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Organochlorine Pesticides in Water by Gas Chromatography – EPA Method SW846-8081A

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1 Scope and Application

1.1 Method SW846-8081A is used to determine the concentrations of various chlorinated hydrocarbon pesticides in surface and ground water. Samples are extracted at neutral pH with methylene chloride then solvent exchanged with hexane. The extract is analyzed by injection into a temperature programmable gas chromatograph with an electron capture detector. Identifications are obtained by analyzing a standard curve under identical conditions used for samples and comparing resultant retention times. Concentrations of the identified components are measured by relating the response produced for that compound to the standard curve response.

1.2 This method is restricted to analysts who have completed the requirements of the initial demonstration SOP. Refer to SOP reference 13.1.

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 1-052, Organics Data Validation, online revision.

3 Interferences

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

3.2 Glassware must be scrupulously cleaned with hot water detergent followed by de-ionized water then rinsed with methanol followed by acetone. The glassware is rinsed again with extraction solvent, methylene chloride, immediately prior to use.

3.3 The use of high purity reagents and solvents helps 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 contaminants that are co-extracted from the sample.

4 Safety

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

5 Apparatus and Equipment

5.1 Sample container: 1.0L amber bottle with Teflon-lined caps

5.2 Vials: auto-sampler vials, clear, screw top, 2.0mL and 300µL inserts

5.3 Volumetric flasks (Class A): various sizes

5.4 Micro-syringes: various sizes

5.5 Syringes: various sizes

5.6 Drying column: Sodium sulfate

5.7 Glasswool: Baked at 400°C for 4 hours

5.8 Gas chromatograph: capable of temperature programming equipped for split/splitless injection

5.9 Mega bore 30m X 0.53mm, Rtx-CLP1 or equivalent (0.32mm may be used)

5.10 Mega bore 30m X 0.53mm, Rtx-CLP2 or equivalent (0.32mm may be used)

5.11 Electron capture detector

5.12 Chromatography software

5.13 Separatory Funnel: 2.0L with PTFE stopcock

5.14 Separatory Funnel Shaker

5.15 Graduated cylinders (Class A): 100mL & 1000mL

5.16 Erlenmeyer flasks: 250-300mL

5.17 Beakers: various sizes

5.18 pH indicator paper: pH range 0-14

5.19 Balance: Analytical, capable of accurately weighing to the nearest 0.0001g

5.20 Balance: Top-loading, capable of accurately weighing to the nearest 0.01g

5.21 RapidVap or similar concentrator with nitrogen blow down and controlled heating capabilities

5.22 RapidVap or similar concentration tubes with at least 300mL volume

5.23 TurboVap or similar concentrator with nitrogen blow down and controlled heating capabilities

5.24 TurboVap or similar concentration tubes with at least 50mL volume

5.25 Sample extract vials: 10mL culture tubes with caps

5.26 Disposable pipettes and bulbs

5.27 Detergent: Steris Labklenz or equivalent

6 Reagents and Standards

6.1 Methylene chloride: pesticide grade or equivalent

6.2 Hexane: pesticide grade or equivalent

6.3 Acetone: pesticide grade or equivalent

6.4 Isooctane: pesticide grade or equivalent

6.5 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 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.

6.6 Sodium sulfate: granular, anhydrous, certified ACS grade suitable for pesticide residue analysis or equivalent

6.6.1 Sodium sulfate is baked for 4 hours at 450°C then stored in a glass container

6.7 Calibration Standard Solutions

6.7.1 Prepare five different concentrations equivalent to the concentration levels in Section 8.2 by dilution of the stock standard solutions. Standard stock solutions are usually at a concentration of 100µg/mL or 1000µg/mL in various solvents or from neat concentration. Calculations or amounts will vary depending on the stock standard concentration. Prepare the primary dilution standard at 1µg/mL concentration.

6.7.2 Calibration Standards for Chlordane will have 3-5 (or more) peaks chosen for calibration and Toxaphene will have 4-6 (or more) peaks chosen for calibration.

6.8 Initial Calibration Verification Standard Solutions (ICV)

6.8.1 Stock standard solutions prepared from a second source vendor's standards or a different lot from the same vendor as the calibration standards containing all of the analytes listed in Section 8.2, diluted in Hexane.

6.8.2 ICV standards are equivalent to Level 3 calibration standard in concentration listed in Section 8, Tables 8.3.2, 8.4.2, 8.5.2 & 8.6.2.

6.9 QC Spiking Solutions

6.9.1 There are four separate spiking solutions for SW846-8081A samples. A Mix A spike, Mix B spike, Chlordane Spike and Toxaphene Spike. The typical volumes of standards used for preparing spikes are given in Sections 6.9.2 – 6.9.5. These may be adjusted if necessary to meet the final concentration if the concentration of the vendor stock changes.

6.9.2 Mix A Spike: The Mix A 100XA is made from a 10µg/mL Primary Stock #1A, a 10µg/mL Primary Stock #2A and an 8-80µg/mL Mix A mix in Acetone. The surrogates are included in the mix. The Mix A spike is spiked at 1.0mL per sample with a sample extract final volume of 10mL. See Tables 6.9.2.1 – 6.9.2.4.

Table 6.9.2.1 – 8081A Mix A Spiking Primary Stock #1A Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Chlorpyrifos (Dursban)	1000	0.25	10
Total Volume of Standard Aliquot		0.25mL	
Addition of Acetone to Standard Aliquot		24.75mL	
Final Volume of Mix A Primary Stock #1A		25mL	

Table 6.9.2.2 – 8081A Mix A Spiking Primary Stock #2A Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Mirex	1000	0.25	10
Total Volume of Standard Aliquot		0.25mL	
Addition of Acetone to Standard Aliquot		24.75mL	
Final Volume of Mix A Primary Stock #2A		25mL	

Table 6.9.2.3 – 8081A Mix A 100XA Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	8.0	1.25	0.40
SS:DCBP	16		0.80
α-BHC	8.0		0.40
γ-BHC (Lindane)	8.0		0.40
p,p'-DDD	16		0.80
p,p'-DDT	16		0.80
Dieldrin	16		0.80
Endosulfan I	8.0		0.40
Endrin	16		0.80
Heptachlor	8.0		0.40
Methoxychlor	80		4.0
Chlorpyrifos (Dursban)	10	2.0	0.80
Mirex	10	2.0	0.80
Total Volume of Standard Aliquots		5.25mL	
Addition of Acetone to Standard Aliquots		19.75mL	

Table 6.9.2.3 – 8081A Mix A 100XA Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Final Volume of Mix A 100XA Spiking Standard		25mL	

Table 6.9.2.4 – 8081A Mix A 100XA Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCBP	0.80		0.08
α-BHC	0.40		0.04
γ-BHC (Lindane)	0.40		0.04
p,p'-DDD	0.80		0.08
p,p'-DDT	0.80		0.08
Dieldrin	0.80		0.08
Endosulfan I	0.40		0.04
Endrin	0.80		0.08
Heptachlor	0.40		0.04
Methoxychlor	4.0		0.40
Chlorpyrifos (Dursban)	0.80		0.08
Mirex	0.80		0.08
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Mix A Spiking Standard in Sample Extract		10mL	

6.9.3 Mix B Spike: The Mix B 100XB is made from a 10µg/mL Primary Stock #1B and an 8-16µg/mL Mix B mix in Acetone. The surrogates are included in the mix. The Mix B spike is spiked at 1.0mL per sample with a sample extract final volume of 10mL. See Tables 6.9.3.1 – 6.9.3.3.

