samples, MDL_{Blank}. These sets of spiked and blank samples are extracted over 3 separate days and analyzed over a period of 3 separate days. There is a non-analysis day between each of the 3 days. A total of 14 samples are extracted, 7 spiked and 7 blank.

9.2.3 **On a continuous basis,** MDLs are performed by extraction and analysis of one sample spiked as an MDL_{Spike}, at the lowest point of the curve and extracted with every batch of samples along with the method blank, MDL_{Blank}, per each batch of samples. The results of the MDL_{Spike} and MDL_{Blank} will be entered into LabWorks using the blank test code $B_515E, and the MDL test code, $ML515E, and the MDL Spiked Amount, $MA515E. MDL reports will be pulled from LabWorks at a minimum of once per year (See SOP reference 13.6).

9.2.4 The higher value of the 2 MDLs, MDL_{Blank} or MDL_{Spike} will be used as the reporting MDL.

9.3 Refer to References 13.2 for training and certification procedures.

9.4 Refer to Reference 13.3for control charting procedures.

9.5 Control Limits

9.5.1 Default control limits for recovery are based on Section 9.3.2 of EPA Method 515.4. See reference 13.1. Precision limit defaults are set by the EPD Laboratory. In-house limits based on control charts may never exceed the default limits. These control limits are presented to assist in defining control limits established with control charts and are not used as batch acceptance criteria.

Note: Analysts must use the control limits presented in Appendix A. Those limits cannot exceed the default limits presented in Table 0

Table 9.5.1.1 - Default Limits Criteria for EPA Method 515.4

QC type	Analytes	Default LCL %Recovery	Default UCL %Recovery	Precision (%RPD)
LCS/LCSD & MS/MSD	Dalapon	70	130	30
	Dicamba	70	130	30
	2,4 D	70	130	30
	PCP	70	130	30
	Silvex	70	130	30
	Dinoseb	70	130	30
	Picloram	70	130	30
Surrogate	SS: 2,4-Dichlorophenylacetic acid (DCAA)	70	130	
Internal Standard	IS: 4,4'-dibromooctafluoro-byphenyl (DBOFBP)	± 50% of average peak area count		N/A

*LCS/LCSD and Surrogate recovery ranges and LCS/LCSD precision ranges are determined by control charting per reference 13.3.

**Method 515.4 specifies static Matrix Spike / Matrix Spike Duplicate recovery ranges of 70-130%. The EPD Lab sets a static Matrix Spike precision range of 0-30%.

9.6 For this method, an analytical batch considered to be 1 to 20 field samples plus QC and calibration samples. See Section 10.3.

9.7 One method blank is required per analytical batch. See section 10.3 for blank preparation.

9.8 Because method 515.4 utilizes a procedural curve, the method considers CCCs and LCSs to be the same. The EPD laboratory analyses separate CCCs and LCSs.

9.9 One LCS/LCSD pair is required for each analytical batch.

9.9.1 EPA Method 515.4 requires LCS to be analyzed at a frequency rate of 5% of all samples (see Reference 13.1, Section 9.3). The LCSD is used to satisfy precision requirements.

9.9.2 The EPD Laboratory has set the default LCS recovery ranges to be equal to the CCC acceptance range of 70%-130%. The LCS ranges are adjusted overtime through the use of control charts. See Reference 13.3.

9.9.3 The EPD Laboratory has set the LCSD recovery ranges to be equal to the LCS recovery ranges.

9.9.4 The EPD Laboratory sets the LCS/LCSD default precision to be 0-30% RPD. LCS/LCSD precision ranges are adjusted over time through the use of control charts. See reference 13.3

9.10 One MS/MSD pair is required for each analytical batch.

9.10.1 Matrix Spike (MS/MSD) is to be analyzed at a frequency of 5% of all samples.

9.10.2 Per method 515.4, section 9.9, the MS/MSD recovery ranges are static at 70%-130%.

9.10.3 Per method 515.4, section 9.9, the precision ranges are static at 0-30%RPD.

9.10.4 *Note: EPA Method 515.4, Revision 1.0, April 2000 states that Field Duplicates are required for this method however Section 9.9 indicates that the laboratory's MS and MSD samples fulfill this requirement.*

