STANDARD OPERATING PROCEDURE

FOR

POLYCHLORINATED BIPHENYLS (PCBs) BY METHOD 8082A

PHILIS SOP L-A-401 Rev. 2

Revision Date: 06-19-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

	June 19, 2024
PHILIS, Castle Rock Lead Chemist	**Date**
	June 19, 2024
PHILIS, Edison Lead Chemist	**Date**
	June 19, 2024
PHILIS, Quality Assurance Manager	**Date**
Julia Capri	**June 19, 2024**
PHILIS, Program Manager	**Date**

Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis Tiandra Allen	05/17/2021	Program Issue Development
1	James Travis Crystal Chu	11/03/2022	Revision
2	Thomas Antony	04/25/2024	Annual Review

SOP REVISION FORM

SOP Name:	**Polychlorinated Biphenyls (PCB's) By Method 8082A**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Revision	*SOP No. L-A-401*	1	11/18/2022
Requested by:	Thomas Antony	Date:	04/25/2024

New SOP Revision Date:	**06/19/2024**	**New SOP Revision #:** *(If Applicable)*	**2**

For *Revision* : Summary of Revisions (specify sections)

Forms	Updated to current release

For *Review*: Comments

Standard Operating Procedure
Polychlorinated Biphenyls
(PCBs) by Method 8082A
L-A-401 Rev. 2

TABLE OF CONTENTS

TABLES, FIGURES, AND ATTACHMENTS

Standard Operating Procedure Polychlorinated Biphenyls (PCBs) by Method 8082A L-A-401 Rev. 2

1.0 Scope and Application

This Standard Operating Procedure (SOP) documents the PHILIS-2 Program application of EPA SW846 Method 8082A, "Polychlorinated Biphenyl (PCBs) by Gas Chromatography", used in the PHILIS-2 Mobile Labs.

This SOP is executed in accordance with the U.S. Environmental Protection Agency and the National Environmental Laboratory Accreditation Program (NELAP).

1.1 This method may be used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from soil, solid, sediment, tissue, wipe, and aqueous matrices, using open-tubular, capillary columns with electron capture detectors (ECD). The Aroclors listed below have been determined by this method using a dual-column analysis system. The method also may be applied to other matrices such as oils and wipe samples, if appropriate sample extraction procedures are employed.

Compound	CAS Registry No.[1]
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Aroclor 1262	37324-23-5
Aroclor 1268	11100-14-4

Note:
1. Chemical Abstract Service Registry No.

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards.

1.3 The nine Aroclors listed in Sec. 1.1 are those that are commonly specified in EPA regulations. The quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations but is particularly difficult when the Aroclors have been weathered by long exposure in the environment.

1.4 Compound identification based on single-column analysis must be confirmed on a second column with different separation characteristics. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS (e.g., Method 8270) is also recommended as a confirmation technique, provided analyte concentration is high enough to be seen by GCMS.

1.5 This method describes a dual-column hardware configuration in which two GC columns operating in a parallel configuration are connected to a single injection port and to two separate detectors. This configuration allows one injection to be used for dual-column simultaneous analysis.

1.6 Matrix-specific performance data must be established for each analytical batch and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Example chromatograms and GC conditions are provided as guidance.

1.7 Note that the Aroclors are listed in approximate retention time order. Additional Aroclors may be added to this list.

Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 This procedure applies to the analysis of extracts from water, sediment, soil, solid, and wipe matrices. The extracts must be in a solvent suitable for analysis by GC/ECD.

2.2 Aqueous samples are extracted with methylene chloride at neutral pH using either Method 3510 (separatory funnel), or other appropriate technique or solvents. The extracts are cleaned, dried, concentrated to a final volume of 10 mL or less, and exchanged into hexane prior to analyses by GC/ECD. Water samples may be tested in the range of 0.50 µg/L to 30 µg/L using separatory funnel extraction with one hundred milliliters of sample and a final extract volume of 1.0 mL. Higher analyte concentrations may be analyzed using less sample or dilution of the extract.

