

EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF PESTICIDES

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Exhibit D - Analytical Methods for Pesticides

Table of Contents

<u>Section</u>	<u>Page</u>
1.0 SCOPE AND APPLICATION	5
2.0 SUMMARY OF METHOD	6
3.0 DEFINITIONS	6
4.0 INTERFERENCES	7
5.0 SAFETY	7
6.0 EQUIPMENT AND SUPPLIES	8
7.0 REAGENTS AND STANDARDS	14
7.1 Reagents	14
7.2 Standards	15
8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES	21
8.1 Sample Collection and Preservation	21
8.2 Procedure for Sample Storage	21
8.3 Procedure for Sample Extract Storage	21
8.4 Records for Sample and Sample Extract Storage	21
8.5 Contract Required Holding Times	21
9.0 CALIBRATION AND STANDARDIZATION	22
9.1 Gas Chromatograph (GC) Operating Conditions	22
9.2 Initial Calibration	22
9.3 Calibration Verification	29
10.0 PROCEDURE	34
10.1 Sample Preparation	34
10.2 Extract Concentration	41
10.3 Cleanup Procedures	44
10.4 GC/ECD Analysis	54
11.0 DATA ANALYSIS AND CALCULATIONS	58
11.1 Qualitative Identification	58
11.2 Calculations	60
11.3 Technical Acceptance Criteria for Sample Analyses	65
11.4 Corrective Action for Sample Analysis	66
12.0 QUALITY CONTROL (QC)	67
12.1 Blank Analyses	67
12.2 Laboratory Control Sample (LCS)	72
12.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)	73
12.4 Method Detection Limit (MDL) Determination	75
13.0 METHOD PERFORMANCE	77
14.0 POLLUTION PREVENTION	77
15.0 WASTE MANAGEMENT	77
16.0 REFERENCES	78
17.0 TABLES/DIAGRAMS/FLOWCHARTS	79

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1.0 SCOPE AND APPLICATION

- 1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of chlorinated pesticides in hazardous waste samples. These methods were based on USEPA Method 608, Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs). In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis for other USEPA methods to perform the analysis of chlorinated pesticides contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of chlorinated pesticides [and Aroclors in Exhibit D (Analytical Method for the Analysis of Aroclors)] at hazardous waste sites.
- 1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites to determine the presence and concentration of the chlorinated pesticides found in the Target Compound List (TCL) in Exhibit C (Pesticides). The method can be used for determining compound concentrations in the range from the Contract Required Quantitation Limits (CRQLs) to one million times the CRQL in these matrices, when appropriate dilutions are made. The method includes sample extraction, extract cleanup techniques, and Gas Chromatograph/Electron Capture Detector (GC/ECD) analytical methods for pesticides.
- 1.3 Resolution difficulties have been associated with the following pairs of compounds using this method:
- On a DB-608 or equivalent column, DDE and Dieldrin; Methoxychlor and Endrin ketone; and Endosulfan I and gamma-Chlordane; and
 - On a DB-1701 or equivalent column, Endosulfan I and gamma-Chlordane, and Methoxychlor and Endosulfan sulfate.
- 1.4 There are two isomers of heptachlor epoxide, the endo epoxy isomer (Isomer A) and the exo epoxy isomer (Isomer B). The two isomers are separable using current GC capillary columns. Only the exo epoxy isomer (Isomer B) is of environmental significance. This is the isomer that must be used as an analytical standard, identified and quantitated in sample analysis, and reported on appropriate forms as heptachlor epoxide.

Exhibit D Pesticides -- Sections 2 & 3
Summary of Method

2.0 SUMMARY OF METHOD

2.1 Water

Continuous liquid-liquid or separatory funnel extraction procedures are employed for aqueous samples. A 1 L volume of sample is spiked with the surrogate solution and extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried with anhydrous sodium sulfate (or Hydromatrix™), concentrated, and cleaned up. Gel Permeation Chromatography (GPC) is required when higher molecular weight compounds are present that interfere with the analyses of target compounds; GPC is optional for all other circumstances. The extract is then solvent exchanged into hexane, cleaned up by Florisil cartridges or other methods as applicable, and analyzed using a dual column wide-bore capillary Gas Chromatograph/Electron Capture Detector (GC/ECD).

2.2 Soil/Sediment

A 30 g aliquot of sample is dried with anhydrous sodium sulfate (or Hydromatrix), spiked with the surrogates, and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by ultrasonic extraction, Soxhlet extraction, or pressurized fluid extraction. The extract is filtered (for ultrasonic extraction), concentrated, and solvent-exchanged into methylene chloride. The methylene chloride extract is then cleaned up by GPC (mandatory), solvent-exchanged into hexane, cleaned up by a Florisil cartridge or other methods as applicable, and analyzed using a dual column wide-bore capillary GC/ECD.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in Gas Chromatograms. These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing instrument and method blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures in this method must be used to remove such interferences in order to achieve the Contract Required Quantitation Limits (CRQLs).

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analyses.

5.2 Specifically, concentrated sulfuric acid and the 10 N sodium hydroxide solution are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT; 4,4'-DDD; and the 1,2,3,4,5,6-hexachlorocyclohexane (BHCs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

Exhibit D Pesticides -- Section 6
Equipment and Supplies

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor must document any use of alternative equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors

Continuous Liquid-Liquid Extractors - Equipped with polytetrafluoroethylene (PTFE) or glass connecting joints and stopcocks requiring no lubrication or hydrophobic membrane-based extractor.

6.1.2 Separatory Funnels - 2 L with PTFE stopcock.

6.1.3 Beakers - 100 mL, 125 mL, 250 mL, and 400 mL.

6.1.4 Erlenmeyer Flasks - 250 mL.

6.1.5 Syringes - 10 mL with Luer-Lok fitting; 1 mL or 2 mL, 5 mL, 100 µL, and 1000 µL.

6.1.6 Vials and Caps - 10 mL (optional), 20 mL, 40 mL, and 60 mL with screw-cap and PTFE or aluminum foil liner, 2 mL capacity for Gas Chromatograph (GC) auto sampler.

6.1.7 Pipets - Glass volumetric 1 mL or 2 mL.

6.1.8 Centrifuge Tube - 12 to 15 mL with 19 mm ground glass joint (optional).

6.1.9 Class A Graduated Cylinder - 1 L and 100 mL capacity.

6.1.10 Drying Column - Chromatographic column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable borosilicate glass wool for the frit will help prevent cross-contamination of sample extracts).

6.1.11 Class A Volumetric Flasks - 10 mL and 1 or 2 mL.

6.1.12 Bottle or Test Tube - 20 mL with PTFE-lined screw-cap for sulfur removal and a glass bottle - 1 L volume, for use in preparation of Bio Beads for packing into a column.

6.1.13 Powder Funnels - 10 cm diameter, for filtration/drying.

6.1.14 Buchner Funnels - 9 cm diameter, for filtration.

6.1.15 Kuderna-Danish (K-D) Apparatus.

6.1.15.1 Concentrator Tubes - 10 mL, graduated.

6.1.15.2 Evaporative Flasks - 500 mL.

6.1.15.3 Snyder Column - Three-ball macro.

6.1.15.4 Snyder Column - Two-ball micro.

6.2 [Automated] Soxhlet Extraction System

[Automated] Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil must not be used because it destroys the rubber parts. The apparatus must be used in a hood.

6.2.1 Cellulose or Glass Extraction Thimbles - 26 mm ID x 60 mm, contaminant-free.

6.2.2 Glass Extraction Cups (80 mL) - (set of six required for the HT-6).

6.2.3 Thimble Adapters - (set of six required for the HT-6).

6.2.4 Viton Seals.

6.3 Pressurized Fluid Extraction System

Pressurized Fluid Extraction System - Dionex Accelerated Solvent Extractor (ASE-300) or equivalent with appropriately-sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements [2000+ pounds per square inch (psi)] necessary for this procedure. Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.4 Florisil Cleanup Equipment

6.4.1 Florisil - 500 mg or 1 g cartridges with stainless steel or PTFE frits.

6.4.2 Vacuum System for Eluting Multiple Cleanup Cartridges.

6.4.3 Vacuum Trap - Made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

6.4.4 Vacuum Pressure Gauge.

6.5 Gel Permeation Chromatography (GPC) Equipment

6.5.1 GPC System - Systems that perform satisfactorily have been assembled from the following components: a High Performance Liquid Chromatography (HPLC) pump; an auto sampler or a valving system with sample loops; and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements in Section 10.3.1.3.

NOTE: GPC cleanup is required for extracts for all soils/sediments and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target compounds.

6.5.2 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached to that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

Exhibit D Pesticides -- Section 6
Equipment and Supplies (Con't)

- 6.5.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column.
- 6.5.4 Bio Beads (SX-3) - 200 to 400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.
- 6.5.5 UV Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.
- 6.5.6 Strip Chart Recorder - Recording integrator or laboratory data system.
- 6.5.7 Syringe Filter Assembly, disposable.

NOTE: Consult your instrument operation manual to determine the proper size filter disc to use in your system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

- 6.6 pH Paper - Wide range.
- 6.7 Spatula - Stainless steel or PTFE.
- 6.8 Centrifuge - Table top (optional).
- 6.9 Balances - Top loading, capable of weighing accurately to ± 0.01 g, analytical, capable of weighing accurately to ± 0.0001 g. The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with Class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.
- 6.10 Ultrasonic Cell Disruptor - Minimum 300 watt output capability.

NOTE: To ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.
- 6.11 Sonabox Acoustic Enclosure (or equivalent) - For use with disruptor to decrease noise level.
- 6.12 Filter Paper - Whatman No. 41, 9 cm circles, or equivalent.
- 6.13 Filter Disks - 1.91 cm Type D28.
- 6.14 Cell Cap Sealing Disks.
- 6.15 Borosilicate Glass Wool - Rinsed with methylene chloride and dried before use.
- 6.16 Boiling Chips
 - 6.16.1 Silicon carbide boiling chips - Approximately 10 to 40 mesh. Heat the chips to 400°C for 30 minutes or solvent rinse before use.
 - 6.16.2 PTFE Boiling Chips (optional) - Solvent rinse the chips before use.

- 6.17 Water Bath - Heated, with concentric ring cover, capable of temperature control.
 - 6.18 Nitrogen Evaporation Device - Equipped with a heated bath that can be maintained at 35-40°C.
 - 6.19 Oven - Drying.
 - 6.20 Desiccator
 - 6.21 Crucibles - Porcelain crucibles or aluminum weighing pans.
 - 6.22 Aluminum Weighing Dish
 - 6.23 pH Meter - With a combination glass electrode. Calibrate according to manufacturer's instructions. The pH meter must be calibrated prior to each use.
 - 6.24 Magnetic Stirrer Motor
 - 6.25 Magnetic Stirrer Bar - PTFE coated, at least 4 cm long.
 - 6.26 Gas Chromatograph/Electron Capture Detector (GC/ECD) System
 - 6.26.1 Gas Chromatograph (GC)
 - 6.26.1.1 The GC must adequately regulate temperature in order to give a reproducible temperature program and have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must have all required accessories including syringes, analytical columns, and gases.
 - 6.26.1.2 GCs that are available from some manufacturers may have difficulty in meeting certain method QC requirements because of Endrin and DDT breakdown in the injector. This problem can be minimized by operating the injector at 200-205°C, using a borosilicate glass (not quartz) methyl silicone deactivated injector liner, and deactivating the metal parts in the injector with dichlorodimethyl silane. In some cases, using a 0.25 inch packed column injector converted for use with 0.53 mm capillary columns works better than a Grob-type injector. If a Grob-type injector is used, a 4 mm liner may be required to meet breakdown criteria.
 - 6.26.1.3 GC Columns - Wide-bore (0.53mm ID) fused silica GC columns may be used provided that the resolution requirements are met (see Section 9.2.5.2); if two wide-bore (0.53 mm ID) fused silica GC columns are used, then a separate detector is required for each column. The specified analytical columns are a 30 m x 0.53 mm ID, 1.0 µm film thickness DB-1701 (J&W Scientific); SPB 1701 (Supelco); AT 1701 (Alltech); RTX-1701, RTX CLP I, RTX CLP II (Restek); CP-Sil 19CB (Chrompack); 007-1701 (Quadrex); BP-10 (SGE); or equivalent, and a 30 m x 0.53 mm ID, 0.5 to 1.0 µm film thickness DB-608 (J&W Scientific); HP-608 (Agilent); SPB-608 (Supelco); 007-608 (Quadrex); BP-608 (SGE); CP-Sil 8CB (Chrompack); or equivalent.
- NOTE: The column length stated above is the minimum requirement. Longer columns that meet resolution and calibration requirements may be used. A description of the GC columns used for analysis shall be provided in the SDG Narrative.

Exhibit D Pesticides -- Section 6
Equipment and Supplies (Con't)

- 6.26.1.3.1 A capillary column is considered equivalent if:
- The column does not introduce contaminants that interfere with the identification and quantitation of the compounds listed in Exhibit C (Pesticides);
 - The analytical results generated using the column meet the initial calibration and calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Pesticides);
 - The column can accept at least 16 times the low-point concentration level as listed in Section 7.2.2.5 for each compound listed in Exhibit C (Pesticides) without becoming overloaded; and
 - The column pair chosen must have dissimilar phases/chemical properties in order to separate the compounds of interest in different Retention Time (RT) order.
- 6.26.1.3.2 Although the instructions included in the analytical method are for wide bore capillary columns, narrower bore capillary columns may be evaluated for use. Follow manufacturer's instructions for use of its product. Document in the SDG Narrative if other columns are used by specifying the column used.
- 6.26.1.3.3 As applicable, follow the manufacturer's instructions for use of its product.
- 6.26.1.3.4 The Contractor must maintain documentation verifying that the alternate column met the criteria in Sections 9.2.5 and 9.3.5. The minimum documentation is as follows:
- 6.26.1.3.4.1 Manufacturer provided information concerning the performance characteristics of the column.
- 6.26.1.3.4.2 GC chromatograms and data system reports generated on the GC/ECD and used for Contract Laboratory Program (CLP) analyses:
- From instrument blanks which demonstrate that there are no contaminants that interfere with the pesticide analysis when using the alternate column;
 - For initial calibration standards analyzed using the alternate column; and
 - For calibration verification standards analyzed using the alternate column.
- 6.26.1.3.5 Based on the Contractor-generated data described in Section 6.26.1.3.4.2, the Contractor must complete a written comparison and review, signed by the Laboratory Manager, certifying that:
- The alternate column performance is comparable to the required column performance in its ability to produce initial calibrations and calibration verifications that meet the technical acceptance criteria in Sections 9.2.5 and 9.3.5;

- The low-point initial calibration standard analyses have adequate sensitivity to meet the pesticide CRQLs;
- The high-point initial calibration standard analyses were not overloaded; and
- The alternate column does not introduce contaminants which interfere with the identification and quantitation of compounds listed in Exhibit C (Pesticides).

6.26.1.3.6 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the USEPA Regional CLP Project Officer (CLP PO).

6.26.1.3.7 **PACKED COLUMNS CANNOT BE USED.**

6.26.1.4 Columns are mounted in a press-fit Y-shaped glass 3-way union splitter or a Y-shaped fused-silica connector from a variety of commercial sources. The two columns may be mounted in an 8 inch deactivated glass injection tee. The Contractor should follow the manufacturer's recommendations for mounting 0.53 mm capillary columns in injector ports.