9.11 Surrogate recovery criteria are static at 70%-130% per method 515.4, section 9.8.

9.12 Internal standard response must be ±50% of the initial calibration average response.

9.13 Performance Test (PT) Sample:

9.13.1 EPA requires that the Laboratory perform a PT sample every 12 months to maintain certification in EPA method 515.4. Those PT result must fall within acceptable control limits for the PT testing facility. If those results are not within acceptable control limits the Laboratory will have a second chance to pass the PT study within the same 12 months of the study. If the results did not fall within acceptable control limits for the study over the 12-month testing period, the laboratory will be downgraded for those compounds listed in this SOP. With the failure of this nature the laboratory must notify all drinking water facilities within 30 days of the failure after the 12-month period has passed. It is not until the laboratory passes a PT study will the laboratory be able to test for those compounds of interest again.

9.14 Method Detection Limit Study (MDL):

9.14.1 MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.14.2 The actual MDL varies depending on instrument and matrix.

9.14.3 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.

9.14.4 An MDL study may be done two different ways. The two different ways are considered and initial MDL study and a continuous MDL study. Both ways will be explained below.

9.15 Initial MDL study:

9.15.1 An initial MDL study may occur when a new instrument is brought online, changes to the method (which affect the compound of interest's peak area), and lastly major instrument repairs have been made.

9.15.2 An initial MDL study will consist of the following operating parameters, 7 MDL samples and 7 MDL blanks. 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 blanks.

9.16 Continuous MDL study:

9.16.1 A Continuous MDL study is preferred over the initial except in a few cases. For a continuous MDL study to be used on an instrument it must have a minimum of 7 MDL samples and 7 MDL blanks extracted over the course of multiple batches over a year. It is required that at a minimum 2 MDL samples and 2 MDL blanks must be ran per quarter per instrument. If this requirement is not met, then the initial MDL study must be performed for that instrument. (See section 9.15.2 for requirements.)

9.16.2 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.

9.16.3 The results of the MDLBlank will be entered into Labworks using the Method Blank test code, $B_515E. The MDLSpike result will be entered using the $ML515E. The MDL Spiked Amount will be entered into the test code $MA515E. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-515E.

9.16.4 MDL studies must be pulled on a yearly basis or an initial MDL study must be performed before the current MDLs for the instrument expire.

10 Procedure

10.1 Remove the sample bottles, standards, and reagents from cold storage, and allow samples to equilibrate to room temperature prior to sample preparation and/or analysis.

10.2 Place 40mL of the water sample into a pre-cleaned 60mL, glass vial with a PTFE lined screw cap using a graduated cylinder.

10.3 Form a batch consisting of a Blank, Laboratory Control Sample (LCS), Laboratory Control Sample Duplicate (LCSD), Matrix Sample (MS), Matrix Sample Duplicate (MSD), and up to 20 samples. The blank is defined as 40mL of laboratory DI or Milli-Q water (or equivalent). The LCS/LCSD are made up 40mL of DI or Milli-Q water (or

equivalent) spiked with 200µL of a Spiking Stock solution at 0.1-1.0µg/mL of the Herbicides standard. The MS/MSD are 40mL aliquots of the designated batch QC sample spiked with 200µL of a Primary Stock solution at 0.1-1.0µg/mL of the Herbicides standard.

10.4 Add 10uL of surrogate standard (100µg/mL, 2,4-dichlrophenylacetic acid in acetone) to the aqueous sample.

10.5 Add 1mL, of the 4N NaOH solution to each vial. Check the pH with pH paper or a pH meter. If the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 4N NaOH solution. Let the sample sit at room temperature for 1 hour, shaking the contents periodically. NOTE: Since many of the herbicides contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to extraction. This step must be included in the analysis of all extracted field samples, LCSs, MSs and calibration standards. Failure to perform this step may result in data that are biased low for some of the targets in the field samples.