2.3 Soil samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using pressurized solvent extraction (PSE), Method 3545, or other appropriate technique or solvents. An example summary for the three extraction amounts and analyte ranges is provided in 2.3.1-3.

2.3.1 For low level soils, 30 grams are extracted with 50:50 methylene chloride/acetone using PSE. The extracts are cleaned, dried, concentrated to 5.0 mL, and exchanged into hexane prior to analysis by GC/ECD. Soil samples may be tested in the range of 0.0083 mg/Kg to 0.50 mg/Kg using the above procedure.

2.3.2 For medium level soil samples, 5 grams of soil are extracted with 50:50 methylene chloride/acetone using PSE. The extracts are cleaned, dried, concentrated to 10 mL, and exchanged into hexane prior to analysis by GC/ECD. Soil samples may be tested in the range of 0.10 mg/Kg to 6.0 mg/Kg using the above procedure.

2.3.3 For high level soil samples, 1 gram of soil is extracted with 50:50 methylene chloride/acetone using PSE. The extracts are cleaned, dried, concentrated to 10 mL, and exchanged into hexane prior to analysis by GC/ECD. Soil samples may be tested in the range of 0.50 mg/Kg to 30 mg/Kg using the above procedure. Further dilution may be required for samples exceeding this range.

2.4 Extraction procedures are described in PHILIS-2 specific extraction SOPs.

2.5 Extracts for PCB analysis may be subjected to a sulfur cleanup (Method 3660B) followed by a sequential sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove and may destroy many single component organochlorine or organophosphorus pesticides.

2.6 After cleanup, the extract is analyzed by injecting a measured aliquot into a gas chromatograph equipped with narrow-bore fused-silica capillary columns and two electron capture detectors (GC/ECD).

2.7 The chromatographic data may be used to determine the nine Aroclors in Sec. 1.1, or total PCBs.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared

samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. See the applicable method or SW846 8000B table 4.1. Also the period of time a sample may be stored prior to analysis when there is no preparation step.

3.3 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.4 Matrix Spike (spiked sample or fortified sample)‡: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.5 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)‡: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.6 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

3.7 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

3.8 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.9 Required Detection Limit (RDL): Detection limits established by a client or regulatory authority for analytes of concern. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.10 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield contamination and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to Methods 3500, 3600, and 8000D for a discussion of interferences.

4.2 Interferences co-extracted from the samples will vary considerably from matrix to matrix. Positive matrix interferences can be caused by contaminants that are extracted from the sample during the extraction process. Negative matrix interference can occur when samples contain materials that have a strong affinity for the analyte compounds. The amount of matrix interference varies from sample to sample. Cleanup procedures may help eliminate some of the interferences. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Some sources of interference in this method are as follows:

4.2.1 Coelution of related analytes -- All 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If this procedure is expanded to encompass the individual congeners, then the analyst must either document the resolution of the congeners in question or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

4.2.2 Phthalate contamination is commonly observed in PCB analysis, and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis. Sample preparation equipment shall not be composed of plastic materials. Interferences from phthalate esters can be further minimized by checking all solvents and reagents for phthalate contamination.

4.2.3 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations.

4.2.4 Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

4.2.5 These contaminant materials may be removed prior to analysis using sulfuric acid/permanganate cleanup techniques described in CSS's SOP L-P-108 and/or Florisil cleanup techniques (CSS's SOP L-P-110).

4.3 Cross-contamination of clean glassware can routinely occur when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned. See SOP L-M-401 on glassware cleaning.

4.4 Sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur contamination should be expected with sediment samples. Sulfur can be removed using the cleanup techniques described in CSS SOP L-P-109.

4.5 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running MBs with every batch. Method blanks must be evaluated for interferences. If interferences are detected, the lab should attempt to determine the source of interference and take corrective action to eliminate it. High purity reagents, solvents, and gases must be used to minimize interference problems with the sample analysis. Carryover contamination may occur when a sample containing low levels of Aroclors is analyzed immediately following a sample containing high levels of Aroclors. If this situation occurs during a non-monitored analysis, the sample containing the low concentrations of Aroclors may require reanalysis. If the situation occurs during monitored analysis, a blank should be run after the high-level sample to ensure that the system is free of contamination.