6.26.1.5 The carrier gas for routine applications is helium. Laboratories may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative and on all divider pages preceding raw chromatographic data in submissions to USEPA. Laboratories that choose to use hydrogen are advised to exercise caution in its use. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.26.2 Electron Capture Detector (ECD)

The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane) or nitrogen according to the instrument specification. Care must be taken to maintain stable and an appropriate flow of make-up gas to the detector. The GC/ECD system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants that may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.26.3 Data System

A data system must be interfaced to the GC/ECD. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at a minimum, the output of time vs. intensity (peak height or peak area) data. Also, the data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

6.26.4 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

Exhibit D Pesticides -- Section 7
Reagents and Standards

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) for each compound of interest.

7.1.1.1 Reagent water may also be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.1.2 Reagent water may be generated using a water purification system.

7.1.2 Sodium sulfate - Granular anhydrous reagent grade, heated at 400°C for 4 hours, or at 120°C for 16 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by a Gas Chromatograph/Electron Capture Detector (GC/ECD) to demonstrate that it is free of interference before use.

OR

Hydromatrix - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

7.1.3 Methylene chloride, hexane, acetone, toluene, iso-octane, and methanol (optional) - pesticide quality or equivalent. It is recommended that each lot of solvent be analyzed to demonstrate that it is free of interference before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.1.4 Copper powder (optional) - Fine, granular. Copper may be used instead of mercury for sulfur cleanup. Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.

7.1.5 Sodium hydroxide solution (10 N). Carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 mL.

7.1.6 Tetrabutylammonium Sulfite

7.1.7 Sodium Sulfite

7.1.8 Concentrated sulfuric acid (18 N).

7.1.9 Nitric acid - Dilute, for sulfur removal with copper.

7.1.10 10% acetone in hexane (v/v). Prepare by adding 10.0 mL of acetone to 90.0 mL of hexane.

7.2 Standards

Introduction

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from the preparation date. The expiration date of the ampulated standards upon the breaking of the glass seal is 6 months (or sooner if the standard has degraded or evaporated).

7.2.1 Stock Standard Solutions

- 7.2.1.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be purchased or prepared in methylene chloride or another suitable solvent.

7.2.2 Working Standards

7.2.2.1 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to all standards, samples [including Laboratory Control Samples (LCSs)], Matrix Spikes and Matrix Spike Duplicates (MS/MSDs), Performance Evaluation (PE) samples (if required), and required blanks (method/sulfur cleanup/instrument). Prepare a surrogate spiking solution of 0.20 µg/mL for tetrachloro-m-xylene and 0.40 µg/mL for decachlorobiphenyl in acetone. The solution should be checked frequently for stability. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

NOTE: Other concentrations for surrogate standard spiking solutions may be used, provided that the appropriate amount of surrogates are added to all standards, samples (including LCSs), MS/MSDs, PE samples, and blanks.

7.2.2.2 Matrix Spiking Solution

Prepare a matrix spiking solution in acetone or methanol that contains the following pesticides at the concentrations specified. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

Exhibit D Pesticides -- Section 7
Reagents and Standards (Con't)

<u>Pesticide</u>	<u>Concentration (ug/mL)</u>
gamma-BHC (Lindane)	0.50
Heptachlor	0.50
Aldrin	0.50
Dieldrin	1.0
Endrin	1.0
4,4'-DDT	1.0

7.2.2.3 Resolution Check Mixture

The Resolution Check Mixture is composed of all the pesticides listed in Exhibit C and surrogates at the concentrations listed below in hexane or iso-octane. The mixture must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

<u>Compounds</u>	<u>Concentration (ng/mL)</u>
alpha-BHC	10.0
beta-BHC	10.0
delta-BHC	10.0
gamma-BHC	10.0
Aldrin	10.0
Heptachlor	10.0
Heptachlor-epoxide	10.0
alpha-Chlordane	10.0
gamma-Chlordane	10.0
Endosulfan I	10.0
Endosulfan II	20.0
4,4'-DDD	20.0
4,4'-DDE	20.0
4,4'-DDT	20.0
Dieldrin	20.0
Endrin	20.0
Endosulfan sulfate	20.0
Endrin ketone	20.0
Endrin aldehyde	20.0
Methoxychlor	100.0
Tetrachloro-m-xylene	10.0
Decachlorobiphenyl	20.0

7.2.2.4 Performance Evaluation Mixture (PEM)

The PEM is prepared in hexane or iso-octane, as listed below. The PEM must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

<u>Compounds</u>	<u>Concentration (ng/mL)</u>
alpha-BHC	10.0
beta-BHC	10.0
gamma-BHC	10.0
Endrin	50.0

<u>Compounds</u>	<u>Concentration (ng/mL)</u>
4,4'-DDT	100.0
Methoxychlor	250.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

7.2.2.5 Individual Standard Mixtures

The suggested compositions of Individual Standard Mixture A and Mixture B are listed in this section with the concentrations of each target compound and surrogate given for the CS1 Standard A and CS1 Standard B. The CS1 Standard C for Individual Standard Mixture C will contain all target compounds and surrogates for both Mixture A and Mixture B at the same concentrations as the CS1 Standard for Mixture A and Mixture B. The Calibration Standard Mixture solutions must be prepared in either hexane or iso-octane. The analysis of the Resolution Check Mixture will determine whether one or two sets of Individual Standard Mixture solutions will be needed. Prepare calibration standards at a minimum of five concentration levels. The concentrations of the pesticides in the low-point standard mixtures (CS1) correspond to the low-point concentration (see Table in this section) or lower for each analyte. The concentration for each analyte in the high-point standard must be at least 16 times the concentration of the low-point standard, but a higher concentration may be chosen by the Contractor provided that the higher concentration standards meets the technical acceptance criteria in Sections 9.2.5 and 9.3.5. The concentration levels of each target compound for each calibration standard are listed in Table 4. These levels are based upon 10 mL final volume extracts for samples not undergoing Gel Permeation Chromatography (GPC) cleanup, and 5.0 mL final volume extracts for those samples undergoing GPC cleanup. Other concentration levels may be used for more sensitive instrumentation and final extract levels. For example in the case of alpha-BHC, a laboratory may use a final extract volume of 10 mL for samples undergoing GPC cleanup, and a low calibration standard of 2.5 ng/mL. The alternate calibration standards and final volumes may be used as long as the following requirements are met:

- The laboratory can demonstrate that the CRQL for each analyte listed in Exhibit C can be reached using the calibration and final volume scheme. This demonstration is made when there is formal documentation of laboratory Method Detection Limit (MDL) studies indicating that the calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final volume and calibration level scheme.
- All five calibration levels are in the same ratio as that shown in Table 4 (e.g., if a laboratory were using a 2.5 ng/mL low standard, then the other calibration levels must be 5.0, 10, 20, and 40 ng/mL).

The standards must be prepared every 6 months, or sooner if the solutions have degraded or concentrated.

Exhibit D Pesticides -- Section 7
Reagents and Standards (Con't)

Individual Standard Mix A	Low-Point (CS1) Concentration (ng/mL)	Individual Standard Mix B	Low-Point (CS1) Concentration (ng/mL)
alpha-BHC	5.0	beta-BHC	5.0
gamma-BHC	5.0	delta-BHC	5.0
Heptachlor	5.0	Aldrin	5.0
Endosulfan I	5.0	Heptachlor- epoxide (exo- epoxy isomer)	5.0
Dieldrin	10	4,4'-DDE	10
Endrin	10	Endosulfan II	10
4,4'-DDD	10	Endosulfan sulfate	10
4,4'-DDT	10	Endrin ketone	10
Methoxychlor	50	Endrin aldehyde	10
Tetrachloro-m- xylene	5.0	alpha-Chlordane	5.0
Decachlorobiphenyl	10	gamma-Chlordane	5.0
		Tetrachloro-m- xylene	5.0
		Decachloro- biphenyl	10

NOTE: Only the exo-epoxy isomer (Isomer B) of heptachlor epoxide is used as an analytical standard.

7.2.2.6 Toxaphene Standards

Prepare Toxaphene standard solutions at a minimum of five concentration levels. The Toxaphene standards must be prepared in hexane or iso-octane and contain the surrogates at the appropriate concentrations (for CS1, the concentrations of tetrachloro-m-xylene and decachlorobiphenyl should be 5.0 and 10 ng/mL respectively). The concentration of Toxaphene in the low-point standard (CS1) should be 500 ng/mL or lower. The concentration in the high-point standard (CS5) must be at least 16 times the low-point standard for Toxaphene but a higher concentration may be chosen by the Contractor. For most operations, the calibrations standards are to be prepared at 500, 1000, 2000, 4000 and 8000 ng/mL (see discussion on alternate calibration standards and final volumes in Section 7.2.3.5). The standard must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.7 Florisil Cartridge Check Solution

Prepare a 0.10 µg/mL solution of 2,4,5-trichlorophenol in acetone. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.8 Gel Permeation Chromatography (GPC) Calibration and Calibration Verification Solutions

7.2.2.8.1 GPC Calibration Solution

Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations

listed below. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

<u>Analyte</u>	<u>Concentration (mg/mL)</u>
Corn oil	25.0
Bis(2-ethylhexyl)phthalate	0.5
Methoxychlor	0.1
Perylene (CAS # 198-55-0)	0.02
Sulfur (CAS # 7704-34-9)	0.08

7.2.2.8.2 GPC Calibration Verification Solution

Prepare a GPC calibration verification solution in methylene chloride that contains the following compounds. The concentrations listed below are for a 5 mL GPC injection loop. See Section 10.3.1.4.3.1 for compound concentrations if a smaller size loop is being used. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

<u>Compound</u>	<u>Concentration (ng/mL)</u>
gamma-BHC (Lindane)	20.0
Heptachlor	20.0
Aldrin	20.0
4,4'-DDT	40.0
Endrin	40.0
Dieldrin	40.0

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.2.9 Laboratory Control Sample (LCS) Spiking Solution

Prepare an LCS spiking solution that contains each of the analytes at the concentrations listed below in methanol or acetone. The LCS solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

<u>Compounds</u>	<u>Concentration (µg/mL)</u>
gamma-BHC	0.050
gamma-Chlordane	0.050
Heptachlor epoxide	0.050
Dieldrin	0.10
4,4'-DDE	0.10
Endrin	0.10
Endosulfan sulfate	0.10

Exhibit D Pesticides -- Section 7
Reagents and Standards (Con't)

7.2.3 Storage of Standards

7.2.3.1 Store the stock standard solutions at 4°C (±2°C) in polytetrafluoroethylene (PTFE)-lined, screw-cap, amber bottles/vials.

7.2.3.2 Store the working standard solutions at 4°C (±2°C) in PTFE-lined screw-cap, amber bottles/vials. The working standards must be checked frequently for signs of degradation or evaporation.

NOTE: Refrigeration may cause the corn oil in the GPC calibration solution to precipitate. Before use, allow the GPC calibration solution to stand at room temperature until the corn oil dissolves.

7.2.3.3 Protect all standards from light.

7.2.3.4 Samples, sample extracts, and standards must be stored separately.

7.2.3.5 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

Exhibit D Pesticides -- Section 8
Sample Collection, Preservation, Storage, and Holding Times

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

- 8.1.1 Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with screw-caps lined with polytetrafluoroethylene (PTFE). If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the Region.
- 8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

- 8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.
- 8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

- 8.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery of a complete reconciled data package to USEPA.
- 8.3.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.
- 8.3.3 Samples, sample extracts, and standards must be stored separately.

8.4 Records for Sample and Sample Extract Storage

- 8.4.1 The temperature of all sample and sample extract storage refrigerators shall be recorded daily.
- 8.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.
- 8.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.5 Contract Required Holding Times

- 8.5.1 Extraction of water samples by separatory funnel procedures must be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by continuous liquid-liquid extraction must be started within 5 days of VTSR. Extraction of soil/sediment samples must be completed within 10 days of VTSR.
- 8.5.2 As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) Samples as standard extracts that the Contractor is required to prepare per instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the Sample Delivery Group (SDG). The extraction holding time (5 days after VTSR for water samples, 10 days after VTSR for

Exhibit D Pesticides -- Sections 8 & 9
Calibration and Standardization

soil/sediment samples) does not apply for PE samples received as standard extracts.

- 8.5.3 Analysis of sample extracts must be completed within 40 days following the start of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Gas Chromatograph (GC) Operating Conditions

- 9.1.1 The following are the GC analytical conditions. The conditions are recommended, unless otherwise noted.

Carrier Gas:	Helium (Hydrogen may be used, Section 6.10.1.5)
Column Flow:	5 mL/min.
Make-up Gas:	Argon/Methane (P-5 or P-10) or N ₂ (required)
Injector Temperature:	> 200°C (Section 9.1.5)
Injection Technique:	On-column
Injection Volume:	1 or 2 µl (Section 9.1.3)
Injector:	Grob-type, splitless
Initial Temperature:	150°C
Initial Hold Time:	0.5 min.
Temperature Ramp:	5°C to 6°C/min.
Final Temperature:	275°C
Final Hold Time:	After decachlorobiphenyl has eluted

- 9.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples [including Laboratory Control Samples (LCSs), and Matrix Spike and Matrix Spike Duplicates (MS/MSDs)], and required blanks (method/sulfur cleanup/instrument).

- 9.1.3 The same injection volume, 1.0 or 2.0 µL, must be used for all standards, samples (including LCSs and MS/MSDs), and required blanks (method/sulfur cleanup/instrument).

- 9.1.4 The linearity of the Electron Capture Detector (ECD) may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

- 9.1.5 Cold (ambient temperature) on-column injectors that allow injection directly onto a 0.53 mm ID column may be used as long as the initial calibration and calibration verification technical acceptance criteria are met.

9.2 Initial Calibration

9.2.1 Summary of Initial Calibration

Prior to sample (including LCSs and MS/MSDs) and required blank (method/sulfur cleanup/instrument) analysis, each GC/ECD system must be initially calibrated at a minimum of five concentrations for

single component analytes, Toxaphene, and surrogates in order to determine instrument sensitivity and the linearity of GC response.

9.2.2 Frequency of Initial Calibration

Each GC/ECD system must be initially calibrated upon award of the contract, whenever major instrument maintenance or modification is performed (e.g., column replacement or repair, cleaning or replacement of ECD, etc.), or if the calibration verification technical acceptance criteria have not been met.

9.2.3 Procedure for Initial Calibration

9.2.3.1 Set up the GC/ECD system as described in Section 9.1.

9.2.3.2 Prepare the initial calibration standards using the procedures, analytes, and concentrations according to Section 7.2.

9.2.3.3 All standards, sample (including LCSs and MS/MSDs), and required blank (method/sulfur cleanup) extracts must be allowed to warm to ambient temperature before analysis.

9.2.3.4 Choose the appropriate initial calibration sequence (1 or 2), as given below. If two Individual Standard Mixtures are used, choose sequence 2. The appropriate calibration sequence is determined by the results of the Resolution Check Mixture (Section 9.2.5.2). All steps pertaining to the initial calibration sequence must be performed uninterrupted with no more than the length of one chromatographic run separating any step.

NOTE: The steps pertaining to Instrument Blank and Performance Evaluation Mixture (PEM) are used as part of the calibration verification as well (Section 9.3).