10.6 Following hydrolysis, add 5mL of (90:10, v/v) hexane:MTBE and shake vigorously for three minutes. Allow the phases to separate for approximately 5 minutes then remove and discard the top hexane/MTBE layer. This wash aids in the sample cleanup and removes Dacthal from the sample which would interfere with the quantitation of the Dacthal metabolites.

10.7 Adjust the pH to approximately 1 by adding concentrated sulfuric acid. Cap, shake and then check the pH with a pH paper or a meter. Add additional sulfuric acid as needed to properly adjust the pH.

10.8 Quickly add approximately 2g of Copper II Sulfate Pentahydrate and shake until dissolved. This colors the aqueous phase blue and allows the analyst to better distinguish between the aqueous phase and the organic phase in this micro-extraction. (**NOTE**: This may not be necessary because the use of Copper II Sulfate does not change to chemistry in the extraction. It is for differentiating the organic layer from the aqueous layer.)

10.9 Quickly add 16g of muffled sodium sulfate and shake until almost dissolved. Sodium sulfate is added to increase the ionic strength of the aqueous phase and thus further drive the chlorophenoxy acids into the organic phase. The addition of the salt also decreases the solubility of MTBE in the aqueous phase and allows greater volumetric recovery. The addition of the salt and the copper II sulfate pentahydrate should be done quickly so that the heat generated from the addition of the acid will dissolve the salts.

10.10 Add exactly 4.0mL of MTBE fortified with internal standard and shake vigorously for three minutes.

10.11 Allow the phases to separate for 5 minutes.

10.12 Using a Pasteur pipette, transfer the sample extract to a 7mL screw cap vial. Add 0.6g of acidified sodium sulfate and shake. This step is included to dry the MTBE extract.

10.13 Using a Pasteur pipette, transfer the extract to a second 7mL glass vial.

10.14 Add 250µL of the diazomethane solution to each vial. The contents of the vial should remain slightly yellow in color indicating an excess of diazomethane. Additional diazomethane may be added if necessary. Let the esterification reaction proceed for 30 minutes.

10.15 Remove any unreacted diazomethane by adding 0.1g of silica gel. Effervescence is an indication that excess diazomethane was present. Allow the extract to sit for 30 minutes.

10.16 Transfer extract to an auto-sampler vial. A duplicate vial may be filled using the excess extract.

10.17 Analyze the sample extracts as soon as possible.

10.18 Dilutions

10.18.1 Upon analysis of the extract, if a target compound response is greater than that of the highest standard of the calibration curve, the sample must be diluted with the final extraction solvent (MTBE fortified with internal standard) so that, upon analyzing the dilution (in a valid analysis sequence), the target response is between the lowest concentration standard (or the reporting limit, whichever is higher) and the highest concentration stand

10.19 The sample extract may be stored up to 21 days if kept at 0ºC or less. Keep the extracts in an amber glass vials with PTFE lined caps.

10.20 PT Study:

10.20.1 Once every 12-month period a PT study must be performed. An accredited testing facility will send the Laboratory an ampule for the compounds of interest listed in this SOP. The testing facility will send direction on how perform the dilutions necessary for the Analyst to spike into a sample. (Note: Please include a copy of instructions from the facility in the batch folder.)

11 Calculations

11.1 Relative Response Factor (*RRF*):

11.1.1 Calculate the relative response factors (*RRF*) for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

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

11.1.2 Where:

RRF = Relative response factor

A_x = Area of the peak for the compound to be measured

A_{is} = Area of the peak for the internal standard

C_{is} = Concentration of internal standard spiking mixture

C_x = Concentration of the compound in the calibration standard

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 sample extract and QC sample extract introduced into the GC is the same for each analysis. C_{is} and C_x must be in the same units.