Table 6.9.3.1 – 8081A Mix B Spiking Primary Stock #1B Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Hexachlorobenzene	1000	0.25	10
Total Volume of Standard Aliquot		0.25mL	
Addition of Acetone to Standard Aliquot		24.75mL	
Final Volume of Mix B Primary Stock #1B		25mL	

Table 6.9.3.2 – 8081A Mix B 100XB Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	8.0	1.25	0.40
SS:DCBP	16		0.80
Aldrin	8.0		0.40
β-BHC	8.0		0.40
δ-BHC	8.0		0.40
α-Chlordane	8.0		0.40
γ-Chlordane	8.0		0.40
p,p'-DDE	16		0.80
Endosulfan II	16		0.80
Endosulfan Sulfate	16		0.80
Endrin Aldehyde	16		0.80
Endrin Ketone	16		0.80
Heptachlor Epoxide	16		0.80
Hexachlorobenzene	10	1.0	0.40
Total Volume of Standard Aliquots		2.25mL	
Addition of Acetone to Standard Aliquots		22.75mL	
Final Volume of Mix B 100XB Spiking Standard		25mL	

Table 6.9.3.3 – 8081A Mix B 100XB Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCBP	0.80		0.08
Aldrin	0.40		0.04
β-BHC	0.40		0.04
δ-BHC	0.40		0.04
α-Chlordane	0.40		0.04
γ-Chlordane	0.40		0.04
p,p'-DDE	0.80		0.04
Endosulfan II	0.80		0.04
Endosulfan Sulfate	0.80		0.08
Endrin Aldehyde	0.80		0.08
Endrin Ketone	0.80		0.08
Heptachlor Epoxide	0.80		0.08
Hexachlorobenzene	0.40		0.04
Total Volume of Standard Aliquots		1.0mL	
Addition of Hexane to Standard Aliquots		9.0mL	
Final Volume of Mix B 100XB Spiking Standard in Sample Extract		10mL	

6.9.4 Chlordane Spike: The Chlordane 100XC Spike is made from a 4-8µg/mL SS: Surrogate Stock mix and 1000µg/mL Chlordane Stock in Acetone. The Chlordane spike is spiked at 1.0mL per sample with a sample extract final volume of 10mL. See Tables 6.9.4.1, 6.9.4.2 & 6.10.1.

Table 6.9.4.1 – 8081A Chlordane 100XC Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	4.0	2.5	0.40
SS:DCPB	8.0		0.80
Chlordane	1000	0.25	10
Total Volume of Standard Aliquot		2.75mL	

Table 6.9.4.1 – 8081A Chlordane 100XC Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Addition of Acetone to Standard Aliquot		22.25mL	
Final Volume of Chlordane 100XC Spiking Standard		25mL	

Table 6.9.4.2 – 8081A Chlordane 100XC Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCPB	0.80		0.08
Chlordane	10		1.0
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Chlordane 100XC Spiking Standard in Standard Extract		10mL	

6.9.5 Toxaphene Spike: The Toxaphene 100XT Spike is made from a 4-8µg/mL SS: Surrogate Stock mix and 1000µg/mL Toxaphene Stock in Acetone. The Toxaphene spike is spiked at 1.0mL per sample with a sample extract final volume of 10mL. See Tables 6.9.5.1, 6.9.5.2 & 6.10.1.

Table 6.9.5.1 – 8081A Toxaphene 100XT Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	4.0	2.5	0.40
SS:DCPB	8.0		0.80
Toxaphene	1000	0.25	10
Total Volume of Standard Aliquot		2.75mL	
Addition of Acetone to Standard Aliquot		22.25mL	
Final Volume of Toxaphene 100XT Spiking Standard		25mL	

Table 6.9.5.2 – 8081A Toxaphene 100XT Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCPB	0.80		0.08
Toxaphene	10		1.0
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Toxaphene 100XT Spiking Standard in Sample Extract		10mL	

6.10 Surrogate Spiking Solution

6.10.1 The Surrogate Spiking solution is made from a 100-200µg/mL mix in Acetone. Note: Surrogates may be added individually if a mix is not available. Volumes may be adjusted if necessary to meet final concentration of 4-8µg/mL. The surrogates are spiked at 1.0mL per sample with a sample extract final volume of 10mL.

Table 6.10.1 – 8081A SS: Surrogate Spiking Solution 1000XPSS Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	100	2.0	4.0
SS:DCBP	200		8.0
Total Volume of Standard Aliquot		2.0mL	
Addition of Acetone to Standard Aliquot		48mL	
Final Volume of SS Spiking Solution in Acetone		50mL	

6.11 MDL Spikes

6.11.1 MDL Spikes are made by diluting the Mix A 100XA, Mix B 100XB, Chlordane 100XC and the Toxaphene 100XT each by 1:10 in Acetone. They are not mixed.

6.11.2 The Mix A MDL spike and Mix B MDL spikes are each spiked at 0.5mL per MDL with a 10mL sample extract final volume. For Mix A MDL Spikes, see Tables 6.11.2.1 & 6.11.2.2. For Mix B MDL Spikes, see Tables 6.11.2.3 & 6.11.2.4.

Table 6.11.2.1 – 8081A Mix A MDL Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCBP	0.80		0.08
α-BHC	0.40		0.04
γ-BHC (Lindane)	0.40		0.04
p,p'-DDD	0.80		0.08
p,p'-DDT	0.80		0.08
Dieldrin	0.80		0.08
Endosulfan I	0.40		0.04
Endrin	0.80		0.08
Heptachlor	0.40		0.04
Methoxychlor	4.0		0.40
Chlorpyrifos (Dursban)	0.40		0.04
Mirex	0.80		0.08
Total Volume of Standard Aliquot			1.0mL
Addition of Acetone to Standard Aliquot			9.0mL
Final Volume of Mix A MDL Spiking Standard			10mL

Table 6.11.2.2 – 8081A Mix A 100XA Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.04	0.50	0.002
SS:DCBP	0.08		0.004
α-BHC	0.04		0.002
γ-BHC (Lindane)	0.04		0.002
p,p'-DDD	0.08		0.004
p,p'-DDT	0.08		0.004
Dieldrin	0.08		0.004
Endosulfan I	0.04		0.002
Endrin	0.08		0.004
Heptachlor	0.04		0.002
Methoxychlor	0.40		0.02

Table 6.11.2.2 – 8081A Mix A 100XA Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Chlorpyrifos (Dursban)	0.04	0.50	0.002
Mirex	0.08		0.004
Total Volume of Standard Aliquot		0.50mL	
Addition of Hexane to Standard Aliquot		9.5mL	
Final Volume of Mix A MDL Spiking Standard in Sample Extract		10mL	