INITIAL CALIBRATION SEQUENCE 1

1. Resolution Check
2. Performance Evaluation Mixture (PEM)
3. Toxaphene CS1
4. Toxaphene CS2
5. Toxaphene CS3
6. Toxaphene CS4
7. Toxaphene CS5
8. CS1 Individual Standard Mix C
9. CS2 Individual Standard Mix C
10. CS3 Individual Standard Mix C
11. CS4 Individual Standard Mix C
12. CS5 Individual Standard Mix C
13. Instrument Blank
14. PEM

Exhibit D Pesticides -- Section 9
Calibration and Standardization (Con't)

INITIAL CALIBRATION SEQUENCE 2

1. Resolution Check
2. Performance Evaluation Mixture (PEM)
3. Toxaphene CS1
4. Toxaphene CS2
5. Toxaphene CS3
6. Toxaphene CS4
7. Toxaphene CS5
8. CS1 Individual Standard Mix A
9. CS1 Individual Standard Mix B
10. CS2 Individual Standard Mix A
11. CS2 Individual Standard Mix B
12. CS3 Individual Standard Mix A
13. CS3 Individual Standard Mix B
14. CS4 Individual Standard Mix A
15. CS4 Individual Standard Mix B
16. CS5 Individual Standard Mix A
17. CS5 Individual Standard Mix B
18. Instrument Blank
19. PEM

9.2.4 Calculations for Initial Calibration

9.2.4.1 During the initial calibration sequence, absolute Retention Times (RTs) are determined for all single component pesticides, surrogates, and three to five major peaks of Toxaphene.

9.2.4.2 For each single component pesticide, an RT is measured in each of the five calibration standards for all Individual Standard Mixtures C for initial calibration sequence 1 or A and B for initial calibration sequence 2). **If initial calibration sequence 2 is used then the RT for the surrogates is measured from each of the five analyses of Individual Standard Mixture A during the initial calibration.** For Toxaphene, an RT is measured in each of the five calibration standards for the major peaks (3, 4, or 5). The Mean Absolute RT ($\overline{RT}$) is calculated for each single component pesticide, surrogate, and Toxaphene as the average of the five values. Calculate an RT for each single component pesticide, surrogate, and Toxaphene using Equation 1.

EQ. 1 Mean Absolute Retention Time Calculation

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

Where,

$\overline{RT}$ = Mean Absolute Retention Time of analyte.

RT_i = Absolute Retention Time of analyte.

n = Number of measurements (5).

- 9.2.4.3 An RT window is calculated for each single component analyte and surrogate and for the major peaks (3, 4 or 5) of Toxaphene using Table 1. Windows are centered around the $\overline{RT}$ for the analyte established during the initial calibration. Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.
- 9.2.4.4 The linearity of the instrument is determined by calculating a Percent Relative Standard Deviation (%RSD) of the Calibration Factors (CFs) from a five-point calibration curve for each of the single component pesticides and surrogates. Either peak area or peak height may be used to calculate the CFs used in the %RSD equation. For example, it is permitted to calculate linearity for Endrin based on peak area and to calculate linearity for Aldrin based on peak height. It is not permitted within a %RSD calculation for an analyte to use the CFs calculated from both peak area and peak height. For example, it is not permitted to calculate the CF for the CS1 Standard for Endrin using peak height and calculate the CS3 and CS5 Standard CFs for Endrin using peak area.
- 9.2.4.5 Calculate the CFs for each single component pesticide and surrogates over the initial calibration range using Equation 2. The CFs for surrogates are calculated from the five analyses of the Individual Standard Mixture. If two Individual Standard Mixtures are used, calculate the CFs for surrogates from Individual Standard Mixture A only.

EQ. 2 Calibration Factors

$$CF = \frac{\text{Peak area (or Height) of the standard}}{\text{Mass Injected (ng)}}$$

- 9.2.4.6 Calculate the Mean CF ($\overline{CF}$) and the %RSD of the CF for each single component pesticide and surrogate over the initial calibration range using Equations 3 and 4.

EQ. 3 Mean Calibration Factor

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

EQ. 4 Percent Relative Standard Deviation of the Calibration Factors

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

$$SD_{CF} = \sqrt{\frac{\sum_{i=1}^n (CF_i - \overline{CF})^2}{(n-1)}}$$

Exhibit D Pesticides -- Section 9
Calibration and Standardization (Con't)

Where,

%RSD = Percent Relative Standard Deviation.

SD_{CF} = Standard Deviation of Calibration Factors.

CF_i = Calibration Factor.

$\overline{CF}$ = Mean Calibration Factor.

n = Total number of values (5).

9.2.4.7 A CF is calculated for each peak in a selected set of three to five major peaks for Toxaphene using Equation 2. The Mean CF and the %RSD of the CFs for each selected Toxaphene peak are calculated using Equations 3 and 4.

9.2.4.8 Calculate the Percent Breakdown (%Breakdown) of DDT, the Percent Breakdown of Endrin, and the combined breakdown of DDT and Endrin in the PEM using Equations 5, 6, 7, and 8.

EQ. 5 Amount Found

$$\text{Amount found (ng)} = \frac{\text{Peak area (or Peak height) of compound in PEM}}{\overline{CF}}$$

Where,

$\overline{CF}$ = Mean Calibration Factor from the initial calibration (area/ng).

NOTE: If during the initial calibration, linearity was determined based on peak area for the compound, then the $\overline{CF}$ must be based on peak area. If during the initial calibration, the linearity for the compound was determined based on peak height for the compound, then the $\overline{CF}$ must be based on peak height.

EQ. 6 Percent Breakdown of DDT

$$\% \text{Breakdown DDT} = \frac{\text{Amount found (ng) (DDD+DDE)}}{\text{Amount (ng) of DDT injected}} \times 100$$

EQ. 7 Percent Breakdown of Endrin

$$\% \text{Breakdown Endrin} = \frac{\text{Amount found (ng) (endrin aldehyde + endrin ketone)}}{\text{Amount (ng) of endrin injected}} \times 100$$

EQ. 8 Combined Percent Breakdown of DDT and Endrin

$$\text{Combined \%Breakdown} = \% \text{Breakdown DDT} + \% \text{Breakdown Endrin}$$

9.2.4.9 Calculate the Percent Difference (%Difference) between the calculated and nominal concentrations of each pesticide and surrogate in the PEM using Equations 5 and 9.

EQ. 9 Percent Difference Between the Calculated and Nominal Concentrations

$$\% \text{Difference} = \frac{C_{\text{calc}} - C_{\text{nom}}}{C_{\text{nom}}} \times 100$$

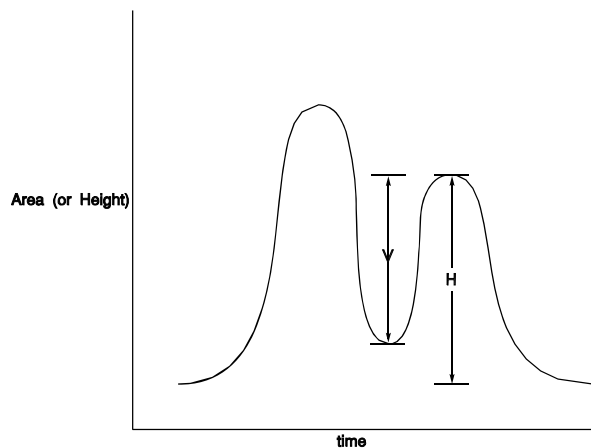
Where,

%Difference = Percent Difference.

C_{calc} = Calculated concentration of each analyte from the analysis of the standard. (Amount found (ng) in Eq. 5).

C_{nom} = Nominal concentration of each analyte.

9.2.4.10 Calculate the resolution between the analytes in the Resolution Check Mixture, PEM, and CS3 Standard concentrations of the Individual Standard Mixtures, using Equation 10.



EQ. 10 Percent Resolution

$$\% \text{Resolution} = \frac{V}{H} \times 100$$

Where,

V = Depth of the valley between the two peaks. The depth of the valley is measured along a vertical line from the level of the apex of the shorter peak to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks.

9.2.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to each GC column.

9.2.5.1 The initial calibration sequence must be analyzed according to the procedure and in the order listed in Section 9.2.3, at the concentrations listed in Section 7.2.2, and at the frequency listed in Section 9.2.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.

Exhibit D Pesticides -- Section 9
Calibration and Standardization (Con't)

- 9.2.5.2 The resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 80.0% for all analytes for the primary column and greater than or equal to 50% for the confirmation column in order to use one Individual Standard Mixture (C). If two Individual Standard Mixtures (A and B) are to be used, then the resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0% for both GC columns.
- 9.2.5.3 All single component pesticides and surrogates in both runs of the PEM must be greater than or equal to 90.0% resolved on each column.
- 9.2.5.4 The absolute RTs of each of the single component pesticides and surrogates in both runs of the PEM must be within the RT window determined from the five-point initial calibration in Section 9.2.4.3.
- 9.2.5.5 The Percent Difference between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in both of the PEM runs of each GC column must be greater than or equal to -25.0% and less than or equal to 25.0% using Equation 9.
- 9.2.5.6 The Percent Breakdown of DDT and Endrin in each of the PEM runs must be less than or equal to 20.0%. The combined breakdown of DDT and Endrin must be less than or equal to 30.0%.
- 9.2.5.7 The %RSD of the CFs for each single component target compound must be less than or equal to 20.0%, except alpha-BHC and delta-BHC. The %RSD of the CFs for alpha-BHC and delta-BHC must be less than or equal to 25.0%. The %RSD of the CFs for the two surrogates must be less than or equal to 30.0%. Up to two single component target compounds (not surrogates) per column may exceed the maximum %RSD of 20.0% (25.0% for alpha-BHC and delta-BHC), but those compounds must have a %RSD of less than or equal to 30.0%. The %RSD of the CFs for Toxaphene must be less than or equal to 30.0%.
- 9.2.5.8 If one Individual Standard Mixture (C) is used then the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture C must be at least 80% for the primary column and 50% for the secondary column. If two Individual Standard Mixtures (A and B) are used, then the resolution between any two adjacent peaks in the CS3 Individual Standard Mixtures (A and B) must be greater than or equal to 90% on both columns.
- 9.2.5.9 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.
- 9.2.5.10 The identification of single component pesticides by GC methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of Toxaphene by GC methods is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and Toxaphene:
- The chromatograms that result from the analyses of the Resolution Check Mixture, the PEM, and the Individual Standard Mixtures during the initial calibration sequence must display the single component analytes present in each standard at

greater than 10% of full scale, but less than 100% of full scale;

- The chromatograms for at least one of the five analyses of each Individual Standard Mixture from the initial calibration sequence must display the single component analytes at greater than 50% and less than 100% of full scale;
- The chromatogram for at least one of the analyses of the Toxaphene standard analyzed during the initial calibration sequence must display the peaks chosen for identification at greater than 25% and less than 100% of full scale;
- For all Resolution Check Mixtures, PEMs, Individual Standard Mixtures, and blanks, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl; and
- If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

9.2.6 Corrective Action for Initial Calibration

- 9.2.6.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake-out the detector, clean the injection port, or take other corrective actions to achieve the technical acceptance criteria.
- 9.2.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. In the case of low-level contamination, baking-out the detector at elevated temperature (350°C) should be sufficient to achieve acceptable performance. In the case of heavy contamination, passing hydrogen through the detector for 1-2 hours at elevated temperature may correct the problem. In the case of severe contamination, the detector may require servicing by the ECD manufacturer. CAUTION: DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.
- 9.2.6.3 If a laboratory cleans out a detector using elevated temperature, the ECD electronics must be turned off during the bake out procedure.
- 9.2.6.4 After bake out or hydrogen reduction, the detector must be recalibrated using the initial calibration sequence.
- 9.2.6.5 Initial calibration technical acceptance criteria MUST be met before any samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup/instrument) are analyzed. Any samples or required blanks analyzed when the initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Calibration Verification

9.3.1 Summary of Calibration Verification

Three types of analyses are used to verify the calibration and evaluate instrument performance, instrument blanks, PEMs, and the CS3 Individual Standard Mixture(s). A calibration verification consists of an instrument blank and PEM or an instrument blank and the CS3 Individual Standard Mixture(s). Sample (including LCS and MS/MSD) and required blank (method/sulfur cleanup) data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEMs, and both Individual Standard Mixtures.

9.3.2 Frequency of Calibration Verification

- 9.3.2.1 An instrument blank and the PEM must bracket one end of a 12-hour period during which sample and required blank data are collected, and a second instrument blank and the CS3 Individual Standard Mixture(s) must bracket the other end of the 12-hour period. If Individual Standard Mixtures A and B were used in the associated initial calibration sequence, then CS3 Individual Standard Mixtures A and B must be used for the calibration verification. If Individual Standard Mixture C was used in the associated initial calibration sequence, then CS3 Individual Standard Mixture C must be used in the calibration verification.
- 9.3.2.2 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence bracket the front end of that 12-hour period. The injection of the instrument blank starts the beginning of the 12-hour period (Section 9.2.3.4). Samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) may be injected for 12 hours from the injection of the instrument blank. The first injections immediately after that 12-hour period must be an instrument blank and the CS3 Individual Standard Mixture(s). The instrument blank must be analyzed first, before the standard(s). If two Individual Standard Mixtures are used they may be analyzed in either order (A, B or B, A).
- 9.3.2.3 The analyses of the instrument blank and CS3 Individual Standard Mixture(s) immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the technical acceptance criteria in Section 9.3.5. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixture(s) fails to meet the technical acceptance criteria in Section 9.3.5. The 12-hour time period begins with the injection of the instrument blank.
- 9.3.2.4 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and PEM must be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard was injected.
- 9.3.2.5 The requirements for running the instrument blanks, PEM, and CS3 Individual Standard Mixture(s) are waived when no samples (including LCSs and MS/MSDs), dilutions, reanalyses, required blanks (method/sulfur cleanup), and Toxaphene standards are analyzed during that 12-hour period. To resume analysis, using the existing initial calibration, the Contractor must first

analyze an instrument blank and PEM that meet the technical acceptance criteria.

- 9.3.2.6 If the entire 12-hour period is not required for the analyses of all samples and blanks to be reported and all data collection is to be stopped, the sequence must be ended with either the instrument blank/PEM combination or the instrument blank/CS3 Individual Standard Mixture(s) combination, whichever was due to be performed at the end of the 12-hour period.
- 9.3.2.7 No more than 14 hours may elapse from the injection beginning the opening Continuing Calibration Verification (CCV) and the injection ending the closing CCV (PEM or Individual Standard Mixture).
- 9.3.3 Procedure for Calibration Verification
- 9.3.3.1 All standards and blanks must warm to ambient temperature prior to analysis.
- 9.3.3.2 Analyze the instrument blank, PEM, and the CS3 Individual Standard Mixture(s) at the required frequencies (Section 9.3.2).
- 9.3.4 Calculations for Calibration Verification
- 9.3.4.1 For each analysis of the PEM used to demonstrate calibration verification, calculate the Percent Difference between the amount of each analyte (including the surrogates) found in the PEM and the nominal amount, using Equation 9.
- 9.3.4.2 For each analysis of the PEM used to demonstrate calibration verification, calculate the Percent Breakdown of Endrin and DDT, and the combined breakdown, using Equations 5, 6, 7, and 8.
- 9.3.4.3 For each analysis of the CS3 Individual Standard Mixture(s) used to demonstrate calibration verification, calculate the Percent Difference between the CF of each analyte (including the surrogates) in the standard mixture and the $\overline{CF}$ from the initial calibration, using Equation 11. Do not attempt to calculate the breakdown of Endrin and DDT in the Individual Standard Mixtures, as these standards contain the breakdown products as well as the parent compounds.

EQ. 11 Percent Difference Between the Calibration Factor
and the Mean Calibration Factor

$$\%Difference = \frac{CF - \overline{CF}}{\overline{CF}} \times 100$$

Where,

%Difference = Percent Difference.

CF = Calibration Factor for CS3 Standard
used for Calibration Verification.

$\overline{CF}$ = Mean Calibration Factor.

Exhibit D Pesticides -- Section 9
Calibration and Standardization (Con't)

9.3.5 Technical Acceptance Criteria for Calibration Verification

All calibration verification technical acceptance criteria apply independently to each GC column.