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

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

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

11.2.2 Where:

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

11.3 Percent Relative Standard Deviation (*%RSD*):

11.3.1 Using the RRFs from the initial calibration, calculate the *%RSD* for all target compounds using the following equations:

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

and

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

11.3.2 Where:

δ_{n-1} = Sample standard deviation of initial response factors (per compound)
RRF_i = Relative response factor at a concentration level
$\overline{RRF}$ = Mean of initial relative response factors (per compound)
n = Number of values

11.4 First Order Linear Regression Response Equation:

$$Y = ax + b$$

11.4.1 This rearranges to:

$$x = Y - b/a$$

11.4.2 Where:
Y = Instrument response
a = Slope of the line

b = Intercept
x = Concentration in the extract or standard

11.4.3 For an internal standard calibration:

$$\frac{A_x}{A_{is}} = a\left(\frac{C_x}{C_{is}}\right) + b$$

11.4.4 Where:
A_x = Area of the peak for the compound to be measured
A_{is} = Area of the peak for the internal standard
C_{is} = Concentration of internal standard spiking mixture
C_x = Concentration of the compound in the calibration standard
a = Slope of the line
b = Intercept

11.4.5 This rearranges to:

$$C_x = C_{is}\left(\left(\frac{A_x}{A_{is}}\right) - \left(\frac{b}{a}\right)\right)$$

11.5 Second Order Quadratic Fit Equation

11.5.1.1 $Y = ax^2 + bx + c$

11.5.1.2 Where:
Y = Instrument response
a = Slope of the line
b = Intercept
c = constant
x = Concentration in the extract or standard

11.5.2 Subtract Y from c to get modified equation $0 = ax^2 + bx + c$

11.5.3 Solve for x using the quadratic formula:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

11.5.5 A positive and negative value will be generated. Use positive value.

11.6 Relative Retention Times (*RRT*):

11.6.1 Calculate the *RRT*s for each target compound over the initial calibration range using the following equation:

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

11.6.2 Where:

RT_c = Retention time of the target compound

RT_{IS} = Retention time of the internal standard

11.7 Mean Relative Retention Time:

$$\overline{RRT} = \sum \frac{RRT}{n}$$

11.7.1 Where:

$\overline{RRT}$ = Mean retention time for target compound

RRT = Retention time for the target compound

n = number of values

11.8 Dilution Factor

11.8.1 When dilutions are required, sample extracts are diluted and a dilution factor (DF) calculated. If the sample volume is not exactly 50mL, that must also be factored into the DF as follows:

$$DF = \frac{V_f}{V_{aliquot}} * \frac{V_s}{V_{ideal}}$$

11.8.2 Where:

DF = Dilution factor

V_f = Final volume after dilution

$V_{aliquot}$ = Amount of extract diluted

V_s = Actual sample volume

V_{ideal} = Ideal sample volume of 40mL

If there is no dilution performed and a sample of exactly 40mL is used, DF = 1.

11.9 Percent Drift, %Drift

$$\%\text{Drift} = \frac{\left(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}}\right)}{\text{Concentration}_{\text{Expected}}} * 100$$

Where:
Concentration $_{Calculated}$ = Concentration calculated from result
Concentration $_{Expected}$ = Theoretical concentration of the standard

11.10 Sample Concentration Calculation for Mean Relative Response Factor Calibrations ($\overline{RRF}$) with Internal Standard:

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

11.10.1 Where:

C_x = Compound concentration
A_x = Area of the compound to be measured
A_{is} = Area of the internal standard
C_{is} = Concentration of the internal standard spiking mixture,
RRF = Mean relative response factor from the initial calibration
DF = Dilution factor. If 40 ml sample and no dilution is performed, DF = 1

NOTE: The equation above is valid assuming a consistent volume and concentration of the internal standard spiking solution throughout calibration and sample analysis.