Table 6.11.2.3 – 8081A Mix B MDL Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCBP	0.80		0.08
Aldrin	0.40		0.04
β-BHC	0.40		0.04
δ-BHC	0.40		0.04
α-Chlordane	0.40		0.04
γ-Chlordane	0.40		0.04
p,p'-DDE	0.80		0.08
Endosulfan II	0.80		0.08
Endosulfan Sulfate	0.80		0.08
Endrin Aldehyde	0.80		0.08
Endrin Ketone	0.80		0.08
Heptachlor Epoxide	0.40		0.04
Hexachlorobenzene	0.80		0.08
Total Volume of Standard Aliquots		1.0mL	
Addition of Acetone to Standard Aliquots		9.0mL	
Final Volume of Mix B MDL Spiking Standard		10mL	

Table 6.11.2.4 – 8081A Mix B MDL Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.04	0.50	0.002
SS:DCBP	0.08		0.004
Aldrin	0.04		0.002
β-BHC	0.04		0.002
δ-BHC	0.04		0.002
α-Chlordane	0.04		0.002
γ-Chlordane	0.04		0.002
p,p'-DDE	0.08		0.004
Endosulfan II	0.08		0.004
Endosulfan Sulfate	0.08		0.004
Endrin Aldehyde	0.08		0.004
Endrin Ketone	0.08		0.004
Heptachlor Epoxide	0.04		0.002
Hexachlorobenzene	0.08		0.004
Total Volume of Standard Aliquots			0.50mL
Addition of Hexane to Standard Aliquots			9.5mL
Final Volume of Mix B MDL Spiking Standard in Sample Extract			10mL

6.11.3 The Chlordane and Toxaphene MDL spikes are each spiked at 1.0mL per MDL with a 10mL sample extract final volume. For Chlordane MDL Spikes, see Tables 6.11.3.1 & 6.11.3.2. For Toxaphene MDL Spikes, see Tables 6.11.3.3 & 6.11.3.4.

Table 6.11.3.1 – 8081A Chlordane MDL Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCPB	0.80		0.08
Chlordane	10		1.0
Total Volume of Standard Aliquot			1.0mL

Table 6.11.3.1 – 8081A Chlordane MDL Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Addition of Acetone to Standard Aliquot		9.0mL	
Final Volume of Chlordane MDL Spiking Standard		10mL	

Table 6.11.3.2 – 8081A Chlordane MDL Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.04	1.0	0.004*
SS:DCPB	0.08		0.008*
Chlordane	1.0		0.10
*Surrogates not at lowest point on the curve. Surrogates not used for MDL study.			
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Chlordane MDL Spiking Standard in Standard Extract		10mL	

Table 6.11.3.3 – 8081A Toxaphene MDL Spiking Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.40	1.0	0.04
SS:DCPB	0.80		0.08
Toxaphene	10		1.0
Total Volume of Standard Aliquot		1.0mL	
Addition of Acetone to Standard Aliquot		9.0mL	
Final Volume of Toxaphene MDL Spiking Standard		10mL	

Table 6.11.3.4 – 8081A Toxaphene MDL Spiking Standard Final Concentration in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.04	1.0	0.004*
SS:DCPB	0.08		0.008*
Toxaphene	1.0		0.10
*Surrogates not at lowest point on the curve. Surrogates not used for MDL study.			
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Toxaphene MDL Spiking Standard in Sample Extract		10mL	

6.12 Breakdown Standard Solution

6.12.1 A standard solution containing Endrin and DDT diluted in Hexane, used to calculate the breakdown of these compounds within the GC before and during the analysis of samples.

6.12.2 The 0.08µg/mL Breakdown Solution is made by diluting 80µL of 100µg/mL p,p'-DDT and 80µL of 100µg/mL Endrin into 100mL final volume Hexane.

Table 6.12.2.1 – 8081A Breakdown Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
DDT	100	0.08	0.08
Endrin	100		0.08
Total Volume of Standard Aliquot		0.08mL	
Addition of Hexane to Standard Aliquot		99.92mL	
Final Volume of Breakdown Standard		100mL	

6.13 Expiration Dates

6.13.1 All standards that are made for SW846-8081A analysis have an expiration date of six months from the opening of the vendor stock ampule or the manufacturer's expiration date if less than six months from opening.

7 Sample Collection

7.1 Aqueous samples for Method SW846-8081A are collected in two to four amber, pre-certified 1000mL glass bottles with Teflon lined screw caps.

7.2 Samples are cooled to 0-6ºC (not frozen) after sample collection. Samples must be extracted within 7 days from collection and analyzed within 40 days of extraction.

8 Calibration

8.1 Calibration Curve

8.1.1 A five-point calibration is performed for all single and multi-peak components. The calibration system uses traceable certified standards. The calibration is an external standard calibration with an average of response factor linear curve fit and should result in a percent relative standard deviation < 20% between calibration levels of each analyte. The origin may not be forced.

8.2 Calibration Standards

Note: It will be necessary to make separate curves for Mix A, Mix B, Chlordane and Toxaphene analyses. These are alternated in QA/QC batching; for instance, one batch will have Chlordane criteria and the next will have Toxaphene until all four have been used over four successive batches. CCCs for all four will be analyzed with each sample batch.

8.3 The Mix A calibration curve consists of the calibration standards at the following concentrations (µg/mL): *A vendor stock of 8-80µg/mL is used to make the Mix A stock at 200XA concentration with Chlorpyrifos and Mirex being at 1000µg/mL. A Primary Stock #1A and #2A is used to dilute Chlorpyrifos and Mirex to 10µg/mL exactly like Section 6.9.2, Tables 6.9.2.1 & 6.9.2.2. While the final solvent of Primary Stock #1A and Primary Stock #2A is still acetone, the final solvent for the Mix A 200XA calibration stock standard is hexane.*

Table 8.3.1 – Mix A 200XA Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	8.0	1.0	0.80
SS:DCBP	16		1.6
α-BHC	8.0		0.80
γ-BHC (Lindane)	8.0		0.80
p,p'-DDD	16		1.6
p,p'-DDT	16		1.6
Dieldrin	16		1.6
Endosulfan I	8.0		0.80
Endrin	16		1.6

Table 8.3.1 – Mix A 200XA Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Heptachlor	8.0	1.0	0.80
Methoxychlor	80		8.0
Chlorpyrifos (Dursban)	10	1.6	1.6
Mirex	10	1.6	1.6
Total Volume of Standard Aliquots		4.2mL	
Addition of Hexane to Standard Aliquots		5.8mL	
Final Volume of Mix A 200XA Stock Standard		10mL	

Table 8.3.2 Mix A Calibration Curve Levels (µg/mL)

Compound	Level 1 0.5XA	Level 2 5XA	Level 3 10XA	Level 4 15XA	Level 5 20XA
SS:TCMX	0.002	0.02	0.04	0.06	0.08
SS:DCBP	0.004	0.04	0.08	0.12	0.16
α-BHC	0.002	0.02	0.04	0.06	0.08
γ-BHC (Lindane)	0.002	0.02	0.04	0.06	0.08
p,p'-DDD	0.004	0.04	0.08	0.12	0.16
p,p'-DDT	0.004	0.04	0.08	0.12	0.16
Dieldrin	0.004	0.04	0.08	0.12	0.16
Endosulfan I	0.002	0.02	0.04	0.06	0.08
Endrin	0.004	0.04	0.08	0.12	0.16
Heptachlor	0.002	0.02	0.04	0.06	0.08
Methoxychlor	0.02	0.20	0.40	0.60	0.80
Chlorpyrifos (Dursban)	0.004	0.04	0.08	0.12	0.16
Mirex	0.004	0.04	0.08	0.12	0.16