5.0 Safety

5.1 This method does not address all safety issues associated with its use. Laboratory personnel are responsible for maintaining a safe work environment and a current awareness of the Chemical Hygiene Plan regarding the safe handling of the chemicals listed in this method.

WARNING: This procedure involves working with hazardous materials. It is the responsibility of the analyst to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous.

5.2 Specific Safety Concerns or Requirements

WARNING: Standard laboratory personal protective equipment (PPE) for routine laboratory functions will include safety glasses with side shields, disposable nitrile gloves, laboratory coat, and closed-toe non-absorbent shoes. Additional PPE may be required as based on increased hazards of the work task performed or abnormal event such as spill clean-up. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar material must be used.

WARNING: GC/ECD instruments and other equipment may have heated zones which can cause severe burns if contacted. Prior to working on any equipment containing a heated source, the equipment will be cooled to a safe temperature.

WARNING: The Agilent Micro Electron Capture Detector (μECD) contains a cell plated with ^{63}Ni, a radioactive isotope, which may be hazardous if ingested or inhaled. Cap the detector inlet and outlet fittings when the detector is not in use. Never introduce corrosive chemicals or any material that may react with ^{63}Ni into the detector, and do not use solvents to clean it. Vent the detector exhaust outside the laboratory.

If the detector needs servicing, turn off the main power, allow the detector to cool to room temperature, cap the inlet and exhaust openings, and return it to the manufacturer. Do not attempt to open the detector.

See Agilent's web site, http://www.chem.agilent.com/library/usermanuals/public/g3430-90013.pdf, for further information on the micro electron capture detectors.

Micro ECD Radiation safety is presented in the PHILIS-2 Laboratory Chemical Hygiene Plan, Chapter 15, and includes requirements for contamination biannual wipe testing to verify no leakage of the source.

WARNING: GC/ECD instruments have high voltage areas. Instrument power must be turned off and the instrument unplugged prior to performing maintenance on any electrical component. The power source of the equipment will be lock-out and/or a tag placed at or near the source to prevent inadvertent operation during a maintenance function.

WARNING: The toxicity and/or carcinogenicity of the reagents and analytes used in this method have not been precisely defined; therefore, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

WARNING: All preparation of standards and sample preparation are required to be conducted in an operating fume hood. Acetone and hexane are highly flammable and require handling caution near any heated source and required storage only in a flammable storage cabinet. Methylene chloride is a highly volatile chemical that poses a significant inhalation hazard if spilled. Methylene chloride is very corrosive to the skin and eyes, therefore extreme care is needed and strict hygiene practices.

5.3 A Safety Data Sheet (SDS) and PHILIS-2 Chemical Hazard Summary sheet are available for each analyte and reagent used in the mobile laboratory to all employees and are required reading/understanding prior to working with the chemical. Special safety precautions for sample preparation (e.g., solvent extraction equipment and methods) are provided in the sample preparation SOPs

6.0 Equipment and Supplies

This section does not list common laboratory glassware (e.g., beakers and disposable pipettes).

6.1 Glassware

6.1.1 Small glass vials (1-mL, 2-mL, and 5-mL sizes) are used for storage of sample extracts, calibration standards and stock standards.

6.1.2 Standards and spiking solutions are stored in 10-mL vials.

6.1.3 Volumetric flasks, Class A - 2-mL, 5-mL and 10-mL, for preparation of standards.

6.2 Solvents

Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane) and the solvents must be exchanged to hexane prior to analysis. Therefore, *n*-hexane will be required in this procedure. All solvents should be pesticide grade in quality or equivalent.

Original containers of reagents shall be labeled with expiration dates in accordance with the OSHA Hazard Communication Program. All original containers and containers of prepared reagents must bear a name, preparation date and must be entered into LIMS.

The following solvents may be necessary for the preparation of standards. All solvent lots must be pesticide grade in quality or equivalent and should be determined to be free of phthalates.