11.11 Alternate Sample Concentration Calculation using linear regression:
Utilizing linear regression calculation 11.4.5 sample concentrations for linear regression internal standard calibrations are calculated as :

$$C_x = C_{is}\left(\frac{\left(\frac{A_x}{A_{is}}\right) - b}{a}\right) * DF$$

11.11.1 Where:

A_x = Area of the peak for the compound to be measured
A_{is} = Area of the peak for the internal standard
C_{is} = Concentration of internal standard spiking mixture
C_x = Concentration of the compound in the calibration standard
a = Slope of the line
b = Intercept
DF = Dilution factor. If 40 ml sample and no dilution is performed, DF = 1

11.11.2 Sample Concentration Calculation (µg/L):

$$\mu g/_{L} = \frac{C_s * 1000\frac{ml}{L} * V_t}{V_s}$$

Where:

C_s = Extract concentration in µg/mL
V_t = Extract volume in mL
V_s = Original sample volume in mL

Assuming an original sample volume of 100mL and an extract volume of 1mL, equation 0reduces to:

$$\mu g/_{L} = C_s * 100$$

11.11.3 Sample Concentration Adjustment for Varying Initial Volume and Dilutions:

$$\mu g/_{L_{Corrected}} = \mu g/_{L_{Uncorrected}} * \frac{(1000\ ml)(DF)}{V_s}$$

Where:

DF = Dilution Factor
V_s = Original sample volume in mL

11.12 Quality Control Calculations

$$\text{LCS/LCSD/ICV \% Recovery} = \frac{R_{spike}}{\text{Expected Result}} X\,100$$

$$\%\ \text{RPD(precision)} = \frac{\left|R_{sample} - R_{duplicate}\right|}{\left(\frac{R_{sample} + R_{duplicate}}{2}\right)} X\,100$$

Where:

R_{spike} =% recovery of spiked sample
R_{sample} =% recovery of sample
$R_{duplicate}$ =% recovery of duplicate sample

11.13 LPC Calculations

11.13.1 An LPC standard is run at the beginning of each sample sequence prior to the analysis of samples to determine sensitivity, chromatographic and column performance. The LPC is equivalent to the lowest standard on the curve.

11.13.2 *Sensitivity*

11.13.2.1 Instrument sensitivity is determined by comparing the LPC recovery of all analytes. The recovery of the analytes must be ± 50% of the true LPC value.

$$\text{LPC \% Recovery} = \frac{R_{spike}}{\text{Expected Result}} X\,100$$

11.14 Sample chromatograms generated from the processing software have calculation formulas already incorporated into the report format (see Calculations, Sections 11.10 and 11.11). Manual adjustments are required for diluted samples, or samples of other than 40mL only (see Calculations, Section 11.8). The RPD calculations are not incorporated into report formats and must be calculated manually or by the use of an Excel spreadsheet. If Excel spreadsheets are used, RPD results may be manually written on LCSD and MSD reports.

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures. SOP 6-015, online revision.

13 References

13.1 EPA Method 515.4, Revision 1.0, 2000

13.2 GA EPD Laboratory SOPs–Initial Demonstration of Capability SOP 6-001, online revision and/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, Fifth Edition, January 2005 or later.

13.6 GA EPD Laboratory SOP– Determination of Method Detection Limit, Method Detection Limit SOP 6-007, Rev. 5 or later.

13.7 GA EPD Laboratory SOP – Organics Data Validation, SOP 1-052, online revision.

13.8 GA EPD Laboratory SOP – Glassware Maintenance, SOP 1-015, online revision.

13.9 GA EPD Laboratory SOP – EPA 500 Series Method Preparation of Sample Kits, SOP 1-037, online revision.

13.10 GA EPD Laboratory SOP – SOP for Muffle Furnace Baking of Sodium Sulfate, Glass Wool, Sodium Chloride and Sand, SOP 1-051, online revision.
13.11 GA EPD Laboratory SOP – SOP for Diazomethane Generation, SOP 1-043, online revision.
13.12 Georgia EPD Laboratory Chemical Hygiene Plan, online revision.
13.13 The Georgia EPD Laboratory Quality Assurance 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 RLs for EPA Method 515.4