- 9.3.5.1 The PEMs, Individual Standard Mixtures, and instrument blanks must be analyzed at the required frequency (Section 9.3.2), on a GC/ECD system that has met the initial calibration technical acceptance criteria.
- 9.3.5.2 All single component pesticides and surrogates in the PEMs used to demonstrate calibration verification must be greater than or equal to 90.0% resolved. If one Individual Standard Mixture is used, the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture C must be at least 80% for the primary column and 50% for the secondary column. If two Individual Standard Mixtures are used, the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture A and B used to demonstrate calibration verification must be greater than or equal to 90.0% for both columns.
- 9.3.5.3 The absolute RT for each of the single component pesticides and surrogates in the PEMs and CS3 Individual Standard Mixture(s) used to demonstrate calibration verification must be within the RT windows determined from the five-point initial calibration in Section 9.2.4.3.
- 9.3.5.4 The Percent Difference between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in the PEM used to demonstrate calibration verification must be greater than or equal to -25.0% and less than or equal to 25.0%.
- 9.3.5.5 The Percent Breakdown of 4,4'-DDT in the PEM must be less than or equal to 20.0% on each column. The Percent Breakdown of Endrin in the PEM must be less than or equal to 20.0% on each column. The combined breakdown of DDT and Endrin must be less than or equal to 30.0% on each column.
- 9.3.5.6 The Percent Difference between the CF of each of the single component pesticides and surrogates in the mid-point concentration of the Individual Standard Mixtures used to demonstrate calibration verification, and the CF from the initial calibration must be greater than or equal to -20.0% and less than or equal to 20.0%.
- 9.3.5.7 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.
- 9.3.5.8 The identification of single component pesticides by GC methods is based primarily on RT data. Since the RT of the apex of a peak can only be verified from an on-scale chromatogram, the following requirements must be met for calibration verification to be acceptable:
- The chromatograms that result from the analyses of the PEM and the Individual Standard Mixtures must display the single component analytes present in each standard at greater than 10% of full scale but less than 100% of full scale;
 - For any PEM, Individual Standard Mixture, or blank, the baseline of the chromatogram must return to below 50% of full

scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl;

- If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram; and
- If the chromatogram of any standard or blank needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram(s) must be submitted in the data package.

9.3.5.9 A Toxaphene calibration verification standard (CS3) must be analyzed on the same instrument upon its detection in a sample. This standard must be analyzed within 72 hours of the analytes detection in a valid 12-hour period. The Percent Difference between the CF of each peak used to identify Toxaphene in the calibration verification standard and the $\overline{CF}$ from the initial calibration must be greater than or equal to -20.0% and less than or equal to 20.0%.

9.3.6 Corrective Action for Calibration Verification

9.3.6.1 If the technical acceptance criteria for the calibration verification are not met, inspect the system for problems and take corrective action to achieve the technical acceptance criteria.

9.3.6.2 Major corrective actions, such as replacing the GC column or baking out the detector, will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.2.5.

9.3.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard (PEM or Individual Standard Mixtures) that originally failed the criteria, and an associated instrument blank immediately after the corrective action, do meet all the technical acceptance criteria.

9.3.6.4 If a PEM or Individual Standard Mixture does not meet the technical acceptance criteria listed above, it must be reinjected immediately. If the second injection of the PEM or Individual Standard Mixture meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be run before more sample data are collected.

9.3.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.4.5, all data collection must be stopped. Appropriate corrective action must be taken to clean out the system, and an acceptable instrument blank must be analyzed before more sample data are collected.

9.3.6.6 Analysts are reminded that running an instrument blank and a PEM or Individual Standard Mixtures once every 12 hours are the minimum contract requirements. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks and standards more often to avoid discarding data.

Exhibit D Pesticides -- Sections 9 & 10
Procedure

- 9.3.6.7 If a successful instrument blank and PEM cannot be run after an interruption in analysis (Section 9.3.2.6), an acceptable initial calibration must be run before sample data may be collected. All acceptable sample (including LCS and MS/MSDs) and required blank (method/sulfur cleanup) analyses must be preceded and followed by acceptable standards and instrument blanks, as described in Section 9.3.2.
- 9.3.6.8 Calibration verification technical acceptance criteria must be met before any samples (including the LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) are reported. Any samples and required blanks associated with a calibration verification that did not meet the technical acceptance criteria will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all of the sample cleanup procedures presented in this Exhibit, including those included by reference. The Contractor may use any of the procedures or combinations of procedures to cleanup the samples prior to analysis, unless the Contractor is specifically directed by the Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including Method Detection Limits (MDLs) and any precision and recovery limits.

10.1 Sample Preparation

- 10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 Multi-phase Samples

If multi-phase samples (e.g., a two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region.

- 10.1.2.1 If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:
- Mix the sample and analyze an aliquot from the homogenized sample;
 - Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases, if required;
 - Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or
 - Do not analyze the sample.

10.1.2.2 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phase(s) and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.3 No other change in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Extraction of Water Samples

Water samples may be extracted by either separatory funnel procedure or a continuous liquid-liquid extraction procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction must be employed. Allow the samples to warm to ambient temperature.

10.1.3.1 Separatory Funnel Extraction

10.1.3.1.1 Measure out each 1 L sample aliquot in a separate graduated cylinder. Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the SDG Narrative. Place the sample aliquot into a 2 L separatory funnel.

10.1.3.1.2 Using a syringe or a volumetric pipet, add 3.0 mL of the surrogate solution (Section 7.2.2.1) to all water samples.

10.1.3.1.3 Rinse the graduated cylinder with 30 mL of methylene chloride and transfer the rinsate to the separatory funnel. If the sample container is empty, rinse the container with 30 mL of methylene chloride and add the rinsate to the separatory funnel. If the sample container is not rinsed, then add another 30 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure.

NOTE: The total volume of solvent used for extraction is 60 mL. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than 1/3 the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration through glass wool, centrifugation, or other physical means. Drain the methylene chloride into a 250 mL Erlenmeyer flask.

10.1.3.1.4 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Proceed to Section 10.2.

10.1.3.2 Continuous Liquid-Liquid Extraction

Exhibit D Pesticides -- Section 10
Procedure (Con't)

10.1.3.2.1 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.2.1.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.1.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom sidearm.

10.1.3.2.1.3 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure the pH of the sample with wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, as required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.1.4 Using a syringe or volumetric pipet, add 3.0 mL of the surrogate standard spiking solution (Section 7.2.2.1) into the sample and mix well.

10.1.3.2.1.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.1.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute. (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.2.2 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.2.2.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.2.2 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor. If the sample container is not rinsed, add 50 mL of methylene chloride to the continuous extractor. Slowly transfer the aliquot to the continuous extractor. Measure the pH of the sample with

wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, as required. Samples requiring pH adjustment must be noted in the SDG Narrative.

- 10.1.3.2.2.3 Using a syringe or volumetric pipet, add 3.0 mL of the surrogate standard spiking solution (Section 7.2.2.1) into the sample and mix well.
- 10.1.3.2.2.4 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor.
- 10.1.3.2.2.5 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours.

NOTE 1: Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane, it may not be necessary to dry the extract with sodium sulfate.

NOTE 3: If low surrogate recoveries occur, assure that 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; 3) there was proper cooling for condensation of solvent. Document the problem and the corrective action.

NOTE 4: Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up. Optimize the extraction procedure.

10.1.4 Soil/Sediment Samples

Mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment to a 100 mL beaker. Add 50 mL of water and stir the solution with a magnetic stirrer for 1 hour. Determine the pH of the sample by using a combination glass electrode and pH meter while the sample is stirred. Report the pH value on the appropriate data sheet. If the pH of the soil/sediment is greater than 9 or less than 5, document any subsequent problems in the analysis related to pH in the SDG Narrative, but do not attempt to adjust the pH of the sample. Discard the portion of the sample used for pH determination.

NOTE: If insufficient weight of soil/sediment is received, use a smaller 1:1 ratio of grams of sample to milliliters of water for the pH determination, and note in the SDG Narrative.

10.1.4.2 Percent Moisture

Weigh 5-10 g of the soil/sediment to the nearest 0.01 g into a tared crucible or aluminum weighing pan. Determine the weight percent volatilized by drying overnight at 105°C (hereafter referred to as Percent Moisture). After the sample is dry, remove the sample and pan and allow them to cool in a desiccator before weighing. Calculate the Percent Moisture according to Equation 12 below. Concentrations of individual analytes will be reported relative to the dry weight of soil/sediment.

CAUTION: Gases volatilized from some soil/sediment samples may require that this drying procedure be carried out in a hood.

EQ. 12 Percent Moisture

$$\% \text{Moisture} = \frac{\text{grams of wet sample} - \text{grams of dry sample}}{\text{grams of wet sample}} \times 100$$

10.1.4.3 Extraction of Soil/Sediment Samples

10.1.4.3.1 Three procedures are provided for the extraction of pesticide compounds from soil/sediment samples:

- Ultrasonic extraction;
- [Automated] Soxhlet extraction; and
- Pressurized fluid extraction.

The Contractor shall use one of the above procedures for the extraction of soil/sediment samples.

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.3.2 For soil/sediment sample extractions, perform the following steps rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample, to the nearest 0.1 g, into a 400 mL beaker. Add 60 g of anhydrous powdered or granulated sodium sulfate, or add 30 g of Hydromatrix, or sufficient quantity, and mix well to produce a sandy texture. Proceed to Section 10.1.4.3.3 for ultrasonic extraction, Section

10.1.4.3.4 for automated Soxhlet extraction, or Section 10.1.4.3.5 for pressurized fluid extraction. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

NOTE: For samples extracted by the Pressurized Fluid Extraction procedure (Section 10.1.4.3.5) the use of sodium sulfate is not recommended.

10.1.4.3.3 Ultrasonic Extraction

10.1.4.3.3.1 Add 3.0 mL of surrogate solution to the sample, then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride.

10.1.4.3.3.2 Place the bottom surface of the tip of the 3/4 inch tapered disruptor horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do not use a microtip probe.

10.1.4.3.3.3 Sonicate for 3 minutes using a 3/4 inch disruptor horn at full power, (output control knob at 10) with pulse on, and percent duty cycle knob set at 50.0%.

NOTE: These settings refer to the Model W-385. When using a sonicator other than Model W-385, refer to the manufacturer's instructions for appropriate output settings.

10.1.4.3.3.4 Decant and filter extracts through Whatman No. 41 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.4.3.3.5 Repeat the extraction two more times with two additional 100 mL portions of 1:1 (v/v) acetone/methylene chloride. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or, very carefully, with the tip of the unenergized probe. Decant the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.2.

10.1.4.3.4 [Automated] Soxhlet Extraction

The Contractor may use either automated or non-automated Soxhlet extraction. The following procedure is based on the use of a Soxtec HT-6 automated Soxhlet extraction system. When using a different system, refer to the instructions provided by the manufacturer for the appropriate procedure.

10.1.4.3.4.1 Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minutes to prevent solvent loss through the condensers.

Exhibit D Pesticides -- Section 10
Procedure (Con't)

- 10.1.4.3.4.2 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to the thimble. Add 3.0 mL of surrogate solution to the sample.
- 10.1.4.3.4.3 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.
- 10.1.4.3.4.4 Insert the extraction cups containing boiling chips, and load each with an appropriate volume 1:1 (v/v) acetone/methylene chloride. Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position.
- NOTE: The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.
- 10.1.4.3.4.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.
- 10.1.4.3.4.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time. After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.
- 10.1.4.3.4.7 When all but 2-5 mL of solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with methylene chloride and add the rinsates to the glass tubes. Proceed to Section 10.2.
- 10.1.4.3.5 Pressurized Fluid Extraction
- 10.1.4.3.5.1 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to an extraction cell of the appropriate size for the aliquot. Add 3.0 mL of surrogate solution to the sample.
- 10.1.4.3.5.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.
- 10.1.4.3.5.3 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

- 10.1.4.3.5.4 The following are recommended extraction conditions:
- Oven temperature: 100°C
- Pressure: 1500-2000 psi
- Static time: 5 min. (after 5 min. pre-heat equilibration)
- Flush volume: 60% of the cell volume
- Nitrogen purge: 60 sec. at 150 psi (purge time may be extended for larger cells)
- Static cycles: 1
- 10.1.4.3.5.5 Optimize the extraction conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.4.3.5.4.
- 10.1.4.3.5.6 Once established, the same pressure should be used for all samples in the same SDG.
- 10.1.4.3.5.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete. Proceed to Section 10.2.
- 10.2 Extract Concentration
- 10.2.1 Concentration by Kuderna-Danish (K-D)
- 10.2.1.1 Assemble a K-D concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the target pesticides listed in Exhibit C.
- 10.2.1.2 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.
- 10.2.1.2.1 For soil/sediment samples, directly transfer the extract to the K-D concentrator.
- 10.2.1.2.2 Rinse the Erlenmeyer flask (for both water and soil/sediment samples) and the column (for water samples) with at least two 20-30 mL portions of methylene chloride to complete the quantitative transfer.
- 10.2.1.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed

with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5.0 mL for water samples (and less than 10 mL for soil/sediment samples), remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.1.4 For water extracts that do not require Gel Permeation Chromatography (GPC) cleanup, and for water and soil/sediment extracts that have been through the GPC cleanup step, proceed with the hexane exchange described in Section 10.2.2.

10.2.1.5 For water extracts that require GPC cleanup, remove the Snyder column, rinse the flask and its lower joint, collect the rinsate in the concentrator tube, and adjust the volume to 10.0 mL with methylene chloride. Proceed to Section 10.3.1.

10.2.1.6 For soil/sediment extracts that have not been cleaned-up using GPC, it is absolutely necessary to further reduce the volume of all soil/sediment extracts to 1 mL in order to remove most of the acetone. This is best accomplished using the nitrogen evaporation technique (Section 10.2.3.2). The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups. Adjust the soil/sediment extract volume to 10 mL with methylene chloride. Proceed to Section 10.3.1 for mandatory GPC.

10.2.2 Solvent Exchange into Hexane

This procedure applies to both extracts of water samples and extracts of soil/sediment samples.

10.2.2.1 With the extract in a K-D apparatus, momentarily remove the Snyder column, add 50.0 mL of hexane and a new boiling chip, and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as described previously (Section 10.2.1), but increase the temperature of the water bath (80-90°C is recommended). When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.2.2 Remove the Snyder column; using 1-2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a 10 mL vial by using hexane.

10.2.2.3 For samples that have not been subjected to GPC cleanup, adjust the volume of the hexane extract to 10 mL. For samples that have been subjected to GPC cleanup, concentrate the hexane extract to 5.0 mL using a Micro Snyder Column or nitrogen evaporation, as described in Section 10.2.3.1 or 10.2.3.2, then proceed to Section 10.3.2 for Florisil cartridge cleanup.

10.2.3 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before Florisil cleanup or extract volume before instrumental analysis. They are the Micro Snyder Column and the Nitrogen

Evaporation Technique. If the Region requests lower Contract Required Quantitation Limits (CRQLs) than those listed in Exhibit C Pesticides, the extracts may be further concentrated (2.0 mL instead of 10 mL when GPC cleanup is not required, or 1.0 mL instead of 5.0 mL when GPC is required), provided a proper MDL study (see Sections 7.2.2.5 and 12.4) is performed. The MDL study must demonstrate that the lower CRQLs can be achieved.