6.2.1 Acetone, $(CH_3)_2CO$—Pesticide grade or equivalent

6.2.2 Toluene, $C_6H_5CH_3$—Pesticide grade or equivalent

6.2.3 Hexane, C_6H_{14}—Pesticide grade or equivalent

6.3 Reagent Water

6.3.1 Water free of PCB's and is used for all QC samples and blanks. This water may be purchased bottled water or water generated from a deionizing source. Other water such as tap water may be used provided there are no positive or negative interferences.

6.4 Reagent soil

6.4.1 Ottawa sand or other material free of PCB's and is used for all QC samples and blanks.

6.5 Gases

6.5.1 Carrier gas: Helium, ultra-high purity (UHP) grade, 99.999%, or greater such as Research Grade, 99.9999%.

6.5.2 Make up gas: Nitrogen, ultra-high purity (UHP) grade. P-5 or P-10 gases may also be used.

6.6 Syringes

6.6.1 Gas-tight micro syringes - various sizes for transferring the concentrated extracts, diluting samples, adding internal standards to extracts, and preparing calibration standards.

6.6.2 Autosampler syringe: 10 µL Gerstel syringe, or equivalent. A 5-µL syringe may be used as an alternate

6.7 Instrumentation

6.7.1 Gas chromatograph: an analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, gases. This method requires dual GC columns for identification, quantitation and confirmational analysis; therefore, the gas chromatograph must be equipped with two separate electron capture detectors (ECDs).

6.7.2 GC Columns used at the Edison facility:

6.7.2.1 Primary column: Rtx®-CLPesticides fused-silica column, 30 m x 0.25 mm ID, with a film thickness of 0.25 µm, Restek catalogue number 11123.

6.7.2.2 Secondary column: Rtx®-CLPesticides2 fused-silica column, 30 m x 0.25 mm ID, with a film thickness of 0.20 µm, Restek catalogue number 11323.

6.7.2.3 Alternate columns may be used if they provide acceptable performance.

6.7.3 Column rinsing kit -- Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent

6.7.4 Autosampler: Gerstel MPS-2 rail system or equivalent.

6.7.5 Data System: Agilent ChemStation software for data acquisition and processing or equivalent.

6.8 Analytical balance, capable of weighing to 0.0001 g.

6.9 Top loading balance, capable of weighing to 0.01 g.

7.0 Reagents and Standards

7.1 Reagents

See Section 6 for a listing of the reagents, solvents and gases needed for this method.

7.2 Standards

The following sections (7.2.1 to 7.2.6) describe the preparation of stock, intermediate, spiking and calibration standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application.

Stock, intermediate, calibration, surrogate and spiking standards must be stored at < 6°C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. All Standards are to be replaced twelve months after opening, or if the manufacturer's expiration date comes first, or in-house QC cannot be met. Unopened standards must be replaced as per the manufacturer's expiration date.

The standards below are examples and may be purchased from another vendor provided they are equivalent.

7.2.1 Stock Standards

The recommended stock standards for this method are:

7.2.1.1 Aroclor 1016/1260 Mix, 1000 µg/mL in hexane, Restek (Bellefonte, PA, USA) catalogue number 32039.

7.2.1.2 Pesticide Surrogate Mix (TCMX and DCB), 200 µg/mL in acetone, Restek catalogue number 32457.

7.2.1.3 DDT Analog mix, Supelco mix of DDT(Catalog # 40124), DDD (Catalog # 40092), and DDE (Catalog # 40091) at 5000 µg/mL in methanol, or equivalent. The analog mix used for retention time checks is made by diluting the stocks to a mid-level concentration (e.g. 500 µg/L) in acetone.

7.2.2 Second source standards:

7.2.2.1 Aroclor 1016, 1000 µg/mL, AccuStandard catalog number C-216S-H-10x.

7.2.2.2 Aroclor 1260, 1000 µg/mL, AccuStandard catalog number C-260S-H-10x.

7.2.3 Stocks of other Aroclors listed in Section 1.1 may be purchased at 1000 µg/mL from Restek or other reputable vendor.

7.2.3.1 Commercially prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.2.3.2 Stock standards may also be prepared from pure standard materials.