Table 8.3.3 Aliquots of Mix A Calibration Stock to make up all the levels in Table 8.3.2

(Aliquots corresponds to each level directly above each column)

	Level 1 0.5XA	Level 2 5XA	Level 3 10XA	Level 4 15XA	Level 5 20XA
Aliquot of Mix A Calibration Stock 200XA (see Table 8.3.1)	0.025mL (25µL)	0.25mL (250µL)	0.50mL (500µL)	0.75mL (750µL)	1.0mL (1000µL)

Note: Bring all levels (points of the curve) up to 10mL by using **Hexane**

8.4 The Mix B calibration curve consists of the calibration standards at the following concentrations (µg/mL): *A vendor stock of 8-16µg/mL is used to make the Mix B stock at 200XB concentration with Hexachlorobenzene being at 1000µg/mL. A Primary Stock #1B is used to dilute Hexachlorobenzene to 10µg/mL exactly like Section 6.9.3, Table 6.9.3.1. While the final solvent of Primary Stock #1B is still acetone, the final solvent for the Mix B 200XB calibration stock standard is hexane.*

Table 8.4.1 – Mix B 200XB Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	8.0	1.0	0.80
SS:DCBP	16		1.6
Aldrin	8.0		0.80
β-BHC	8.0		0.80
δ-BHC	8.0		0.80
α-Chlordane	8.0		0.80
γ-Chlordane	8.0		0.80
p,p'-DDE	16		1.6
Endosulfan II	16		1.6
Endosulfan Sulfate	16		1.6
Endrin Aldehyde	16		1.6
Endrin Ketone	16		1.6
Heptachlor Epoxide	16		1.6
Hexachlorobenzene	10	0.80	0.80
Total Volume of Standard Aliquots		1.8mL	
Addition of Hexane to Standard Aliquots		8.2mL	
Final Volume of Mix B 200XB Stock Std		10mL	

Table 8.4.2 Mix B Calibration Curve Levels (µg/mL)

Compound	Level 1 0.5XB	Level 2 5XB	Level 3 10XB	Level 4 15XB	Level 5 20XB
SS:TCMX	0.002	0.02	0.04	0.06	0.08
SS:DCBP	0.004	0.04	0.08	0.12	0.16
Aldrin	0.002	0.02	0.04	0.06	0.08
β-BHC	0.002	0.02	0.04	0.06	0.08
δ-BHC	0.002	0.02	0.04	0.06	0.08
α-Chlordane	0.002	0.02	0.04	0.06	0.08

Table 8.4.2 Mix B Calibration Curve Levels (µg/mL)

Compound	Level 1 0.5XB	Level 2 5XB	Level 3 10XB	Level 4 15XB	Level 5 20XB
γ-Chlordane	0.002	0.02	0.04	0.06	0.08
p,p'-DDE	0.004	0.02	0.04	0.06	0.08
Endosulfan II	0.004	0.04	0.08	0.12	0.16
Endosulfan Sulfate	0.004	0.04	0.08	0.12	0.16
Endrin Aldehyde	0.004	0.04	0.08	0.12	0.16
Endrin Ketone	0.004	0.04	0.08	0.12	0.16
Heptachlor Epoxide	0.004	0.04	0.08	0.12	0.16
Hexachlorobenzene	0.002	0.02	0.04	0.06	0.08

Table 8.4.3 Aliquots of Mix A Calibration Stock to make up all the levels in Table 8.4.2

(Aliquots corresponds to each level directly above each column)

	Level 1 0.5XB	Level 2 5XB	Level 3 10XB	Level 4 15XB	Level 5 20XB
Aliquot of Mix B Calibration Stock 200XB (see Table 8.4.1)	0.025mL (25µL)	0.25mL (250µL)	0.50mL (500µL)	0.75mL (750µL)	1.0mL (1000µL)

Note: Bring all levels (points of the curve) up to 10mL by using **Hexane**

8.5 The Chlordane calibration curve is made from a 4000-8000µg/mL SS: Surrogate Stock mix and 1000µg/mL Chlordane Stock.

Table 8.5.1 – 8081A Chlordane 200XC Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	4000	5.0	0.80
SS:DCPB	8000		1.6
Chlordane	1000	0.50	20
Total Volume of Standard Aliquot		5.5mL	
Addition of Hexane to Standard Aliquot		19.5mL	
Final Volume of Chlordane 200XC Stock Standard		25mL	

Table 8.5.2 Chlordane Calibration Curve Levels (µg/mL)

Compound	Level 1 1XC	Level 2 5XC	Level 3 10XC	Level 4 15XC	Level 5 20XC
SS:TCMX	0.002	0.02	0.04	0.06	0.08
SS:DCBP	0.004	0.04	0.08	0.12	0.16
Chlordane	0.10	0.50	1.0	1.5	2.0

Table 8.5.3 Aliquots of Chlordane Calibration Stock to make up all the levels in Table 8.5.2

(Aliquots corresponds to each level directly above each column)

	Level 1 1XC	Level 2 5XC	Level 3 10XC	Level 4 15XC	Level 5 20XC
Aliquot of Chlordane Calibration Stock 200XC (see Table 8.5.1)	0.050mL (50µL)	0.25mL (250µL)	0.50mL (500µL)	0.75mL (750µL)	1.0mL (1000µL)

Note: Bring all levels (points of the curve) up to 10mL by using **Hexane**

8.6 The Toxaphene calibration curve is made from a 4000-8000µg/mL SS: Surrogate Stock mix and 1000µg/mL Toxaphene Stock.

Table 8.6.1 – 8081A Toxaphene 200XT Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	4000	5.0	0.80
SS:DCPB	8000		1.6
Toxaphene	1000	0.50	20
Total Volume of Standard Aliquot		5.5mL	
Addition of Hexane to Standard Aliquot		19.5mL	
Final Volume of Toxaphene 200XT Stock Standard		25mL	

Table 8.6.2 Toxaphene Calibration Curve Levels (µg/mL)

Compound	Level 1 1XT	Level 2 5XT	Level 3 10XT	Level 4 15XT	Level 5 20XT
SS:TCMX	0.002	0.02	0.04	0.06	0.08
SS:DCBP	0.004	0.04	0.08	0.12	0.16
Toxaphene	0.10	0.50	1.0	1.5	2.0

Table 8.6.3 Aliquots of Toxaphene Calibration Stock to make up all the levels in Table 8.6.2

(Aliquots corresponds to each level directly above each column)

	Level 1 1XT	Level 2 5XT	Level 3 10XT	Level 4 15XT	Level 5 20XT
Aliquot of Toxaphene Calibration Stock 200XT (see Table 8.6.1)	0.050mL (50µL)	0.25mL (250µL)	0.50mL (500µL)	0.75mL (750µL)	1.0mL (1000µL)

Note: Bring all levels (points of the curve) up to 10mL by using **Hexane**

8.7 Calibration Verification

8.7.1 Second source calibration verification (ICV) must be analyzed after each initial calibration. All analytes must be within ± 15% of the expected value.

8.7.2 The ICVs for all pesticide mixes are equivalent in concentration to Level 3 of the corresponding calibration curve.