NOTE: If the Region requests lower CRQLs than those listed in Exhibit C Pesticides, sufficient surrogate spiking solution must be added to samples [including LCS and Matrix Spike and Matrix Spike Duplicate (MS/MSD)] and blanks, such that the expected surrogate concentrations after final concentration of the extract are 12 times the surrogate concentrations in the low standard (CS1) of the associated initial calibration.

10.2.3.1 Micro Snyder Column Concentration

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath (80-90°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 mL of hexane. If GPC cleanup is needed and not yet performed, adjust the volume to 10.0 mL with methylene chloride and proceed to Section 10.3.1 for GPC cleanup. For water samples that do not require GPC cleanup, adjust the volume to 10.0 mL with hexane and proceed to Section 10.3.2 for Florisil cleanup. For soil/sediment samples that have already undergone GPC cleanup, adjust the volume with hexane to 5.0 mL and proceed to Section 10.3.2 for Florisil cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot used for Florisil and/or sulfur cleanup (1.0 or 2.0 mL) and proceed to Section 10.4 for Gas Chromatograph/Electron Capture Detector (GC/ECD) analysis.

10.2.3.2 Nitrogen Evaporation Technique (taken from ASTM Method D5812)

10.2.3.2.1 Place the Concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to the final volume by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) onto the solvent. DO NOT ALLOW THE EXTRACT TO GO DRY.

If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.3.1 for GPC cleanup. For water samples that do not require GPC cleanup, adjust the volume to 10.0 mL with hexane and proceed to Section 10.3.2 for Florisil cleanup. For soil/sediment samples that have already undergone GPC cleanup, adjust the volume with hexane to 5.0 mL and proceed to Section 10.3.2 for Florisil cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot

used for Florisil and/or sulfur cleanup (1.0 or 2.0 mL) and proceed to Section 10.4 for GC/ECD analysis.

10.2.3.2.2 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or polytetrafluoroethylene (PTFE) tubing. Plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.

10.2.3.2.3 During evaporation, the tube solvent level must be kept below the water level of the bath.

10.3 Cleanup Procedures

There are three cleanup procedures specified in this method: GPC; Florisil cartridge; and sulfur cleanup. GPC must be performed for all soil/sediment extracts. GPC must be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. Florisil cartridge cleanup is mandatory for all extracts. Sulfur cleanup must be performed for all sample extracts contaminated with sulfur. Method blanks must be subjected to the same cleanup procedures as the samples [including Laboratory Control Samples (LCSS) and MS/MSDs]. The following cleanup methods may be used in addition to those described here, so long as all technical acceptance criteria are met: SW-846 methods 3610B (Alumina); 3630C (Silica Gel); and 3650B (Acid/Base Partition).

10.3.1 Sample Cleanup by GPC

10.3.1.1 Introduction

GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural (and synthetic) macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.3.1.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternate column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC calibration checks, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the pesticide compounds. Follow the manufacturer's instructions for preparation of the GPC column.

10.3.1.3 Calibration of GPC

10.3.1.3.1 Summary of GPC Calibration

10.3.1.3.1.1 The GPC calibration procedure is based on monitoring the elution of standards with an ultraviolet (UV) detector connected to the GPC column.

10.3.1.3.1.2 The UV detector calibration procedure described in Section 10.3.1.3.3 is needed for the analyses of organochlorine pesticides and Toxaphene listed in Exhibit C. IT MUST NOT

BE USED FOR THE ANALYSIS OF GAS CHROMATOGRAPH/MASS SPECTROMETRY (GC/MS) EXTRACTABLES OR OTHER ANALYTES WITHOUT A RECOVERY STUDY.

10.3.1.3.2 Frequency of GPC Calibration

Each GPC system must be calibrated upon award of the contract, when the GPC calibration verification solution fails to meet criteria, when the column is changed, when channeling occurs, and once every 7 days.

10.3.1.3.3 Procedure for GPC Calibration

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte Retention Times (RTs) and must be monitored.

10.3.1.3.3.1

Using a 10 mL syringe, load the calibration solution (Section 7.2.2.8.1) onto the GPC. Determine the elution times for Bis(2-ethylhexyl)phthalate, methoxychlor, and perylene. Bis(2-ethylhexyl)phthalate will elute first; perylene will elute last.

Choose a "DUMP" time that removes greater than 85% of the phthalate. Choose a "COLLECT" time so that greater than 95% of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a "WASH" time of 10 minutes.

NOTE: The "DUMP" and "COLLECT" times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

Analyze a GPC blank of methylene chloride. Concentrate the methylene chloride that passed through the system during the collect cycle using a K-D evaporator. Exchange the solvent to hexane and analyze the concentrate by GC/ECD according to the procedure in Section 10.2.2 (usual protocol). Assuming that the blank represents the extract from a 1 L water sample, calculate the analyte concentrations using Equation 14.

10.3.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.1.3.4.1

The GPC system must be calibrated at the frequency described in Section 10.3.1.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution;

Exhibit D Pesticides -- Section 10
Procedure (Con't)

- Corn oil and phthalate peaks should exhibit greater than 85% resolution;
 - Phthalate and methoxychlor peaks should exhibit greater than 85% resolution;
 - Methoxychlor and perylene peaks should exhibit greater than 85% resolution; and
 - Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.
- 10.3.1.3.4.2 The solvent flow rate and column pressure must be within the manufacturer's specified ranges.
- 10.3.1.3.4.3 The RTs for bis (2-ethylhexyl) phthalate and perylene must not vary more than $\pm 5\%$ between calibrations. If the RT shift is greater than 5%, take corrective action. Excessive RT shifts are caused by the following:
- Poor laboratory temperature control or system leaks;
 - An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight; and/or
 - Excessive laboratory temperatures causing outgassing of the methylene chloride.
- 10.3.1.3.4.4 The analyte concentrations in a GPC blank must be less than the Contract Required Quantitation Limit (CRQL) of any compound in Exhibit C (Pesticides).
- 10.3.1.3.4.5 A copy of the two most recent UV traces of the calibration solution must be submitted with the data for the associated samples. If UV traces using the same GPC system are submitted with data for analysis of samples for semivolatile compounds, no additional UV traces are required.
- 10.3.1.3.5 Corrective Action for GPC Calibration
- 10.3.1.3.5.1 If the flow rate and/or column pressure do not fall within the manufacturer's specified ranges, a new column should be prepared.
- 10.3.1.3.5.2 A UV trace that does not meet the criteria in Section 10.3.1.3.4 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.
- 10.3.1.3.5.3 If the concentration of any target compound in the GPC blank is equal to, or exceeds the CRQL listed in Exhibit C (Pesticides), pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.
- 10.3.1.4 GPC Calibration Verification
- 10.3.1.4.1 Summary of GPC Calibration Verification

The GPC calibration must be routinely verified with two check mixtures (Sections 7.2.2.8.1 and 7.2.2.8.2).

10.3.1.4.2 Frequency of GPC Calibration Verification

10.3.1.4.2.1 The calibration verification must be performed at least once every 7 days (immediately following the GPC Calibration) whenever samples, including MS/MSDs, and blanks, are cleaned up using the GPC.

10.3.1.4.2.2 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore, system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every 7 days.

10.3.1.4.3 Procedure for GPC Calibration Verification

The instructions below are for a GPC injection loop of 5 mL. If a 2 mL injection loop is used, the Contractor should adjust the volume to 4 mL instead of 10 mL before injection extract on the GPC.

10.3.1.4.3.1 The pesticide GPC calibration verification solution contains the following six compounds in methylene chloride: gamma-BHC (Lindane), Heptachlor and Aldrin, each at a concentration of 20 ng/mL for a 5 mL GPC loop (50 ng/mL when a 2 mL GPC loop is used); and 4,4'-DDT, Endrin, and Dieldrin at 40 ng/mL (100 ng/mL for a 2 mL loop).

10.3.1.4.3.2 Load the 5 mL sample loop by using a 10 mL syringe containing 8 mL of the pesticide GPC calibration verification solution. Fractions are collected in an auto sequence by using the GPC program established by the UV detector calibration procedure (Section 10.3.1.3).

10.3.1.4.3.3 The collected GPC calibration verification fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10 mL portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced according to Section 10.2.1. After cooling, the solvent is exchanged to hexane according to the instructions in Section 10.2.2. The final volume is adjusted to 10 mL, and the sample is analyzed by GC according to the procedure in Section 10.4. The analysis must be performed on only one of the GC columns used for sample analysis.

10.3.1.4.3.4 The recovery of each single component analyte must be determined for evaluation and reporting purposes. Calculate the Percent Recovery of each single component analyte using Equation 13 in Section 10.3.2.2.3.

10.3.1.4.4 Technical Acceptance Criteria for GPC Calibration Verification

The recovery of each of the single component analytes must be between 80-110%.

10.3.1.4.5 Corrective Action for GPC Calibration Verification

The Contractor may continue to use the GPC column if the technical acceptance criteria for the GPC calibration verification are met. If the recoveries are out of the acceptance window, the columns must be replaced and the GPC recalibrated according to the instructions in Section 10.3.1.3 before proceeding with any GPC cleanup on samples (including LCSs and MS/MSDs) and required method blanks.

10.3.1.5 Daily UV Calibration Check (Optional)

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Section 7.2.2.8.1) and the UV detector calibration procedure (Section 10.3.1.3.3). The UV detector should be used to monitor the elution times for the phthalate, methoxychlor, and perylene, respectively. The precalibrated GPC program should "DUMP" greater than 85% of the phthalate and should "COLLECT" greater than 95% of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., greater than 0.5 minutes) indicate that the column is out of calibration and must be recalibrated or replaced.

10.3.1.6 Sample Cleanup by GPC

10.3.1.6.1 Introduction to Sample Cleanup by GPC

10.3.1.6.1.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, RTs will shift, and the "DUMP" and "COLLECT" times determined by the calibration standard will no longer will be appropriate. The ideal laboratory temperature, to prevent outgassing of the methylene chloride, is 22°C.

10.3.1.6.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 40 mg/mL of non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or another suitable container. When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected.

10.3.1.6.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is injected onto the column. Viscous extracts, or extracts containing a large amounts of non-volatile residue will cause problems with injecting the proper amount of sample extract onto the column using automated injection systems. After the sample extract has been processed, the remaining sample extract in an injection vial must be checked to assure that the proper amount of extract was injected on the column before proceeding with the sample analysis. If the proper amount of extract was not injected, the sample must be reprepared and the sample extract must be either diluted and loaded into several loops or the sample extract must be injected manually.

10.3.1.6.2 Frequency of Sample Cleanup by GPC

GPC cleanup must be performed at least once for each soil/sediment extract, water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes, and all associated Quality Control (QC) samples (blanks, LCSs, and MS/MSDs). If the cleanup procedure is inadequate, contact SMO.

10.3.1.6.3 Procedure for Sample Cleanup by GPC

- 10.3.1.6.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap). Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

NOTE: Some GPC instrument manufacturer's recommend using a smaller micron size filter disc. In this instance, follow the manufacturer's recommended operating instructions.

- 10.3.1.6.3.2 INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

- 10.3.1.6.3.3 Follow the manufacturer's instructions for operation of the GPC system being utilized.

NOTE: These instructions were written for a 5 mL GPC injection loop. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL loop is used, concentrate the 10 mL extract to 4 mL, and then inject 2 mL from the 4 mL.

- 10.3.1.6.3.4 If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action, following the manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

- 10.3.1.6.3.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

- 10.3.1.6.3.6 After loading all sample loops, process each sample using the collect and dump cycle times established in Section 10.3.1.3.3.1.

- 10.3.1.6.3.7 Collect each sample in a 250 mL Erlenmeyer flask covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes

collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure;
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used; and/or
- Leaks in the system or significant variances in room temperature.

10.3.1.6.3.8 After the appropriate GPC fraction has been collected for each sample, concentrate the extract as per Section 10.2.1 and proceed to solvent exchange into hexane as described in Section 10.2.2 and Florisil cleanup in 10.3.2.

10.3.1.6.3.9 Any samples that were loaded into two or more loops must be recombined before proceeding with concentration.

10.3.2 Florisil Cleanup

10.3.2.1 Introduction

Florisil cartridge cleanup significantly reduces matrix interference caused by polar compounds and is required for all extracts. The same volume of the concentrated extract taken for Florisil cleanup must be maintained after Florisil cleanup (1 or 2 mL).

10.3.2.2 Florisil Cartridge Performance Check

10.3.2.2.1 Summary of Florisil Cartridge Performance Check

Every lot number of Florisil cartridges must be tested before they are used for sample cleanup.

10.3.2.2.2 Frequency of Florisil Cartridge Performance Check

Cartridge performance check must be conducted at least once on each lot of cartridges used for sample cleanup or every 6 months, whichever is most frequent.

10.3.2.2.3 Procedure for Florisil Cartridge Performance Check

Add 0.5 mL of 2,4,5-trichlorophenol solution (0.1 µg/mL in acetone; Section 7.2.2.7) and 0.5 mL of Individual Standard Mixture A or C (mid-point concentration; Section 7.2.2.5) to 4 mL of hexane. Reduce the volume to 0.5 mL using nitrogen (Section 10.2.3.2). Place the mixture onto the top of a washed Florisil cartridge, and elute it with 9 mL of hexane/acetone [(90:10) (V/V)]. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the standard from the cartridge. Concentrate to a final volume of 1 mL and analyze the solution by GC/ECD using at least one of the GC columns specified for sample analysis. Determine the recovery of each analyte for evaluation and reporting purposes. Calculate the Percent Recovery (%R) using Equation 13.

EQ. 13 Percent Recovery

$$\text{Percent Recovery} = \frac{(Q_d \times DF)}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis.

Q_a = Quantity added.

DF = Dilution Factor

NOTE: For Florisil Cartridge Performance Check, use DF = 1.0 in calculations.

10.3.2.2.4 Technical Acceptance Criteria for Florisil Cartridge Performance Check

10.3.2.2.4.1 The cartridge performance check solution must be analyzed on a GC/ECD meeting the initial calibration and calibration verification technical acceptance criteria.

10.3.2.2.4.2 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80-120%, if the recovery of trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected.

10.3.2.2.5 Corrective Action for Florisil Cartridge Performance Check

Any lot of Florisil cartridges that does not meet the criteria above must be discarded and a new lot, meeting criteria, must be used for sample cleanup.

10.3.2.3 Sample Cleanup by Florisil Cartridge

The required Florisil cartridge size and the final volume of the extract after Florisil cleanup are a function of the GC autosampler that a laboratory uses. If the autosampler operates reliably with 1.0 mL of sample extract, then a 500 mg cartridge is used and the required final volume is 1.0 mL. If the autosampler requires more sample, prepare 2.0 mL of sample extract using a 1 g cartridge. Manual injection requires only a 1.0 mL final extract and a 500 mg cartridge.

10.3.2.3.1 Frequency of Sample Cleanup by Florisil Cartridge

All samples (including LCSs and MS/MSDs) and method blank extracts are required to be cleaned up by the Florisil cartridge technique.

10.3.2.3.2 Procedure for Sample Cleanup by Florisil Cartridge

10.3.2.3.2.1 Attach the vacuum manifold to a water aspirator or to a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5 and 10 lbs of vacuum.