Parameter/Method	Analyte	Matrix (Water)	
		RL	Unit
EPA 515.4	**Dalapon**	2.20	µg/L
	Dicamba	0.44	µg/L
	2,4 D	0.22	µg/L
	PCP	0.088	µg/L
	Silvex	0.44	µg/L
	Dinoseb	0.44	µg/L
	Picloram	0.22	µg/L

Table 14.1.2 Summary of Calibration and QC procedures for Method 515.4						
Method	**Applicable Parameter**	**QC check**	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**
515.4	Herbicides	6 point initial calibration for all analytes	Initial calibration prior to sample analysis	Linear mean RSD for all analytes < 20% with linear least squares regression r≥ 0.980 or r^2≥0.960 for all analytes. All analytes must be within ±30% of expected values for each level except lowest calibration level which must be ±50% of expected values for each analyte	Correct problem then repeat initial calibration	
		ICV – Second source calibration verification	Once per 6 point initial calibration	All analytes within ±30% of expected values	Correct problem then repeat initial calibration	
		Retention time window calculated for each analyte	Once per year and after major maintenance of instrument	± 3 times standard deviation for each analyte retention time for standard analytical batch sequence	Correct problem then reanalyze all samples since the last retention time check	
		Retention time window update	Must be done every analytical sequence	First CCC of each sequence and the first CCC of each 24 hour period.		
		Initial calibration verification	Daily, before sample analysis	All analytes within ± 30% of expected value	Correct problem then repeat initial calibration	
		CCC - Calibration Verification	Beginning each analysis sequence prior to the analysis of the samples, after every 10 samples and at the end of the analysis. Sequence will alternate between Mid CCC and a High CCC.	All analytes within ±30% of expected values. If the continuing calibration fails because the calculated concentration is greater than 130% (150% for the low-level CCC) for a particular target compound	If the continuing calibration fails because the calculated concentration is greater than 130% (150% for the low-level CCC) for a particular target compound, and field sample extracts show no detection for that target compound, non-detects may be reported without re-analysis.	If out of range high, high bias with no detects, generate a corrective action and use data.

Table 14.1.2 Summary of Calibration and QC procedures for Method 515.4

Method	Applicable Parameter	QC check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
515.4	Herbicides	Demonstrate the ability to generate acceptable accuracy and precision using 4 replicate analyses of the QC check sample, a Blind and a Blank Analyst must also produce a passing MDL study with 7 MDL spikes and 7 MDL blanks	One per analyst	QC acceptance criteria Appendix A, Table A.1. **See section 9.14 for MDL requirements**	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Method blank	One per analytical batch	No analytes detected >RL	Correct problem; then re-prep and analyze method blank and all samples processed with the contaminated blank	If unable to re-extract, flag samples with a "B"
		Surrogate Spike	Every sample, spiked sample, standard and method blank	QC acceptance criteria Appendix A, Table A.1	Correct problem and re-analyze or re-extract samples	
		LCS/LCSD for all analytes	One LCS/LCSD per batch	QC acceptance criteria Appendix A, Table A.1	Reanalyze once. If they fail a second time, correct problem the reanalyze or re-extract the LCS/LCSD and all samples in the affected batch	Flag QC sample report if LCSD exceeds upper acceptable control limits with passing RPD when high bias with no detects
		MS/MSD for all analytes	One MS/MSD per batch	QC acceptance criteria Appendix A, Table A.1	Flag report if recoveries are out of acceptable range	
		Internal Standard	Every sample, spiked sample, standard and method blank	±50% deviation from expected value	Re-analyze extract. If it fails the second analysis, re-extract and re-analyze sample	
		IDC Blank	Once per analyst, prior to IDC replicate analysis	All target analyts are < ⅓ RL or lowest point on curve	Correct problem and re-analyze or re-extract IDCs	