8.7.3 The Mix A ICV consists of the calibration standards at the following concentrations (µg/L): *A vendor stock of 5-50µg/mL is used to make the Mix A stock at 125XA concentration with Chlorpyrifos at 1000µg/mL and Mirex at 100µg/mL. A Primary Stock #1A-ICV and #2A-ICV is used to dilute Chlorpyrifos and Mirex to 10µg/mL. See Tables 8.7.3.1 & 8.7.3.2. If the Vendor Stock is the same concentration as the Primary Standard, then the Mix A ICV will be made exactly as the primary calibration curve at Level 3 in Section 8.3.*

Table 8.7.3.1 – 8081A Mix A Spiking Primary Stock #1A-ICV Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Chlorpyrifos (Dursban)	1000	0.25	10
Total Volume of Standard Aliquot		0.25mL	
Addition of Acetone to Standard Aliquot		24.75mL	
Final Volume of Mix A ICV Stock #1A-ICV		25mL	

Table 8.7.3.2 – 8081A Mix A Spiking Primary Stock #2A-ICV Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Mirex	100	1.0	10
Total Volume of Standard Aliquot		1.0mL	
Addition of Acetone to Standard Aliquot		9.0mL	
Final Volume of Mix A ICV Stock #2A-ICV		10mL	

Table 8.7.3.3 – Mix A ICV 125XA-ICV Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	5.0	1.0	0.50
SS:DCBP	10		1.0
α-BHC	5.0		0.50
γ-BHC (Lindane)	5.0		0.50
p,p'-DDD	10		1.0
p,p'-DDT	10		1.0
Dieldrin	10		1.0
Endosulfan I	5.0		0.50
Endrin	10		1.0
Heptachlor	5.0		0.50
Methoxychlor	50		5.0
Chlorpyrifos (Dursban)	10	1.0	1.0
Mirex	10	1.0	1.0
Total Volume of Standard Aliquots		3.0mL	
Addition of Hexane to Standard Aliquots		7.0mL	
Final Volume of Mix A ICV 125XA-ICV Stock Standard		10mL	

Table 8.7.3.4 – Mix A ICV 10XA-ICV Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.50		0.04

Table 8.7.3.4 – Mix A ICV 10XA-ICV Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:DCBP	1.0	0.80	0.08
α-BHC	0.50		0.04
γ-BHC (Lindane)	0.50		0.04
p,p'-DDD	1.0		0.08
p,p'-DDT	1.0		0.08
Dieldrin	1.0		0.08
Endosulfan I	0.50		0.04
Endrin	1.0		0.08
Heptachlor	0.50		0.04
Methoxychlor	5.0		0.40
Chlorpyrifos (Dursban)	1.0		0.08
Mirex	1.0		0.08
Total Volume of Standard Aliquots		0.80mL	
Addition of Hexane to Standard Aliquots		9.2mL	
Final Volume of Mix A ICV 10XA-ICV Standard		10mL	

8.7.4 The Mix B ICV consists of the calibration standards at the following concentrations (µg/L): *A vendor stock of 5-10µg/mL is used to make the Mix B stock at 125XB concentration with Hexachlorobenzene at 100µg/mL. A Primary Stock #1B-ICV is used to dilute Hexachlorobenzene to 10µg/mL. See Table 8.7.4.1. If the Vendor Stock is the same concentration as the Primary Standard, then the Mix B ICV will be made exactly as the primary calibration curve at Level 3 in Section 8.4.*

Table 8.7.4.1 – 8081A Mix B Spiking Primary Stock #1B-ICV Standard in Acetone

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Hexachlorobenzene	100	1.0	10
Total Volume of Standard Aliquot		1.0mL	
Addition of Acetone to Standard Aliquot		9.0mL	
Final Volume of Mix B ICV Stock #1B-ICV		10mL	

Table 8.7.4.2 – Mix B ICV 125XB-ICV Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	5.0	1.0	0.50
SS:DCBP	10		1.0
Aldrin	5.0		0.50
β-BHC	5.0		0.50
δ-BHC	5.0		0.50
α-Chlordane	5.0		0.50
γ-Chlordane	5.0		0.50
p,p'-DDE	5.0		0.50
Endosulfan II	10		1.0
Endosulfan Sulfate	10		1.0
Endrin Aldehyde	10		1.0
Endrin Ketone	10		1.0
Heptachlor Epoxide	10		1.0
Hexachlorobenzene	10	0.50	0.50
Total Volume of Standard Aliquots		1.5mL	
Addition of Hexane to Standard Aliquots		8.5mL	
Final Volume of Mix B ICV 125XB-ICV Stock Standard		10mL	

Table 8.7.4.3 – Mix B ICV 10XB-ICV Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
SS:TCMX	0.50	0.80	0.04
SS:DCBP	1.0		0.08
Aldrin	0.50		0.04
β-BHC	0.50		0.04
δ-BHC	0.50		0.04
α-Chlordane	0.50		0.04
γ-Chlordane	0.50		0.04
p,p'-DDE	0.50		0.04
Endosulfan II	1.0		0.08
Endosulfan Sulfate	1.0		0.08
Endrin Aldehyde	1.0		0.08

Table 8.7.4.3 – Mix B ICV 10XB-ICV Calibration Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Endrin Ketone	1.0		0.08
Heptachlor Epoxide	1.0		0.08
Hexachlorobenzene	0.50		0.04
Total Volume of Standard Aliquots		0.80mL	
Addition of Hexane to Standard Aliquots		9.2mL	
Final Volume of Mix B ICV 10XB-ICV Standard		10mL	

8.7.5 The Chlordane ICV is made from a 100µg/mL Chlordane Stock. If the ICV vender stock is the same concentration as the Primary standard, then the ICV is made exactly like the primary calibration curve at Level 3 in Section 8.4. Surrogates are not included.

Table 8.7.5.1 – 8081A Chlordane ICV 100XC-ICV Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Chlordane	100	1.0	10
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Chlordane ICV 100XC-ICV Stock Standard		10mL	

Table 8.7.5.2 – 8081A Chlordane ICV 10XC-ICV Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Chlordane	10	1.0	1.0
Total Volume of Standard Aliquot		1.0mL	

Table 8.7.5.2 – 8081A Chlordane ICV 10XC-ICV Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Chlordane ICV 10XC-ICV Standard		10mL	

8.7.6 The Toxaphene ICV is made from a 100µg/mL Toxaphene Stock. If the ICV vender stock is the same concentration as the Primary standard, then the ICV is made exactly like the primary calibration curve at Level 3 in Section 8.5. Surrogates are not included.