Exhibit D Pesticides -- Section 10
Procedure (Con't)

- 10.3.2.3.2.2 Place one Florisil cartridge into the vacuum manifold for each sample extract.
- 10.3.2.3.2.3 Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge on the vacuum manifold, by pulling a vacuum, and by passing at least 5 mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.
- 10.3.2.3.2.4 After the cartridges on the manifold are washed, the vacuum is released, and a rack containing labeled 10 mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.
- 10.3.2.3.2.5 After the volumetric flasks are in place, the vacuum to the manifold is restored, and a volume of extract equal to the required final volume (1.0 or 2.0 mL) from each sample, blank, or Matrix Spike extract is transferred to the top frit of the appropriate Florisil cartridge. This must equal the final volume after Florisil cleanup.
- 10.3.2.3.2.6 Because the volumes marked on concentrator tubes are not necessarily accurate at the 1 mL level, the use of a syringe or a volumetric pipet is required to transfer the extract to the cleanup cartridge.
- 10.3.2.3.2.7 The pesticides in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL volumetric flasks held in the rack inside the vacuum manifold.
- 10.3.2.3.2.8 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10 mL vial. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the cartridge eluate.
- 10.3.2.3.2.9 Adjust the extract to the same 1 or 2 mL aliquot volume as was taken for cleanup using either of the blowdown technique (Section 10.2.3.1 or 10.2.3.2). Measure the final volume with a syringe or by transferring the extract to a volumetric flask.
- 10.3.2.3.2.10 If sulfur cleanup is to be performed, proceed to Section 10.3.3. Otherwise, transfer the sample to a GC vial and label the vial. The extract is ready for GC/ECD analysis.

10.3.3 Sulfur Cleanup

10.3.3.1 Introduction

- 10.3.3.1.1 Sulfur contamination will cause a rise in the baseline of a chromatogram and may interfere with the analyses of the later eluting pesticides. If crystals of sulfur are evident or if the presence of sulfur is suspected, sulfur removal must be performed. Interference which is due to sulfur is not acceptable. Sulfur can be removed by one of two methods,

according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and remove the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

- 10.3.3.1.2 If only part of a set of samples require sulfur cleanup, then, a sulfur cleanup blank is required for that part of the set (Section 12.1.3).

10.3.3.2 Frequency of Sulfur Cleanup

Sulfur removal is required for all sample extracts that contain sulfur.

10.3.3.3 Procedure for Sulfur Cleanup

10.3.3.3.1 Removal of Sulfur using Tetrabutylammonium (TBA) Sulfite

- 10.3.3.3.1.1 The TBA Sulfite procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble. TBA sulfite causes the least amount of degradation to a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

- 10.3.3.3.1.2 Add 2.0 mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to the extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more aliquots (approximately 0.65 g) to the extract and observe. Place the samples on the wrist shaker for 45 minutes observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5 mL organic free water and shake for 10-15 minutes. Place the samples into the centrifuge and spin at a setting and duration appropriate to spin down the solids. Transfer the hexane layer to a clean 10 mL and cap. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume.

10.3.3.3.2 Copper Technique

Add approximately 2 g of cleaned copper powder to the extract in the centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipet, and transfer the extract to a clean vial. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume. The separation of the extract from the copper powder is necessary to prevent degradation of the pesticides. If the copper appears bright, proceed to Section 10.4 and analyze the extracts. If the copper changes color, repeat the sulfur removal procedure as necessary.

10.4 GC/ECD Analysis

10.4.1 Introduction

10.4.1.1 Before samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) can be analyzed, the instrument must meet the initial calibration and calibration verification technical acceptance criteria. All sample extracts, required blanks, and calibration standards must be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature before preparation/analysis. Sample analysis on two different non-equivalent GC columns (see Section 6.26.1.3) is required for all samples and blanks.

10.4.1.2 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used (Section 9.1), the injector must be heated to at least 200°C. The optimized GC conditions from Section 9.1 must be used.

10.4.2 Procedure for Sample Analysis by GC/ECD

The injection must be made on-column by using either automatic or manual injection. 1.0 or 2.0 µL injector volumes may be used provided that all associated standards, samples, and blanks use the same injection volume. The same injection volume must be used for all standards, samples (including LCSs and MS/MSDs), and blanks associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2 µL. However, the same injection volume must be used for all analyses.

10.4.2.1 Analytical Sequence

All acceptable samples must be analyzed within a valid analysis sequence as given below.

NOTE: The injection # will depend on whether initial calibration sequence 1 or 2 is used. The analytical sequence specific to using the initial calibration sequence 1 is depicted in bold font.

<u>Time</u>	<u>Injection #</u>	<u>Material Injected</u>
	1-17	First 17 steps of the initial calibration sequence 2
	1-12	First 12 steps of the initial calibration sequence 1
0 hr.	18	Instrument Blank at end of initial calibration sequence 2
	13	Instrument Blank at end of initial calibration sequence 1
	19	PEM at end of initial calibration sequence 2
	14	PEM at end of initial calibration sequence 1
	20	First sample if using initial calibration sequence 2

<u>Time</u>	<u>Injection #</u>	<u>Material Injected</u>
	15	First sample if using initial calibration sequence 1
	.	Subsequent samples
	.	
	.	
12 hrs.	.	Last Sample
	1st injection past 12 hours	Instrument blank
	2nd and 3rd injections past 12 hours	Individual Standard Mixtures A and B
	2nd injection past 12 hours	Individual Standard Mixture C
	.	Sample
	.	
	.	
	.	Subsequent samples
	.	
Another 12 hrs.	.	Last Sample
	1st injection past 12 hours	Instrument blank
	2nd injection past 12 hours	PEM
	.	Sample
	.	
	.	Subsequent samples
	.	
Another 12 hrs.	.	Last Sample
	1st injection past 12 hours	Instrument blank
	2nd and 3rd injections past 12 hours	Individual Standard Mixtures A and B
	2nd injection past 12 hours	Individual Standard Mixture C
	.	Sample
	.	
	etc.	

10.4.2.1.1 For initial calibration sequence 2, the first 12 hours are counted from injection #18 (the Instrument Blank at the end of the initial calibration sequence), not from injection #1. Samples and required blanks may be injected until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. If more than 12 hours elapse between the injection of two instrument blanks that bracket a 12-hour period in which samples or required blanks are analyzed then the time between the injection of the second instrument blank and the preceding sample may not exceed the length of one chromatographic run. While the 12-hour period may not be

exceeded, the laboratory may run instrument blanks and standards more frequently, for instance, to accommodate staff working on 8-hour shifts. No more than 14 hours may elapse from the injection beginning the opening Continuing Calibration Verification (CCV) (instrument blank) and the injection ending the closing CCV (PEM or Individual Standard Mixture).

- 10.4.2.1.2 After the initial calibration, the analysis sequence may continue as long as acceptable instrument blanks, PEMs, and Individual Standard Mixtures (A and B) or C are analyzed at the required frequency. This analysis sequence shows only the minimum required blanks and standards. More blanks and standards may be run at the discretion of the Contractor; however, the blanks and standards must also satisfy the criteria presented in Section 9 in order to continue the run sequence.
- 10.4.2.1.3 An analysis sequence must also include all samples and required blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.
- 10.4.2.1.4 The requirements for the analysis sequence apply to both GC columns and for all instruments used for these analyses.

10.4.3 Sample Dilutions

- 10.4.3.1 All samples must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography as defined in Section 11.3 (injection taken from the 1.0 or 2.0 mL final extract after the cleanup steps).
- 10.4.3.2 If the response of any single component pesticide is greater than the response of the high standard (CS5) of the initial calibration range on both GC columns, then the extract must be diluted. The response of the pesticide compound(s) in the diluted extract must be between the initial calibration low-point (CS1) and high-point (CS5) standards for the lower column response of the two analyses.
- 10.4.3.3 If the response of any Toxaphene peak used for quantitation is greater than the response of the corresponding Toxaphene peak in the high standard (CS5) on both columns, then the sample must be diluted to have the response of the same peak be between the mid-point (CS3) and high-point (CS5) standards of Toxaphene.
- 10.4.3.4 If dilution is employed solely to bring a peak within the calibration range or to get the Toxaphene pattern on scale, the results for both the greater and the less concentrated extracts must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.
- 10.4.3.5 If the Dilution Factor (DF) is greater than 10, an additional extract 10 times more concentrated than the diluted sample extract must be analyzed and reported with the sample data. If the DF is less than or equal to 10, but greater than 1, the results of the original undiluted analysis must also be reported.
- 10.4.3.6 If the analysis of the most concentrated extract does not meet the requirement for dilution in Section 10.4.3.2 and 10.4.3.3, then the analysis is at no additional cost to USEPA.

- 10.4.3.7 When diluted, the chromatographic data for the single component pesticide must be able to be reported at greater than 10% of full scale but less than 100% of full scale.
- 10.4.3.8 When diluted, Toxaphene must be able to be reported at greater than 25% of full scale but less than 100% of full scale.
- 10.4.3.9 Samples with analytes detected at a level greater than the high calibration point must be diluted until the response is within the linear range established during calibration, or to a maximum of 1:100,000.
- 10.4.3.10 If the response is still above the high calibration point after the dilution of 1:100,000, the Contractor shall contact SMO immediately.
- 10.4.3.11 Use the results of the original analysis to determine the approximate DF required to get the largest analyte peak (for the lower of the two column responses) within the initial calibration range.
- 10.4.3.12 Sample dilutions must be made quantitatively. Dilute the sample extract with hexane.
- 10.4.3.13 If more than two analyses (i.e., from the original sample extract and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO for guidance.

Exhibit D Pesticides -- Section 11
Data Analysis and Calculations

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

- 11.1.1.1 The laboratory will identify single component analyte peaks based on the Retention Time (RT) windows established during the initial calibration sequence. Single component analytes are identified when peaks are observed in the RT window for the analyte on both Gas Chromatograph (GC) columns.
- 11.1.1.2 A set of three or four major peaks is selected for Toxaphene. RT windows for each peak are determined from the initial calibration analysis. Identification of Toxaphene in the sample is based on pattern recognition in conjunction with the elution of three or four sample peaks within the RT window of the corresponding peaks of the standard on both GC columns.
- 11.1.1.3 If Toxaphene is detected in a sample then a Toxaphene CS3 standard must be run within 72 hours of its detection in a sample chromatogram, within a valid 12-hour sequence.
- 11.1.1.4 The choice of the peaks used for Toxaphene identification and the recognition of those peaks may be complicated by the environmental alteration of Toxaphene, and by the presence of coeluting analytes, matrix interferences, or both. Because of the alteration of Toxaphene in the environment, it may give patterns in samples similar to, but not identical with, those of the standards.

11.1.2 Gas Chromatography/Mass Spectrometry (GC/MS) Confirmation

- 11.1.2.1 Any pesticide listed in Exhibit C (Pesticides) for which a concentration is reported from GC/Electron Capture Detector (GC/ECD) analysis must have the identification confirmed by GC/MS if the concentration is sufficient for that purpose. The following paragraphs are to be used as guidance in performing GC/MS confirmation. If the Contractor fails to perform GC/MS confirmation as appropriate, USEPA may require reanalysis of any affected samples at no additional cost to USEPA.
- 11.1.2.2 The GC/MS confirmation may be accomplished by one of three general means:
- Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data]; or
 - A second analysis of the semivolatile extract; or
 - Analysis of the pesticide extract, following any solvent exchange and concentration steps that may be necessary.
- 11.1.2.3 The semivolatile GC/MS analysis procedures outlined in Exhibit D (Analytical Methods for Semivolatiles) are based on the injection into the instrument of approximately 10 ng of a target compound in a 2.0 µL volume. The semivolatile Contract Required Quantitation Limit (CRQL) values in Exhibit C (Semivolatiles) are based on the sample concentration that corresponds to an on-column concentration (extract concentration) of 5.0 ng/µL of target analyte. Although these are quantitation limits, and the detection of analytes and generation of reproducible mass spectra

will routinely be possible at levels 3-10 times lower, the sample matrix may prevent detection of target analytes at less than 5.0 ng/μL. If any single component pesticide has an on-column concentration of greater than or equal to 5.0 ng/μL for both columns, then GC/MS confirmation is required. Similarly, for Toxaphene, if an individual peak concentration is greater than or equal to 125 ng/μL for both columns then GC/MS confirmation is required.

- 11.1.2.3.1 For water samples prepared according to the method described in Section 10, 10.0 ng/2.0 μL corresponds to a sample concentration of 50.0 μg/L for single component pesticides and a sample concentration of 1250 μg/L for Toxaphene.
- 11.1.2.3.2 For soil/sediment samples prepared according to the method described in Section 10, the corresponding sample concentration is 1700 μg/kg for single component pesticides and 42000 μg/kg for Toxaphene.
- 11.1.2.4 In order to confirm the identification of Toxaphene, the laboratory must also analyze a reference standard for Toxaphene. In order to demonstrate the ability of the GC/MS system to identify Toxaphene, the concentration of the standard should be 125 ng/μL.
- 11.1.2.5 To facilitate the confirmation of the single component pesticide analytes from the semivolatile library search data, the laboratory may wish to include these analytes in the semivolatile continuing calibration standard at a concentration of 5.0 ng/μL or less. Do not include Toxaphene in the semivolatile initial and continuing calibration standard. If added to this GC/MS standard, the response factors, RTs, etc., for these analytes would be reported on the GC/MS quantitation report, but not on the GC/MS calibration data reporting forms. As only a single concentration of each analyte would be analyzed, no linearity (%RSD) or Percent Difference criteria would be applied to the response factors for these additional analytes.
- 11.1.2.6 The Contractor is advised that library search results from the NIST (2002 release or later) mass spectral library will not likely list the name of the pesticide analyte as it appears in this analytical method, hence, the mass spectral interpretation specialist is advised to compare the Chemical Abstracts Service (CAS) Registry Numbers for the pesticides to those from the library search routine.
- 11.1.2.7 If the analyte cannot be confirmed from the semivolatile library search data for the original semivolatile GC/MS analysis, the laboratory may analyze another aliquot of the semivolatile sample extract after further concentration of the aliquot. This second aliquot must either be analyzed as part of a routine semivolatile GC/MS analysis, including instrument performance checks (DFTPP), calibration standards containing the pesticides as described in Section 11.1.2.5, or it must be analyzed along with separate reference standards for the analytes to be confirmed.
- 11.1.2.8 If the analyte cannot be confirmed by either the procedures in Sections 11.1.2.5 or 11.1.2.7, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS, following any necessary solvent exchange and concentration steps. As in Section 11.1.2.4, analysis of a reference standard is

Exhibit D Pesticides -- Section 11
Data Analysis and Calculations (Con't)

required if the GC/MS continuing calibration standard does not contain the analyte to be confirmed.

- 11.1.2.9 Regardless of which of the three approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the semivolatile extract, then the semivolatile method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the extract prepared for the GC/ECD analysis, then the pesticide method blank extracted with the sample must be analyzed.
- 11.1.2.10 If the identification of the analyte cannot be confirmed by any of the GC/MS procedures above, and the concentration calculated from the GC/ECD analysis is greater than, or equal to, the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form I with one of the laboratory-defined qualifiers ("X," "Y," or "Z"). In this instance, define the qualifier explicitly in the Sample Delivery Group (SDG) Narrative, and describe the steps taken to confirm the analyte in the SDG Narrative.
- 11.1.2.11 For GC/MS confirmation of single component analytes, the required deliverables are copies of the library search results (best TIC matches) or analyte spectrum and the spectrum of the reference standard. For Toxaphene, spectra of three characteristic peaks are required for both the sample component and the reference standard.
- 11.1.2.12 The purpose of the GC/MS analysis for the single component pesticides is for identification. The purpose of the GC/MS analysis for Toxaphene is to confirm the presence of chlorinated camphenes. The GC/MS analytical results for the pesticides shall not be used for quantitation and the GC/MS results shall not be reported on Form I and Form X. The exception noted in Section 11.1.2.10 applies only to analytes that cannot be confirmed above the reference standard concentration.