7.2.3.3 If pure standard materials are to be used, prepare stock standard solutions of Aroclors by accurately weighing 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10- mL volumetric flask. Stock standards of the surrogates may be prepared in a similar manner except acetone is used as the solvent. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution.

7.2.4 Calibration standards for Aroclors

7.2.4.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other seven Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Aroclors. A minimum of six concentrations is required for a linear regression or a quadratic calibration curve. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample.

7.2.4.2 Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock or intermediate standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

7.2.4.3 Single standards of each of the other seven Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in this section have been used to demonstrate the linearity of the detector, the single standards of the remaining seven Aroclors (Section 1.1) also may be used to determine the calibration factor for each Aroclor when a linear calibration model through the origin is chosen (see Sections 10 and 12). Prepare a standard for each of the other Aroclors. The concentrations should generally correspond to the mid-point of the linear range of the detector, but lower concentrations may be employed at the discretion of the analyst based on project requirements.

7.2.4.4 The examples below are recommended procedures for preparing calibration standards of Aroclors 1016 and 1260.

Intermediate Stock Solution – Dilute 200 µL of the Aroclor 1016/1260 stock at 1000 µg/mL plus 200 µL of the surrogate stock at 200 µg/mL to 2.00 mL in a volumetric flask with hexane. The concentration of the Aroclors in the intermediate solution will be 100 µg/mL, and the concentration of each surrogate will be 20 µg/mL.

Calibration Solutions – Dilute 5, 10, 25, 50, 75 100, or 300 µL of the intermediate stock to 10.0 mL with hexane in seven individual volumetric flasks. The final concentrations of Aroclor 1016 and Aroclor 1260 will be 50, 100, 250, 500, 750, 1000, and 3000 µg/L, and the surrogate concentrations in these standards will be 10, 20, 50, 100, 150, 200, and 600 µg/L, respectively.

Continuing Calibration Verification (CCV) Solution – The recommended CCV solution is prepared at a concentration near the middle of the calibration range established by the initial calibration. For this method, the recommended CCV has a concentration of 500 µg/L and is prepared as described above.

7.2.5 Laboratory Control Spiking Solutions are prepared at 500 µg/L. The LCS shall include all compounds of interest. The LCS is prepared using the same source as the instrument calibration or from a source different than used for the instrument calibration. Other levels could be used as long as the resulting concentration of the LCS is near the midpoint of the calibration curve. Spiking amounts are given in the sample preparation SOPs.

7.2.6 Surrogate Spiking Solution

7.2.6.1 The recommended surrogates of this method are tetrachloro-*m*-xylene (TCMX, [877-09-8]) and decachlorobiphenyl (DCB, [2051-24-3]). Other surrogates may be used, provided that the analyst can demonstrate and document performance appropriate for the data quality needs of the particular application.

7.2.6.2 Recommended preparation of surrogate spiking solutions:

7.2.6.3 For water samples, prepare a solution at 2.0 µg/mL in acetone by diluting 50 µL of the stock at 200 µg/mL (Sec. 7.2.1.2) to 5.0 mL.

7.2.6.4 For soil or solid samples, prepare a solution at 20.0 µg/mL in acetone by diluting 500 µL of the stock at 200 µg/mL (Sec. 7.2.1.2) to 5.0 mL.

7.2.7 DDT analog standard -- Used to determine if the commonly found DDT analogs (DDT, DDE, and DDD) elute at the same retention times as any of the target analytes (congeners or Aroclors). A single standard containing all three compounds should be sufficient. The concentration of the standard is left to the judgment of the analyst, but it is recommended to prepare it a mid-level concentration (e.g., 50 – 100 µg/mL) in acetone.

7.2.8 Preparation of the Instrument Blank

An instrument blank contains the surrogates in hexane at a concentration at or near the mid-point of the calibration range. A recommended concentration for this method would be 100 µg/L of each surrogate.

7.2.9 Matrix Spike Solution is the same as the Laboratory Control Spiking Solution.

7.2.10 Other standards (e.g., other Aroclors) and other calibration approaches (e.g., non-linear calibration for individual Aroclors) may be employed to meet project needs. When the nature of the PCB contamination is already known, use standards of those particular Aroclors. See Method 8000D for information on non-linear calibration approaches.