Table 8.7.6.1 – 8081A Toxaphene ICV 100XT-ICV Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Toxaphene	100	1.0	10
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Toxaphene ICV 100XT-ICV Stock Standard		10mL	

Table 8.7.6.2 – 8081A Toxaphene ICV 10XT-ICV Stock Standard in Hexane

Compound	Initial Concentration (µg/mL)	Aliquot (mL)	Final Concentration (µg/mL)
Toxaphene	10	1.0	1.0
Total Volume of Standard Aliquot		1.0mL	
Addition of Hexane to Standard Aliquot		9.0mL	
Final Volume of Toxaphene ICV 10XT-ICV Standard		10mL	

8.8 Record Keeping

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

8.9 Daily Calibration Verification and Continuing Calibration

8.9.1 A continuing calibration standard (CCC) ensures the instruments target compound retention times and quantitation parameters meet method performance criteria. For any 12-hour analysis period, prior to sample analysis, a mid-point daily continuing calibration verification is performed for each pesticide and multi-component mix. Continuing calibration standards are analyzed during the analysis period to verify that instrument calibration accuracy does not exceed ±15% of the initial calibration, i.e. %Drift ≤ 15% (calculation 11.7). If the continuing calibration does not meet method performance criteria, then the instrument must be re-calibrated. A CCC is required after running the standard curve and initial calibration verification. After performing an initial calibration, an ICV may be substituted for a CCC if it meets method criteria for a CCC.

8.10 Average Response Factor Calibration

8.10.1 To evaluate the linearity of the initial calibration, calculate the mean response factor (RF), the standard deviation (σ_{n-1}) and the relative standard deviation expressed as a percentage (%RSD). If the %RSD of the response factors is ≤ 20% over the calibration range, then linearity through the origin may be assumed, and the average calibration or response may be used to determine sample concentrations. See Calculations 11.2.

8.11 Linear Calibration using First Order Least Squares Regression

8.11.1 Linearity through the origin is not assumed in a least squares fit. The instrument responses versus the concentration of the standards for the 5 points are evaluated using the instrument data analysis software. The regression will produce the slope and intercept terms for a linear equation. The regression calculation will regenerate a correlation, r, a measure of goodness of fit of the regression line to the data. A value of 1.0 is a perfect fit. An acceptable correlation of coefficient should be $r \geq 0.990$ (or $r^2 \geq 0.980$). See Calculations 11.4.

8.11.2 Alternatively, second order quadratic fit may be used with an acceptable correlation of coefficient of $r \geq 0.990$ (or $r^2 \geq 0.980$). Note: quadratic fit will be calculated by chromatographic software. See Calculation 11.5.

8.12 Retention Time Windows

8.12.1 The width of the retention time window for each analyte, surrogate and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time of CCCs established over a 72 hour period from beginning injection to final injection over four days, with final injection occurring at a time earlier than the first injection so as to not exceed 72 hours. See Calculation 11.6.

8.12.2 CCCs used for RT Studies only are not required to meet continuing calibration criteria.

8.13 Daily Retention Time Update

8.13.1 Retention Times (RT) are updated once every 12 hours when ran on a GC for 8081A analysis. Each CCC is processed using Totalchrom software and the subsequent new RTs are saved in a copy of the Totalchrom method used for analyzing this batch of samples. To the existing Totalchrom method an extension is added by using "Month-Day-Year." The vial number where the update occurred may also be added to prevent confusion as there may be up to three or more RT updates in a single sequence. Hard copies of the calibration parameters are included with the data package for that batch of samples.

8.14 Verification of Linear Calibrations

8.14.1 Calibration verification for linear calibrations involves the calculations of % drift of the instrument response between the initial calibration and each subsequent analysis of the verification standard. The % drift may be no more than ± 15%. See Calculation 11.7.

8.15 Sample Concentration

8.15.1 Sample results are expressed in µg/L. See Calculation 11.9.

8.15.2 If an analyte response is calibrated by Average Response Factor, $\overline{RF}$, the chromatographic software calculates the concentration of the extract per equation 11.8, Calculations in µg/mL.

8.15.3 If an analyte response is calibrated by linear regression, the chromatographic software calculates the concentration of the extract solving for x per equation 11.4, Calculations in µg/mL.

8.15.4 If an initial volume of other than 1000mL is used or a dilution of the extract is analyzed, the final sample result is multiplied by the factor determined per equation 11.10.

9 Quality Control

9.1 Refer to Table 14.1 for Reporting Limits (RLs), Appendix A, Table A.1 for Quality Assurance criteria and Table 14.2 for a summary of Quality Control procedures associated with this method.

9.2 A Method Detection Limit Study for all analytes must be performed once per year. Refer to SOP Reference 13.4.

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_8081H, and the MDL test code, $ML8081H, and the MDL Spiked Amount, $MA8081H. MDL reports will be pulled from LabWorks at a minimum of once per year (See SOP reference 13.4).

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 SOP Reference 13.1 for training and certification procedures.

9.4 Refer to SOP Reference 13.2 for control charting procedures.

9.5 LCS control limits are used to monitor LCSD recovery. LCSD recovery is not used to validate batch data; however, the LCS/LCSD precision (%RPD) is used for batch validation.

9.6 MS/MSD pairs are analyzed at a minimum of 5% of all samples analyzed.

9.7 Control Limits

9.7.1 Note: Analysts must use the control limits presented in Appendix A, Table A.1 for LCS/LCSDs. Those limits cannot exceed the default limits presented in Table 9.7.1.

Table 9.7.1: Default QC Limits*

	Compound	Default LCL %Recovery	Default UCL %Recovery	Default Precision %RPD
LCS/LCSD				
	Aldrin	10	200	30
	α-BHC	10	200	30
	β-BHC	10	200	30
	δ-BHC	10	200	30
	γ-BHC (Lindane)	10	200	30
	Chlordane	10	200	30
	α-Chlordane	10	200	30
	γ-Chlordane	10	200	30
	Chlorpyrifos (Dursban)	10	200	30
	p,p'-DDD	10	200	30
	p-p'-DDE	10	200	30
	p,p'-DDT	10	200	30
	Dieldrin	10	200	30
	Endosulfan I	10	200	30

Table 9.7.1: Default QC Limits*

	Compound	Default LCL %Recovery	Default UCL %Recovery	Default Precision %RPD
	Endosulfan II	10	200	30
	Endosulfan Sulfate	10	200	30
	Endrin	10	200	30
	Endrin Aldehyde	10	200	30
	Endrin Ketone	10	200	30
	Heptachlor	10	200	30
	Heptachlor Epoxide	10	200	30
	Hexachlorobenzene	10	200	30
	Methoxychlor	10	200	30
	Mirex	10	200	30
	Toxaphene	10	200	30
Surrogate				
	TCMX (Surrogate)	10 (0.04µg/L)	200 (0.80µg/L)	NA
	DCBP (Surrogate	10 (0.08µg/L)	200 (1.6µg/L)	NA
MS/MSD	Same as LCS/LCSD*			

*Methods 8000B and 8081A do not specify a range limit for Surrogate, LCS or MS recoveries or precisions. LCS recoveries are derived from Control Charting. The EPD lab will use the LCS/LCSD limits for the MS/MSD recovery limits. No recovery may be less than 10% or higher than 200%. The EPD Lab sets a default of no higher than 70% for the LCL and no less than 130% for the UCL. Precision RPD will be set at 30% default.

9.8. Method Detection Limit Study (MDL):

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

9.8.2. The actual MDL varies depending on instrument and matrix.

9.8.3. 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.

9.8.4. 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.

9.9. Initial MDL study:

9.9.1. 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.

9.9.2. 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.

9.10. Continuous MDL study:

9.10.1. 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 9.9.2 for requirements.)

9.10.2. 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.

9.10.3. The results of the MDLBlank will be entered into Labworks using the Method Blank test code, $B_8081H. The MDLSpike result will be entered using the $ML8081H. The MDL Spiked Amount will be entered into the test code $MA8081H. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-8081H.