Table 14.1.2 Summary of Calibration and QC procedures for Method 515.4

Method	Applicable Parameter	QC check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
515.4	Herbicides	IDC - Demonstrate ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample plus a blind & a blank	Once per analyst	QC acceptance criteria Appendix A, Table A.1	Correct problem and re-analyze or re-extract IDCs	
		CDC – Continuing Demonstration of Capability	Required every six months after IDC for each analyst	QC acceptance criteria Appendix A, Table A.1	Correct problem and re-analyze or re-extract CDCs	
		Second column confirmation	100% for all positive results	Same as for primary column analysis	Same as for primary column analysis if used for quantitation	
		MDL study	Once per year or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	None
		MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	None
		Results reported between MDL and RL	None	None	None	
		Quarterly ICV	Once per Quarter	All analytes within ±30% of expected value	Correct problem then repeat initial calibration	

Table 14.1.2 Summary of Calibration and QC procedures for Method 515.4						
Method	**Applicable Parameter**	**QC check**	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**
		LPC - Laboratory Performance Check (equivalent to Low CCC referenced in Table 14 of EPA Method 515.4, Rev. 1.0, 2000)	One at the beginning each analysis sequence prior to the analysis of the samples	All analytes within ± 50% of expected value	Correct problem then repeat initial calibration	If out of range high, high bias with no detects, generate a corrective action and use data. If low bias or with detects, rerun LPC and affected samples. If rerun passes, use data. If reruns do not pass, correct problem, repeat LPC and reanalyze all samples.
515.4	Herbicides	Residual Chlorine check	Whenever needed. If collector does not check residual chlorine.	Must be checked for every sample.	Check residual chlorine levels and add information to extraction sheet.	

15 Associated LabWorks Test Codes

15.1 Parent Test Code
15.1.1 $515E – Analysis Results
15.2 Extraction Test Code
15.2.1 515EE – Sample Extraction
15.3 QC Test Codes
15.3.1 $B_515E – Extraction Blank Results
15.3.2 $LA515E – LCS/LCSD Spike Amount
15.3.3 $LS515E – LCS Results
15.3.4 $LD515E – LCSD Results
15.3.5 $LR515E – LCS Percent Recovery
15.3.6 $L2515E – LCSD Percent Recovery
15.3.7 $LP515E – LCS/LCSD Precision
15.3.8 $A_551E – MS/MSD Spike Amount
15.3.9 $S_515E – MS Results
15.3.10 $D_515E – MSD Results
15.3.11 $R_515E – MS Percent Recovery
15.3.12 $RD515E – MSD Percent Recovery

15.3.13 $P_515E – MS/MSD Precision
15.3.14 $MA515E – MDL Spike Amount
15.3.15 $ML515E – MDL Results

Appendix A, Table A.1 – Quality Assurance Criteria for Method EPA 515.4

QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
LCS/LCSD*	2,4-D	70	-	130	17
	Dalapon	82	-	130	15
	Dicamba	70	-	130	16
	Dinoseb	70	-	130	15
	Pentachlorophenol (PCP)	76	-	126	15
	Picloram	70	-	130	17
	Silvex	70	-	130	19
MS/MSD**	2,4-D	70	-	130	30
	Dalapon	70	-	130	30
	Dicamba	70	-	130	30
	Dinoseb	70	-	130	30
	Pentachlorophenol (PCP)	70	-	130	30
	Picloram	70	-	130	30
	Silvex	70	-	130	30
Surrogate**	DCAA	70	-	130	NA
	DCAA (ug/L)	17.5	-	32.5	NA

*LCS/LCSD recovery and precision limits based on control charts of data collected from 12/31/2018-01/01/2021.
**Surrogate and MS/MSD accuracy limits are specified by the method as 70-130% and are therefore static. Precision limits are specified as 0-30% RPD by the EPD Laboratory as static.

Updates
Appendix A added.
ICN Rev. 1 for SOP 1-050 incorporated.
Updated for online revision.