8.0 Sample Collection, Preservation, and Storage

8.1 PHILIS-2 personnel do not take field samples. Samples are collected by field crews in 1 L amber bottles or 8-oz jars and are put on ice to maintain a temperature of ≤ 6°C and shipped to the laboratory. See SOPs for sample receipt, login and storage procedures (CSS SOPs L-P-001, L-P-002 and L-P-003).

8.2 Samples received on the collection day shall be considered acceptable if there is evidence that the chilling process has begun such as arrival on ice. In such cases, sample temperatures that are in excess of 6°C upon receipt are acceptable.

8.3 Samples are maintained at the temperature range from 0°C - 6°C.

8.4 For PCBs, there is no holding time limit between sample collection and extraction per SW846. It is highly recommended that 7 days to extraction is used for the aqueous samples and 14 days to extraction for solid samples. A documented QAP will override the use of 7 and 14 day holding times.

8.5 Extracts should be stored under refrigeration in the dark or stored in amber glass and should be analyzed within 40 days of extraction.

9.0 Quality Control

QC requirements include the initial demonstration of capability and ongoing QC requirements that must be met when analyzing samples.

Quality control procedures are necessary to evaluate the GC system operation, and they include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

9.1 Initial Demonstration of Capability (DOC)

An initial Demonstration of Capability (DOC) is an evaluation that must be successfully performed by an analyst prior to analyzing any field samples. The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained, whenever major method modifications are made, when significant changes in instrumentation are made, or when one year has passed since the last DOC.

A DOC study must start with an acceptable instrument calibration following the procedure outlined in Section 10 of this SOP. After a successful IC and SCV, a MB is then analyzed to demonstrate that the background contamination is low enough to not interfere with analytes. A DOC study may be analyzed in one analytical batch or in separate batches and is comprised of the analysis of the following:

9.1.1 An initial calibration (IC, Section 9.2)

9.1.2 An initial calibration verification (SCV, Section 9.3)

9.1.3 A method blank (MB, Section 9.4)

9.1.4 A CCV (A CCV is analyzed at the start of a sequence if an IC is not performed and after a maximum of 20 samples). (See Section 9.6.)

9.1.5 A Precision and Accuracy Study (Section 9.8)

9.1.6 An MDL Study (Section 9.9)

9.1.7 An analyst DOC consists of analyzing a method blank and a precision and accuracy study.

9.2 Initial Calibration (IC)

9.2.1 The procedure for performing an initial calibration is given in Section 10.

9.2.2 The RSD of the calibration factors must be ≤ 20% for each selected Aroclor peak and both surrogates.

9.2.3 If the RSD for a compound in the initial calibration is > 20%, then the calibration points may be fit to a linear or a nonlinear curve, such as a second-order polynomial. A curve fit should not be employed in lieu of the average CF to compensate for instrumentation problems or needed maintenance.

9.2.4 Linear curve-fits may be used if there are five (5) or more ICAL levels. Quadratic (second-order) curve-fits may be used if there are 6 or more ICAL levels. The use of a weighted linear regression is recommended to improve accuracy of quantitation at the low end of the curve. Curve-fits can be used if it is determined that the curve will generate accurate results across the calibration range. If a curve-fit is used, a re-quantitation of the low point of the ICAL against the ICAL must show recovery within 30% of the anticipated value.

9.2.5 If a linear curve-fit is used, the coefficient of determination (R_2) must be ≥ 0.990. For quadratic curve-fits, the intercept and degree of curvature should be examined to be sure that the results will be reliable throughout the working range and the coefficient of determination must be ≥ 0.990. Quadratic curve-fits should not be used to compensate for detector saturation or to avoid proper instrument maintenance.

9.3 Initial Calibration Verification (SCV)

Acceptance criteria for SCV: The value determined from the second source check should be within 30% of the expected concentration.

9.4 Method Blank (MB)

9.4.1 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank.