9.10.4. 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 Refer to GA EPD Laboratory SOP – Separatory Funnel Liquid-Liquid Extraction – EPA Method 3510C, SOP 1-028, Rev. 7 or later for the sample prep and extraction procedure.

10.2 Upon completion of the extraction procedure, samples are diluted if necessary and vialed in 2mL autosampler vials using 300µL inserts to preserve sample volume if desired.

10.3 Analyze all sample extracts and QC using a gas chromatograph equipped with an electron capture detector.

10.4 Sample response is measured against the calibration curves. If the response exceeds the upper limit of the curve, the sample extract is diluted and re-analyzed.

10.4.1 Dilutions: 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 (Hexane) 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 standard.

10.5 A detect is considered to be positive if the quantitation amount is greater than the Reporting Limit for that compound. When a positive detect is found, the sample must be re-analyzed on a second, dissimilar confirmation column. If the difference between the quantitation amount found for the detected compound on the primary column and the confirmation column is greater than 40%, the detected compound is considered to be not confirmed. The Blanks, LCS and MS values are taken from the primary column. If the results of this column are out of acceptable range due to matrix interferences or other problems, the results may be reported from the confirmation column provided the calibration criteria are met.

10.6 Single peak analytes are identified as positive if detected within its appropriate retention time window on both columns. For multi-component analytes, a fingerprint pattern and retention time match is required.

10.6.1 Chlordane will be quantitated when the pattern in the sample reasonably matches that of the standard. Heptachlor, Heptachlor Epoxide, α-Chlordane and γ-Chlordane are calculated separately. The area of a minimum of three peaks, but preferably five or more peaks, should be summed and averaged for use in determining the Chlordane concentration. Weathered Chlordane no longer showing the characteristic pattern will be qualified as estimated (J).

10.6.2 Toxaphene concentration is determined using four to six (or more) peaks. When front end degradation of the Toxaphene is apparent on the chromatogram, then the peaks should be taken from the latter half of the Toxaphene pattern. The chosen peaks should not be disproportionately larger or smaller in the sample compared to the standard. The areas of the four to six peaks should be summed and averaged for use in determining the Toxaphene concentration. Weathered Toxaphene no longer showing the characteristic pattern will be qualified as estimated (J).

11 Calculations

11.1 Response Factor, RF, for a peak

$$RF = \frac{\text{Area}_{\text{Analyte}}}{\text{Concentration}_{\text{Analyte}}}$$

11.1.1 Where:

RF = Response Factor
Area $_{\text{Analyte}}$ = Area of the peak of the analyte of interest
Concentration $_{\text{Analyte}}$ = Concentration of the analyte of interest in µg/ml

11.2 Average Response Factor, $\overline{RF}$

$$\overline{\mathrm{RF}} = \sum \frac{RF_i}{n}$$

11.2.1 Where:
$\overline{\mathrm{RF}}$ = Mean response factor
RF_i = Response factor of compound at each level *i*
n = Number of calibration standards

11.3 Sample Standard Deviation (n – 1) (σ_{n-1}) of response factors

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(RF_i - \overline{RF})^2}{n-1}}$$

11.3.1 Where:
σ_{n-1} = Sample Standard Deviation
$\overline{\mathrm{RF}}$ = Mean response factor
RF_i = Response factor of compound at each level *i*
n = Number of calibration standards

11.4 First Order Linear Regression Response Equation

$$Y = ax + b$$

This rearranges to:
$$x = Y - b/a$$

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

11.5 Second Order Quadratic Fit Equation

11.5.1 $Y = ax^2 + bx + c$

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

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

11.5.4 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 Average Retention Time, $\overline{RT}$

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

11.6.1 Where:
$\overline{RT}$ = Mean retention time for the target compound
RT = Retention time for the target compound
n = Number of values

11.7 Percent Drift, %Drift

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

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

11.8 Extract Concentration Calculation (µg/mL)

$$\mu g/mL = \frac{(A_s)}{(\overline{RF})}$$

11.8.1 Where:
A_s = Peak area of analyte
$\overline{RF}$ = Average Response Factor

11.9 Sample Concentration Calculation (µg/L)

$$\mu g/L = \frac{(A_s)(V_t)(D)}{(RF)(V_i)(V_s)}$$

11.9.1 Where:
A_s = Area of peak for analyte in sample
V_t = Extract volume in mL
D = Dilution factor
RF = Mean response factor (area per µg)
V_i = Volume of sample injected in µL
V_s = Original sample volume in mL

11.10 Sample Concentration Adjustment for Varying Initial Volume and Dilutions

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

11.10.1 Where:
DF = Dilution Factor
V_s = Original sample volume in mL

11.11 Quality Control Calculations

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

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

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

11.12 Breakdown Calculations

11.12.1 Endrin and DDT breakdown due to active sites in the injector or on the column with Endrin being oxidized and DDT being subjected to dechlorination. In addition, Endrin is subject to oxidation as a result of air leaking into the system or not being adequately scrubbed from the gases used for flow and makeup.

11.12.2 Breakdown for each main compound is calculated by determining the % recovery of each compound with respect to the total amount of main compound plus derivatives.

11.12.3 Endrin Breakdown:

$$\%\text{Recovery of Endrin} = \left(\frac{\text{Area}_{\text{E}}}{\text{Area}_{\text{E}} + \text{Area}_{\text{EA}} + \text{Area}_{\text{EK}}}\right) * 100$$

11.12.4 DDT Breakdown:

$$\%\text{Recovery of DDT} = \left(\frac{\text{Area}_{\text{DDT}}}{\text{Area}_{\text{DDT}} + \text{Area}_{\text{DDE}} + \text{Area}_{\text{DDD}}}\right) * 100$$

11.12.5 Where:
Area_{E} = Area of Endrin peak in breakdown chromatogram
Area_{EA} = Area of Endrin aldehyde
Area_{EK} = Area of Endrin Ketone
Area_{DDT} = Area 4,4'-DDT
Area_{DDE} = Area 4,4'-DDE
Area_{DDD} = Area 4,4'-DDD

12 Waste Management

12.1 See GA EPD Laboratory SOP – EPD Laboratory Waste Management Standard Operating procedures, SOP6-015, Rev. 1 or later.