11.2 Calculations

11.2.1 Target Compounds

- 11.2.1.1 Quantitation for all analytes and surrogates must be performed and reported for each GC column.
- 11.2.1.2 Manual integration of peaks (e.g., measuring peak height with a ruler) is only permitted when accurate electronic integration of peaks cannot be done. If manual integration of peaks is required, it must be documented in the SDG Narrative.
- 11.2.1.3 The Contractor must quantitate each single component analyte and surrogate based on the Mean Calibration Factors (CFs) from the most recent initial calibration. Do not use the analyses of the Individual Standard Mixtures used to demonstrate calibration verification for quantitation of samples.

- 11.2.1.4 The Contractor must quantitate Toxaphene based on the Mean Calibration Factors ($\overline{CF}$ s) from the most recent initial calibration.
- 11.2.1.5 The chromatograms of all samples [including Laboratory Control Samples (LCSSs), Matrix Spikes and Matrix Spike Duplicates (MS/MSDs)], standards, and required blanks must be reviewed by a qualified pesticide analyst before they are reported.
- 11.2.1.6 Calculate the sample concentration and on-column concentration of the single component pesticides and surrogates by using the following equations.
- 11.2.1.6.1 Water
- 11.2.1.6.1.1 EQ. 14 Concentration Calculation of Target Compounds in Water Samples

$$\text{Concentration } \mu\text{g/L} = \frac{(A_x) (V_t) (DF) (GPC)}{(\overline{CF}) (V_o) (V_i)}$$

Where,

A_x = Response (peak area or height) of the compound to be measured.

$\overline{CF}$ = Mean Calibration Factor from the initial calibration (area/ng).

V_{in} = Volume of extract loaded onto GPC column.

V_{out} = Volume of extract collected after GPC cleanup.

V_t = Volume of concentrated extract (μL). (If GPC is not performed, then $V_t = 10,000 \mu\text{L}$. If GPC is performed, then $V_t = V_{out}$.)

V_i = Volume of extract injected (μL). (If a single injection is made onto two columns, use $\frac{1}{2}$ the volume in the syringe as the volume injected onto each column).

$GPC = \frac{V_{in}}{V_{out}}$ = Gel Permeation Chromatography factor. (If no GPC is performed, $GPC = 1.0$)

V_o = Volume of water extracted (mL). (NOTE: for instrument blanks and sulfur cleanup blanks, assume a 1,000 mL volume).

DF = Dilution Factor. The DF is defined as follows:

$$\frac{\mu\text{L most concentrated extract used to make dilution} + \mu\text{L clean solvent}}{\mu\text{L most concentrated extract used to make dilution}}$$

If no dilution is performed, $DF = 1.0$.

The $\overline{CF}$ s used in Equations 14 - 17 are those from the most recent initial calibration. If the CF s used to determine the linearity of the initial calibration were based on peak area, then the concentration of the analyte in the sample

Exhibit D Pesticides -- Section 11
Data Analysis and Calculations (Con't)

must be based on peak area. Similarly, if peak height was used to determine linearity, use peak height to determine the concentration in the sample.

11.2.1.6.1.2 EQ. 15 On-Column Concentration of Water Sample Extract

$$\text{On-Column Concentration (ng/}\mu\text{L)} = \frac{(A_x)}{(\overline{CF}) (V_i)}$$

Where,

A_x = Same as EQ. 14.

$\overline{CF}$ = Same as EQ. 14.

V_i = Volume of extract injected (μL). (If a single injection is made onto two columns, use $\frac{1}{2}$ the volume in the syringe as the volume injected onto each column).

11.2.1.6.2 Soil/Sediment

11.2.1.6.2.1 EQ. 16 Concentration of Target Compounds in Soil/Sediment Samples

$$\text{Concentration } \mu\text{g/Kg (Dry weight basis)} = \frac{(A_x) (V_t) (DF) (GPC)}{(\overline{CF}) (V_i) (W_s) (D)}$$

Where,

A_x = Same as EQ. 14.

$\overline{CF}$ = Same as EQ. 14.

V_t = Same as EQ. 14.

V_i = Volume of extract injected (μL). (If a single injection is made onto two columns, use $\frac{1}{2}$ the volume in the syringe as the volume injected onto each column).

W_s = Weight of sample extracted (g).

DF = Same as EQ. 14.

D = % dry weight or $\frac{100 - \% \text{Moisture}}{100}$

GPC = Same as EQ. 14.

11.2.1.6.2.2 EQ. 17 On-Column Concentration of Soil Sample Extract

$$\text{On-Column Concentration (ng/}\mu\text{L)} = \frac{(A_x)}{(\overline{CF}) (V_i)}$$

Where,

A_x = Same as EQ. 14.

$\overline{CF}$ = Same as EQ. 14.

V_i = Volume of extract injected (μL). (If a single injection is made onto two columns, use $\frac{1}{2}$ the volume in the syringe as the volume injected onto each column).

11.2.1.7 The lower of the two concentrations calculated for each single component pesticide is reported on Form I. In addition, the concentrations calculated for both the GC columns are reported on Form X, along with a Percent Difference (%Difference) comparing the two concentrations. The Percent Difference is calculated according to Equation 18.

EQ. 18 Percent Difference Between Concentrations on Both GC Columns

$$\%D = \frac{\text{Conc}_H - \text{Conc}_L}{\text{Conc}_L} \times 100$$

Where,

Conc_H = The higher of the two concentrations for the target compound in question.

Conc_L = The lower of the two concentrations for the target compound in question.

NOTE: Using this equation will result in Percent Difference values that are always positive.

11.2.1.8 The quantitation of Toxaphene must be accomplished by comparing the heights or the areas of each of the three or four major peaks of in the sample with the CF for the same peaks established during the initial calibration sequence. The concentration of Toxaphene is calculated by using Equations 14 and 16, where A_x is the area for each of the major peaks. The concentration of each peak is determined and then a mean concentration for the three or four major peaks is determined on each column.

11.2.1.9 The reporting requirement for Toxaphene is similar to that for the single component analytes, except that the lower mean concentration (from three or four peaks) is reported on Form I, and the two mean concentrations reported on Form X. The two mean concentrations are compared by calculating the Percent Difference using Equation 18.

Exhibit D Pesticides -- Section 11
Data Analysis and Calculations (Con't)

11.2.2 CRQL Calculation

11.2.2.1 Water Samples

EQ. 19 CRQL for Water Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{\text{Contract Sample Vol (1000 mL)}}{V_o} \times \text{DF} \times \frac{V_t}{(V_c)}$$

Where,

Contract CRQL = The CRQL value reported in Exhibit C (Pesticides).

V_o = Same as EQ. 14.

DF = Same as EQ. 14.

V_t = Same as EQ. 14.

V_c = Contract concentrated extract volume [10,000 μ L if Gel Permeation Chromatography (GPC) was not performed and $V_c = V_{out}$ if GPC was performed].

11.2.2.2 Soil/Sediment Samples

EQ. 20 CRQL for Soil/Sediment Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{\text{Contract Sample Wt. (30 g)}}{W_s} \times \text{DF} \times \frac{V_t}{V_c} \times \frac{100}{(100 - M_p)}$$

Where,

Contract CRQL = The CRQL value reported in Exhibit C (Pesticides).

W_s = Same as EQ. 16.

DF = Same as EQ. 16.

V_t = Same as EQ. 16.

V_c = Same as EQ. 19.

M_p = Percent Moisture.

11.2.3 Surrogate Recoveries

11.2.3.1 The concentrations of the surrogates are calculated separately for each GC column in a similar manner as the other analytes, using Equations 14 and 16. Use the $\overline{CF}$ s from the initial calibration. If two Individual Standard Mixtures are used, $\overline{CF}$ s from Individual Standard Mixture A are to be used.

11.2.3.2 The recoveries of the surrogates are calculated for each GC column according to Equation 13, Percent Recovery (%R).

11.3 Technical Acceptance Criteria for Sample Analyses

The requirements below apply independently to each GC column and to all instruments used for these analyses (see exception in Section 11.3.8). Quantitation must be performed on each GC column.

- 11.3.1 Samples must be analyzed under the GC/ECD operating conditions in Section 9.1. The instrument must have met all initial calibration and calibration verification technical acceptance criteria. Samples must be cleaned-up, when required, with GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration verification. Samples must be cleaned-up using Florisil that meets the technical acceptance criteria for Florisil. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, Performance Evaluation Mixtures (PEMs), and Individual Standard Mixture(s), as described in Section 10.4.2.1.
- 11.3.2 The sample must be extracted and analyzed within the contract holding times.
- 11.3.3 The LCS associated with the samples must meet the LCS technical acceptance criteria.
- 11.3.4 The samples must have an associated method blank meeting the method blank technical acceptance criteria. If a sulfur cleanup blank is associated with the samples, that blank must meet the sulfur cleanup blank technical acceptance criteria.
- 11.3.5 The RT for each of the surrogates must be within the RT window as calculated in Section 9.2.4.3, for both GC columns.
- 11.3.6 The Percent Recovery for the surrogates must be between 30-150%, inclusive. Up to one surrogate may fail this criteria per column.

NOTE: The surrogate recovery requirements do not apply to a sample that has been diluted.
- 11.3.7 No target compound responses may exceed the upper limit responses of the initial calibration or else extracts must be diluted and reanalyzed (Section 10.4.3).
- 11.3.8 A Toxaphene calibration verification standard (CS3) must be analyzed on the same instrument upon its detection in a sample. This standard must be analyzed within 72 hours of the analytes detection in a valid 12-hour period.
- 11.3.9 The identification of single component pesticides by GC methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of Toxaphene by GC methods is based primarily on recognition of the pattern of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component analytes and Toxaphene.
 - 11.3.9.1 When no compounds are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low-point standard of the initial calibration associated with those analyses.
 - 11.3.9.2 Chromatograms must display single component pesticides detected in the sample at less than full scale.

Exhibit D Pesticides -- Section 11
Data Analysis and Calculations (Con't)

- 11.3.9.3 Chromatograms must display the largest peak of Toxaphene detected in the sample at less than full scale.
- 11.3.9.4 If an extract must be diluted (Section 10.4.3), chromatograms must display single component pesticides between 10-100% of full scale.
- 11.3.9.5 If an extract must be diluted (Section 10.4.3), chromatograms must display Toxaphene between 25-100% of full scale.
- 11.3.9.6 For any sample or blank, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.
- 11.3.9.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.4 Corrective Action for Sample Analysis

- 11.4.1 Sample analysis technical acceptance criteria MUST be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank or sulfur cleanup blank will require reextraction and reanalysis at no additional cost to USEPA. Any samples analyzed that do not meet the technical acceptance criteria will require reextraction and/or reanalysis at no additional cost to USEPA.
- 11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reanalyzed at no additional cost to USEPA after the corrective action.
- 11.4.3 The extract from samples that were cleaned up by GPC using an automated injection system and that have both surrogate recoveries outside the lower surrogate acceptance limits must be checked to assure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample must be reprepared and reanalyzed at no additional cost to USEPA.
- 11.4.4 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g., carryover, column bleed, dirty ECD, contaminated gases, leaking septum, etc.). After correcting the problem, analyze an instrument blank to demonstrate that the system is functioning properly. Reanalyze the sample extracts. If the problem with the samples still exists, then those samples must be reextracted and reanalyzed. Samples that cannot be made to meet the given specifications after one reextraction and minimum three-step cleanup (GPC, Florisil, and sulfur cleanups) are reported in the SDG Narrative and do not require further analysis.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Introduction

There are two types of blanks required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may also be required if some, but not all of the samples are subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective technical acceptance criteria for the sample analysis technical acceptance criteria to be met.

NOTE: Under no circumstances should blanks (method/instrument/sulfur cleanup) be analyzed at a dilution (i.e., blanks should always have a DF = 1.0).

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a volume of a clean reference matrix (reagent water for aqueous samples, or purified sodium sulfate or Hydromatrix for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2.2 Frequency of Method Blank

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike and Matrix Spike Duplicates (MS/MSDs), Performance Evaluation (PE) samples, and Laboratory Control Samples (LCSs)]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples; and
- Be analyzed on each Gas Chromatograph/Electron Capture Detector (GC/ECD) system used to analyze associated samples.

12.1.2.3 Procedure for Method Blank

For water samples, measure 1.0 L of reagent water for each method blank aliquot and spike with 3.0 mL of the surrogate spiking solution (Section 7.2.2.1). For soil/sediment samples, measure 30 g of sodium sulfate or Hydromatrix and spike with 3.0 mL of the surrogate spiking solution. Extract, concentrate, and analyze the method blank according to Section 10.

12.1.2.4 Calculations for Method Blank

Calculate method blank results according to Section 11.

Exhibit D Pesticides -- Section 12
Quality Control (Con't)

12.1.2.5 Technical Acceptance Criteria for Method Blank

- 12.1.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.
- 12.1.2.5.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2.2, using the procedure in Section 12.1.2.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria. Method blanks must undergo Gel Permeation Chromatography (GPC) cleanup, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. Method blanks must be cleaned-up using Florisil meeting the technical acceptance criteria for Florisil.
- 12.1.2.5.3 Method blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, Performance Evaluation Mixtures (PEMs), and Individual Standard Mixtures, as described in Section 10.4.2.1.
- 12.1.2.5.4 The concentration of the target compounds [Exhibit C (Pesticides)] in the method blank must be less than the Contract Required Quantitation Limit (CRQL) for each target compound.
- 12.1.2.5.5 The method blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.9.
- 12.1.2.5.6 Surrogate recoveries must fall within the acceptance window of 30-150%. These limits are not advisory.
- 12.1.2.5.7 Method blanks must be analyzed at the original concentration only (i.e., DF = 1.0).
- 12.1.2.6 Corrective Action for Method Blank
 - 12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of QC limits.
 - 12.1.2.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples (including LCSs, MS/MSDs, and PE samples) processed with a method blank that does not meet the method blank technical acceptance criteria (i.e., contaminated) will require reextraction and reanalysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.
 - 12.1.2.6.3 If surrogate recoveries in the method blank do not meet the technical acceptance criteria listed in Section 12.1.2.5.6, first reanalyze the method blank. If the surrogate recoveries do not meet the technical acceptance criteria after reanalysis, then the method blank and all samples (including LCSs, MS/MSDs, and PE samples) associated with that method blank must be reextracted and reanalyzed at no additional cost to USEPA.

- 12.1.2.6.4 If the method blank fails to meet a technical acceptance criteria other than Sections 12.1.2.5.4 and 12.1.2.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary) and reanalyze the method blank.

12.1.3 Sulfur Cleanup Blank

12.1.3.1 Summary of Sulfur Cleanup Blank

The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup and analysis procedures. The purpose of the sulfur cleanup is to determine the levels of contamination associated with the separate sulfur cleanup steps.

12.1.3.2 Frequency of Sulfur Cleanup Blank

The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set that required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then no separate sulfur cleanup blank is required.

12.1.3.3 Procedure for Sulfur Cleanup Blank

The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. The sulfur blank must also contain the surrogates at the same concentrations as the sample extracts (assuming 100.0% recovery). Therefore, add 0.6 mL of the surrogate spiking solution (Section 7.2.2.1) to 1.4 mL of hexane in a clean vial.

- 12.1.3.3.1 Proceed with the sulfur removal (Section 10.3.3) using the same technique (mercury or copper) as the samples associated with the blank.

- 12.1.3.3.2 Analyze the sulfur blank according to Section 10.4.2.

12.1.3.4 Calculations for Sulfur Cleanup Blank

- 12.1.3.4.1 Assuming that the material in the sulfur blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 14 in Section 11.2.1.6.1.1. Compare the results to the CRQL values in Exhibit C (Pesticides).