9.4.2 For aqueous samples, the method blank is reagent water, and for soil samples it is Ottawa sand or an analyte-free sand. The method blank is free of the analytes of interest and is spiked with the surrogates at 100 µg/L. At least one method blank must be prepared with every preparation batch.

9.4.3 Acceptance Criteria: The result for the method blank must be less than the RL or less than 10% of the analyte concentration found in the associated samples, whichever is higher, to report definitive results.

9.5 Instrument Blank (IB)

Instruments must be evaluated for contamination during every sequence. This can be accomplished by analysis of a MB. If a MB is unavailable, an instrument blank must be analyzed. An instrument blank consists of hexane with the surrogate standards added at the mid-point level, e.g., 100 µg/L if the levels in Table 2 are used. It is evaluated the same way as a method blank. No detectable Aroclors may be present in an instrument blank.

9.6 Continuing Calibration Verification (CCV)

9.6.1 Verify continuing calibration verification (CCV) prior to conducting any sample analyses. A CCV must also be injected once every 20 samples (after every 10 samples is recommended to minimize the number of samples requiring reinjection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard is normally a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence. If the requirement is for a specific Aroclor, then the CCV would be the same as the Aroclor used in the initial calibration. The CCV should be ≤ 50% of the highest standard.

9.6.2 The calibration factor (CFv) for each analyte and surrogate calculated from the CCV must not exceed a difference of more than ±20% when compared to the mean calibration factor from the initial calibration curve. %Drift must also be less than 20% for linear or quadratic methods of calibration.

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

9.7 Laboratory Control Sample (LCS)

9.7.1 An LCS is required in all preparation batches. In a DOC study (Sections 12.1 and 12.8) at least four LCSs are required.

9.7.2 The LCS is prepared using reagent water for aqueous samples or analyte-free sand for soil samples. A laboratory control sample is prepared and analyzed with every batch of samples. The compounds must be spiked at a concentration that falls within the working range of the calibration.

9.7.3 A laboratory control sample (LCS) must be included with each preparation batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000D for information on developing acceptance criteria for the LCS.

9.7.4 Acceptance Criteria: All analytes must be within the control limits to report definitive data. Recommended control limits are in Table 6. Control limits are reviewed and revised on a semi-annual basis.

9.8 Precision and Accuracy Study

9.8.1 Calculate the average recovery and the standard deviation of the recoveries of the analytes in each of the four QC reference samples. Refer to Method 8000D for procedures for evaluating method performance.

9.8.2 Recovery limits will be established when adequate data are available. The acceptable range will be set using the control charts and updated every six months.

9.8.3 The Precision and Accuracy samples must contain PCBs as Aroclors at a concentration near the middle of the calibration range. An extract concentration of 500 µg/L for water and solid samples is recommended. A 1-mL volume of this concentrate spiked into 100 mL of reagent water will result in a sample concentration of 10-50 µg/L. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the QC reference sample. Other concentrations may be used, as appropriate for the intended application.

9.8.4 Method precision and accuracy are demonstrated by analyzing four (4) replicate LCSs as described above. Precision and accuracy are calculated.

9.8.5 Acceptable precision is RSD $\leq$ 30%. Once adequate points are available, laboratory limits will be established.

9.8.6 Once adequate points are available, laboratory acceptance limits will be established.

9.9 MDL Procedure

MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL and seven blank replicates. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

MDL's are determined using a 1016 and 1260 Aroclor standard. Since these two Aroclors contain many of the congeners of other Aroclors determined by this method, MDL's may be calculated by selecting peaks in each Aroclor and recalculating the specific MDL. MDL's for projects where a specific Aroclor is targeted, will be determined as per the procedure in 40 CFR Part 136, Appendix B, Revision 2.

9.9.1 Initial MDLs

9.9.1.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped and analyzed over three separate days. The MDL should be spiked 1 to 5 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.9.1.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one-sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL studies are repeated annually and verified each time they are prepared. MDL results are stored in Element each time they are calculated. This calculation must be performed separately for the spikes and blanks. If all seven blanks are non-detect, then the spiked MDL is used. If not all blanks are non-detect the use the largest value at the MDL blank. If all seven MDL blanks are detects, calculate the MDL as above and add the average of the results. The larger of the two values will be used as the MDL.