13 References

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

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

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

13.4 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

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

13.6 GA EPD Laboratory SOP – Separatory Funnel Liquid-Liquid Extraction – EPA Method 3510C, SOP 1-028, online revision.

13.7 EPA Method SW846-8000B – Determinative Chromatographic Separation, Rev. 2, December 1996.

13.8 EPA Method SW846-8081A – Organochlorine Pesticides by Gas Chromatography, Rev. 1, December 1996.

13.9 EPA Method SW846-3510C – Separatory Funnel Liquid-Liquid Extraction, Rev. 3, December 1996.

13.10 GA EPD Laboratory Chemical Hygiene 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 RLs for EPA Method SW846-8081A in Water

Parameter/Method	Analyte	Matrix (Water)	
		RL	Unit
SW846-8081A (Water)	Aldrin	0.05	µg/L
	α-BHC	0.05	µg/L
	β-BHC	0.05	µg/L
	δ-BHC	0.05	µg/L
	γ-BHC (Lindane)	0.05	µg/L
	Chlordane	5.0	µg/L
	α-Chlordane	0.05	µg/L
	γ-Chlordane	0.05	µg/L
	Chlorpyrifos (Dursban)	0.10	µg/L
	p,p'-DDD	0.10	µg/L
	p-p'-DDE	0.10	µg/L
	p,p'-DDT	0.10	µg/L
	Dieldrin	0.10	µg/L
	Endosulfan I	0.05	µg/L
	Endosulfan II	0.10	µg/L
	Endosulfan Sulfate	0.10	µg/L
	Endrin	0.10	µg/L
	Endrin Aldehyde	0.10	µg/L
	Endrin Ketone	0.10	µg/L
	Heptachlor	0.05	µg/L
	Heptachlor Epoxide	0.05	µg/L

Table 14.1 RLs for EPA Method SW846-8081A in Water

Parameter/Method	Analyte	Matrix (Water)	
		RL	Unit
SW846-8081A (Water)	Hexachlorobenzene	0.05	µg/L
	Methoxychlor	0.50	µg/L
	Mirex	0.10	µg/L
	Toxaphene	5.0	µg/L

Table 14.2 Summary of Calibration and QC Procedures for EPA Method SW846-8081A in Water

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA Method SW846-8081A (Water)	Chlorinated hydrocarbon pesticides	5-point initial calibration for all analytes	Initial calibration prior to sample analysis	RSD for all analytes ≤ 20% linear-least squares regression $r \geq 0.990$ or $r^2 \geq 0.980$	Correct problem then repeat initial calibration	
		Initial calibration verification (CCC)	Beginning each analysis sequence prior to the analysis of samples, after every 12 hours, and at the end of the analysis sequence	All analytes within ± 15% of expected values	If out of range high, high bias with no detects, generate a corrective action and use data. If low bias or with detects, rerun CCC and affected samples. If rerun passes, use data. If reruns do not pass, correct problem, repeat initial calibration verification and re-analyze all samples since last successful calibration verification	
		Second source calibration verification (ICV)	Once per initial calibration	All analytes within ± 15% of expected value	Correct problem then repeat initial calibration	
		Retention Time window calculated for each analyte	Once per year or after major maintenance that would affect RTs	± 3 times standard deviation for each analyte retention time for standard analytical batch sequence	Correct problem then re-analyze all samples analyzed since the last retention time check	

Table 14.2 Summary of Calibration and QC Procedures for EPA Method SW846-8081A in Water

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA Method SW846-8081A (Water)	Chlorinated hydrocarbon pesticides	Retention time window update	Must be done every 12 hours with each CCC and prior to sample analysis	First CCC of each sequence and then every 12 hours	None	
		Breakdown check (Endrin & DDT)	Prior to analysis then every 12 hours	Degradation ≤ 15% for either Endrin or DDT	Correct problem and re-analyze	
		IDC- Demonstrate ability to generate acceptable accuracy and precision using four replicate analyzes of a QC check sample, a Blind and a Blank	Once per analyst	QC acceptance criteria Table A.1, Appendix A	Locate and fix problem then re-run or re-extract demonstration for those analytes that did not meet criteria	
		Surrogate spike	Every sample, spiked sample, standard and method blank	QC acceptance criteria Table A.1, Appendix A	Analyze second extract aliquot, if this does not pass, correct problem then re-extract and re-analyze the sample	
		Method Blank Solvent Blank	One per analytical batch of 20 or less samples	No analytes detected >RL	Analyze second extract aliquot, if this does not pass, correct problem then re-analyze or re-extract the blank and all samples in the affected batch	
		LCS/LCSD for all analytes	One per analytical batch of 20 or less samples	QC acceptance criteria Table A.1, Appendix A	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	Minimum of 5% of all samples analyzed	QC acceptance criteria Table A.1, Appendix A	Flag QC sample report	

Table 14.2 Summary of Calibration and QC Procedures for EPA Method SW846-8081A in Water

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA Method SW846-8081A (Water)	Chlorinated hydrocarbon pesticides	Second-column confirmation	100% for all positive results, ≤ 40% RPD for confirmation	If used for quantitation, same as for initial or primary column analysis	Same as for initial or primary column analysis	
		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	

15 Associated LabWorks Test Codes

15.1 Parent Test Code

15.1.1 $8081H

15.2 Extraction Test Code

15.2.1 EXTN_P

15.3 QC Test Codes

15.3.1 $B_8081H – Extraction Blank Results

15.3.2 $LA8081H – LCS/LCSD Spike Amount

15.3.3 $LS8081H – LCS Results

15.3.4 $LD8081H – LCSD Results

15.3.5 $LR8081H – LCS Percent Recovery

15.3.6 $L28081H – LCSD Percent Recovery
15.3.7 $LP8081H – LCS/LCSD Precision
15.3.8 $A_8081H – MS/MSD Spike Amount
15.3.9 $S_8081H – MS Results
15.3.10 $D_8081H – MSD Results
15.3.11 $R_8081H – MS Percent Recovery
15.3.12 $RD8081H – MSD Percent Recovery
15.3.13 $P_8081H – MS/MSD Precision
15.3.14 $MA8081H – MDL Spike Amount
15.3.15 $ML8081H – MDL Results

Appendix A – Quality Assurance Criteria for EPA Method SW846-8081A in Water

Table A.1

QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
LCS/LCSD*	Aldrin	33	-	130	30
	α-BHC	52	-	140	30
	β-BHC	70	-	130	30
	δ-BHC	39	-	134	30
	γ-BHC (Lindane)	56	-	138	30
	Chlordane	62	-	141	30
	α-Chlordane	70	-	130	30
	γ-Chlordane	42	-	130	30
	Chlorpyrifos (Dursban)	66	-	136	30
	p,p'-DDD	64	-	142	30
	p-p'-DDE	70	-	130	30
	p,p'-DDT	60	-	130	30
	Dieldrin	58	-	133	30
	Endosulfan I	63	-	137	30
	Endosulfan II	66	-	130	30
	Endosulfan Sulfate	41	-	138	30
	Endrin	65	-	139	30
	Endrin Aldehyde	65	-	130	30
	Endrin Ketone	10	-	200	30
LCS/LCSD*	Heptachlor	47	-	138	30

Table A.1					
QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
	Heptachlor Epoxide	70	-	130	30
	Hexachlorobenzene	58	-	130	30
	Methoxychlor	57	-	130	30
	Mirex	51	-	132	30
	Toxaphene	43	-	146	30
Surrogate**	TCMX	23.5	-	162	NA
	TCMX (as ug/L)	0.0940	-	0.650	NA
	DCBP	15.0	-	146	NA
	DCBP (as µg/L)	0.120	-	1.17	NA
MS/MSD***	Same as LCS Recoveries	See Above			30

*LCS/LCSD recovery based on Control Charts of data collected from 12/31/2010 to 1/01/2021. The EPD lab sets a default of 30% RPD for all compounds.

** Surrogate recoveries based on Control Charts of data collected from 12/31/2010 to 1/01/2021.

*** The EPD lab sets the MS/MSD recoveries and precisions as the same as the LCS/LCSDs.

Updates: Appendix A added. Updated for online revision.