- 12.1.3.4.2 See Section 11.2 for the equations for the other calculations.

12.1.3.5 Technical Acceptance Criteria for Sulfur Cleanup Blanks

- 12.1.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each column.

- 12.1.3.5.2 All sulfur cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 using the procedure in Section 12.1.3.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

Exhibit D Pesticides -- Section 12
Quality Control (Con't)

- 12.1.3.5.3 Sulfur cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixtures, as described in Section 10.4.2.1.
- 12.1.3.5.4 The concentration of the target compounds [Exhibit C (Pesticides)] in the sulfur cleanup blank must be less than the CRQL for each target compound.
- 12.1.3.5.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.9.
- 12.1.3.5.6 Surrogate recoveries must fall within the acceptance windows of 30-150%. These limits are not advisory.
- 12.1.3.6 Corrective Action for Sulfur Cleanup Blank
 - 12.1.3.6.1 If a sulfur cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out-of-control.
 - 12.1.3.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures **MUST** be taken and documented before further sample analysis proceeds. Further, all samples processed with a sulfur cleanup blank that does not meet the sulfur cleanup blank technical acceptance criteria (i.e., contaminated) will require reextraction and reanalysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.
 - 12.1.3.6.3 If surrogate recoveries in the sulfur cleanup blank do not meet the technical acceptance criteria in Section 12.1.3.5.6, first reanalyze the sulfur cleanup blank. If the surrogate recoveries do not meet the technical acceptance criteria after reanalysis, then the sulfur cleanup blank and all samples associated with that sulfur cleanup blank must be re-prepared/reextracted and reanalyzed at no additional cost to USEPA.
 - 12.1.3.6.4 If the sulfur cleanup blank fails to meet a technical acceptance criteria other than Sections 12.1.3.5.4 and 12.1.3.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary), and reanalyze the sulfur cleanup blank.

12.1.4 Instrument Blank

12.1.4.1 Summary of Instrument Blank

An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis, particularly with regard to carryover of analytes from standards or highly contaminated samples into other analyses.

12.1.4.2 Frequency of Instrument Blank

The first analysis in a 12-hour analysis sequence (Section 9.3.2) must be an instrument blank. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks (Section 10.4.2.1). If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an instrument blank must be analyzed to initiate a new 12-hour sequence (Section 9.3.2).

12.1.4.3 Procedure for Instrument Blank

12.1.4.3.1 Prepare the instrument blank by spiking the surrogates into hexane or iso-octane for a concentration of 20.0 ng/mL of tetrachloro-m-xylene and 40.0 ng/mL of decachlorobiphenyl.

12.1.4.3.2 Analyze the instrument blank according to Section 10.4, at the frequency listed in Section 12.1.4.2.

12.1.4.4 Calculations for Instrument Blank

12.1.4.4.1 Assuming that the material in the instrument blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 14 in Section 11.2.1.6.1.1. Compare the results to the CRQL values for water samples in Exhibit C (Pesticides).

12.1.4.4.2 See Section 11.2 for the equations for the other calculations.

12.1.4.5 Technical Acceptance Criteria for Instrument Blanks

12.1.4.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed and reported independently on Form I PEST for each GC column.

12.1.4.5.2 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.4.2, using the procedure in Section 10.4 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.4.5.3 The concentration of each target compound [Exhibit C (Pesticides)] in the instrument blank must be less than the CRQL for that analyte.

12.1.4.5.4 The instrument blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.9.

12.1.4.5.5 Instrument blanks must be analyzed at the original concentration only (i.e., DF = 1.0).

12.1.4.6 Corrective Action for Instrument Blank

12.1.4.6.1 If compounds are detected at concentrations greater than the CRQL, or the surrogate Retention Times (RTs) are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples that were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. All samples (including LCSs, MS/MSDs, and PE samples) and required blanks that were run after the last acceptable instrument blank must

Exhibit D Pesticides -- Section 12
Quality Control (Con't)

be reinjected during a valid run sequence and must be reported at no additional cost to USEPA.

12.2 Laboratory Control Sample (LCS)

12.2.1 Summary of LCS

The LCS is an internal laboratory QC sample designed to assess [on a Sample Delivery Group (SDG)-by-SDG basis] the capability of the Contractor to perform the analytical method listed in this Exhibit.

12.2.2 Frequency of LCS

The LCS must be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, per SDG. The LCS must be extracted and analyzed concurrently with the samples in the SDG using the same extraction protocol, cleanup procedure, and instrumentation as the samples in the SDG.

12.2.3 Procedure for LCS

For water samples, measure 1.0 L of reagent water and spike with 1.0 mL of the LCS spiking solution and 3.0 mL of the surrogate spiking solution (Section 7.2.2). For soil/sediment samples, measure 30 g of a clean reference matrix (e.g., sodium sulfate, Hydromatrix, sand) and spike with 1.0 mL of the LCS spiking solution and 3.0 mL of the surrogate spiking solution. Extract, concentrate, and analyze the LCS according to Section 10.

12.2.4 Calculations for LCS

12.2.4.1 Calculate the results according to Section 11.

12.2.4.2 Calculate individual compound recoveries of the LCS using Equation 13.

12.2.5 Technical Acceptance Criteria For LCS

12.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.2.5.2 The LCS must be analyzed at the frequency described in Section 12.2.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.2.5.3 The LCS must be prepared as described in Section 12.2.3.

12.2.5.4 The LCS must meet all sample technical acceptance criteria in Sections 11.3.5, 11.3.7, and 11.3.9.

12.2.5.5 The Percent Recovery (%R) for each of the compounds in the LCS (water and soil/sediment) must be within the recovery limits listed in Table 2.

12.2.5.6 Surrogate recoveries must fall within the acceptance windows of 30-150%. These limits are not advisory.

12.2.6 Corrective Action for LCS

12.2.6.1 If the LCS technical acceptance criteria for the surrogates or the LCS compound recovery are not met, check calculations, the

surrogate and LCS solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and LCS recovery criteria.

- 12.2.6.2 LCS technical acceptance criteria MUST be met before data are reported. LCS contamination from laboratory sources or any LCS analyzed not meeting the technical acceptance criteria will require reextraction and reanalysis of the LCS at no additional cost to USEPA.
- 12.2.6.3 All samples (including MS/MSD and PE samples) and required blanks, prepared and analyzed in an SDG with an LCS that does not meet the technical acceptance criteria, will also require reextraction and reanalysis at no additional cost to USEPA.

12.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.3.1 Summary of MS/MSD

To evaluate the effects of the sample matrix on the methods used for pesticide analyses, USEPA has prescribed a mixture of pesticide target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.3.2 Frequency of MS/MSD Analysis

- 12.3.2.1 An MS/MSD must be extracted and analyzed for every 20 field samples of a similar matrix in an SDG.
- 12.3.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field blanks may be delivered to a laboratory for analysis. Do not perform MS/MSD analysis on a water rinsate sample or field blank.
- 12.3.2.3 If the USEPA Region requesting an MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify the Sample Management Office (SMO) that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.
- 12.3.2.4 If there is insufficient sample volume remaining in any of the samples in an SDG to perform the requested MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.
- 12.3.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.3.2.1, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If

Exhibit D Pesticides -- Section 12
Quality Control (Con't)

this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.3.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.3.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis when the Region did not designate a sample to be used for this purpose.

12.3.3 Procedure for Preparing MS/MSD

12.3.3.1 For water samples, measure out two additional 1 L aliquots of the sample chosen for spiking. Adjust the pH of the samples (if required) and fortify each with 1.0 mL of the matrix spiking solution and 3.0 mL of the surrogate spiking solution (Section 7.2.2). Extract, concentrate, cleanup, and analyze the MS/MSD according to Section 10.

12.3.3.2 For soil/sediment samples, weigh out two additional 30 g aliquots of the sample chosen for spiking. Add 1.0 mL of the matrix spiking solution and 3.0 mL of the surrogate spiking solution (Section 7.2.2). Extract, concentrate, cleanup, and analyze the MS/MSD according to Section 10.

12.3.3.3 MS/MSD samples must be analyzed at the same concentration as the most concentrated extract for which the original sample results will be reported. Do not dilute the MS/MSD samples further to get either spiked or non-spiked analytes within calibration range.

12.3.4 Calculations for MS/MSD

The Percent Recoveries and the Relative Percent Difference (RPD) between the recoveries of each of the compounds in the MS/MSD samples will be calculated and reported by using the following equations:

EQ. 21 Percent Recovery of Spike Compounds in MS/MSD Samples

$$\text{Matrix Spike Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

Where,

SSR = Spike Sample Result.

SR = Original Sample Result.

SA = Spike Added.

EQ. 22 Relative Percent Difference Between MS/MSD Spike Recoveries

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2} (MSR + MSDR)} \times 100$$

Where,

RPD = Relative Percent Difference.

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

12.3.5 Technical Acceptance Criteria for MS/MSD

12.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.3.5.2 All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.3.2, using the procedure above and in Section 10, on a GC/ECD system meeting the initial calibration, calibration verification, and blank technical acceptance criteria. MS/MSDs must be cleaned up with GPC, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. MS/MSDs must be cleaned-up using Florisil meeting the technical acceptance criteria for Florisil. MS/MSDs must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixture(s) (A, B, or C) as described in Section 10.4.2.1.

12.3.5.3 The samples must be extracted and analyzed within the contract required holding times.

12.3.5.4 The RT for each of the surrogates must be within the RT window as calculated in Section 9 for both GC columns.

12.3.5.5 The limits for Matrix Spike compound recovery and RPD are given in Table 3. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.3.6 Corrective Action for MS/MSD

Any MS/MSD which fails to meet the technical acceptance criteria in Sections 12.3.5.1, 12.3.5.2, and 12.3.5.4 must be reanalyzed at no additional cost to USEPA.

12.4 Method Detection Limit (MDL) Determination

12.4.1 Before any field samples are analyzed under the contract, the MDL for each single compound pesticide target compound and Toxaphene shall be determined on each instrument used for analysis. MDL determination is matrix- and level-specific (i.e., the MDL shall be determined for water and soil samples). The MDLs must be verified annually thereafter (see Section 12.4.2 for MDL verification procedures), until the contract expires or is terminated, or after major

Exhibit D Pesticides -- Section 12
Quality Control (Con't)

instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the detector and replacement of the GC column.

- 12.4.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for water samples is achieved by analyzing a single reagent water blank (see method blank for water samples in Section 12.1.2) spiked with each single component pesticide target compound and Toxaphene at a concentration equal to two times the analytically determined MDL. MDL verification for soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for soil samples in Section 12.1.2) spiked with each single component pesticide target compound and Toxaphene at a concentration equal to 2 times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1.1. Samples used for MDL determination and verification must be subjected to the same extraction and cleanup procedures used for field samples. The resulting chromatograms of each target compound must meet the qualitative identification criteria outlined in Sections 11.1.1 for both columns.
- 12.4.3 The determined concentration of the MDL must be less than the CRQL.
- 12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, to comply with the letter and spirit of any sewer discharge permits and regulations, and to comply with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

Exhibit D Pesticides -- Section 16
References

16.0 REFERENCES

- 16.1 American Society of Testing and Materials. Standard Test Method for Determination of Organochlorine Pesticides in Water by Capillary Column Gas Chromatography. D5812-96(2002)e1.
- 16.2 US Environmental Protection Agency. Organochlorine Pesticides by Gas Chromatography. SW-846 Method 8081B, Revision 2. January 1998.
- 16.3 US Environmental Protection Agency. Separatory Funnel Liquid-Liquid Extraction. SW-846 Method 3510C, Revision 3. December 1996.
- 16.4 US Environmental Protection Agency. Continuous Liquid-Liquid Extraction. SW-846 Method 3520C, Revision 3. December 1996.
- 16.5 US Environmental Protection Agency. Automated Soxhlet Extraction. SW-846 Method 3541, Revision 0. September 1994.
- 16.6 US Environmental Protection Agency. Pressurized Fluid Extraction (PFE). SW-846 Method 3545A, Revision 1. January 1998.
- 16.7 US Environmental Protection Agency. Ultrasonic Extraction. SW-846 Method 3550C, Revision 3. November 2000.
- 16.8 US Environmental Protection Agency. Alumina Cleanup. SW-846 Method 3610B, Revision 2. December 1996.
- 16.9 US Environmental Protection Agency. Silica Gel Cleanup. SW-846 Method 3630C, Revision 3. December 1996.
- 16.10 US Environmental Protection Agency. Gel-Permeation Cleanup. SW-846 Method 3640A, Revision 1. September 1994.
- 16.11 US Environmental Protection Agency. Acid-Base Partition Cleanup. SW-846 Method 3650B, Revision 2. December 1996.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Retention Time Windows for Single Component
Analytes, Toxaphene, and Surrogates

Compound	RT Window (minutes)
alpha-BHC	± 0.05
beta-BHC	± 0.05
gamma-BHC (Lindane)	± 0.05
delta-BHC	± 0.05
Heptachlor	± 0.05
Aldrin	± 0.05
alpha-Chlordane	± 0.07
gamma-Chlordane	± 0.07
Heptachlor epoxide	± 0.07
Dieldrin	± 0.07
Endrin	± 0.07
Endrin aldehyde	± 0.07
Endrin ketone	± 0.07
4,4'-DDD	± 0.07
4,4'-DDE	± 0.07
4,4'-DDT	± 0.07
Endosulfan I	± 0.07
Endosulfan II	± 0.07
Endosulfan sulfate	± 0.07
Methoxychlor	± 0.07
Toxaphene	± 0.07
Tetrachloro-m-xylene	± 0.05
Decachlorobiphenyl	± 0.10

Table 2

Laboratory Control Sample Recovery Limits

Compound	Percent Recovery
gamma-BHC	50-120
Heptachlor epoxide	50-150
Dieldrin	30-130
4,4'-DDE	50-150
Endrin	50-120
Endosulfan sulfate	50-120
gamma-Chlordane	30-130

NOTE: The recovery limits for any of the compounds in the LCS may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

Table 3

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
gamma-BHC (Lindane)	56-123	0-15	46-127	0-50
Heptachlor	40-131	0-20	35-130	0-31
Aldrin	40-120	0-22	34-132	0-43
Dieldrin	52-126	0-18	31-134	0-38
Endrin	56-121	0-21	42-139	0-45
4,4'-DDT	38-127	0-27	23-134	0-50

Table 4
Concentration Levels of Calibration Standards

Compound	Concentration (ng/mL)				
	CS1	CS2	CS3	CS4	CS5
alpha-BHC	5.0	10	20	40	80
gamma-BHC	5.0	10	20	40	80
Heptachlor	5.0	10	20	40	80
Endosulfan I	5.0	10	20	40	80
Dieldrin	10	20	40	80	160
Endrin	10	20	40	80	160
4,4'-DDD	10	20	40	80	160
4,4'-DDT	10	20	40	80	160
Methoxychlor	50	100	200	400	800
beta-BHC	5.0	10	20	40	80
delta-BHC	5.0	10	20	40	80
Aldrin	5.0	10	20	40	80
Heptachlor-epoxide	5.0	10	20	40	80
4,4'-DDE	10	20	40	80	160
Endosulfan II	10	20	40	80	160
Endosulfan sulfate	10	20	40	80	160
Endrin ketone	10	20	40	80	160
Endrin aldehyde	10	20	40	80	160
alpha-Chlordane	5.0	10	20	40	80
gamma-Chlordane	5.0	10	20	40	80
Tetrachloro-m-xylene	5.0	10	20	40	80
Decachlorobiphenyl	10	20	40	80	160
Toxaphene	500	1000	2000	4000	8000

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