9.9.2 Ongoing MDL Data Collection

9.9.2.1 Ongoing MDL's are determined by preparing and analyzing two spiked standards at 1-5 times the estimated MDL and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch, but is not required. If the instruments are being used regularly, the MDL spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used.

9.9.2.2 At least once per year re-evaluate the MDL by, calculating as above in 9.9.1.2. Use the larger of the spiked determinations and blank determinations for the MDL value.

9.9.2.3 If samples are not analyzed during a quarter, ongoing MDLs do not have to be analyzed that month.

9.9.3 Ongoing MDL Annual Verification

9.9.3.1 At least once every thirteen months, re-calculate the MDL spike and MDL blank from the collected spiked samples and method blank results.

9.9.4 Include data generated within the last twenty four months, but only data with the same spiking level. Only documented instances of gross failures (instrument malfunctions, mislabeled samples, cracked vials, etc.) may be excluded from the calculations.

9.10 Matrix Spikes (MS/MSD)

9.10.1 The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures as those used on actual samples.

9.10.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking.

9.10.3 The matrix spike is a second aliquot of one of the samples in the batch, and the matrix spike duplicate is a third aliquot of the same sample. The MS/MSD are spiked with the same analytes and concentration as the LCS. The MS and MSD samples are prepared with every batch. If adequate sample is not available for an MS, duplicate, or MSD, then run an LCSD, which will demonstrate precision.

9.10.4 Acceptance Criteria: The percent recovery must be within the control limits listed in Table 6 until in-house limits are established. The RPD for the pair must be less than or equal to the control limit in Table 6.

9.11 Surrogates - Surrogates are added to monitor the performance of the extraction, cleanup, and matrix of each sample, including QC samples. Because GC/ECD analysis is subject to interferences, two surrogates are to be used. Both surrogates should meet acceptance criteria. If the result(s) is not within acceptance criteria, a thorough evaluation of the data should be performed evaluating peak interference, unstable baseline, instrument parameters, etc. Surrogates outside limits must be flagged and explained in the case narrative. Data reported with surrogate recoveries outside the acceptance criteria will be flagged and addressed in the case narrative.

9.11.1 Control limits are determined for surrogates, laboratory control samples, matrix spike samples and precision and accuracy. Limits can be calculated when 15 – 20 data points are available and monitored every 20 – 30 data points thereafter. They should be evaluated at least every 6 months. The recovery limits are the mean recovery ±3 standard deviations for surrogates, MS, and LCS. Precision limits for the MS/MSD or LCS/LCSD pair are the absolute value of the mean relative percent difference (RPD) ±3 standard deviations.

9.11.2 These limits do not apply to dilutions, but the surrogate and matrix spike recoveries will be reported unless the dilution is 4x or more.

9.11.3 All surrogates, LCS, and MS recoveries (except for dilutions) must be entered into LIMS (Promium Element) so that historical control limits can be generated. For multiple dilutions reported from the same extract, surrogates will be reported for all dilutions of less than 4x.

9.11.4 Each calibration standard, sample, MB, and QC sample is spiked with the surrogate standards. The surrogates must be spiked within the working concentration range of the ICAL. The surrogates are listed in Table 6. After analysis, evaluate the surrogate(s) to determine acceptability. Then, based on the evaluation, accept the data, qualify the data, or if adequate sample is available, re-extract and reanalyze the sample.

9.11.5 If a sample has a surrogate failure and it has an associated MS/MSD, and the surrogate recoveries in the pair also fail, then the sample and the MS/MSD do not require re-extraction. This indicates matrix interference.

9.11.6 If the sample is re-extracted and the surrogates in the re-analysis are acceptable, the re-analysis should be reported. This indicates the failure was within the control of the analyst. However, if the sample is re-extracted outside of the hold time, both sets of results should be reported.

9.11.7 If the re-extraction confirms the surrogate failure, the original results should be reported and the matrix interference should be documented in the report.

9.12 Confirmation Column RPD—% RPD between the reporting column and the confirmation column must be ≤ 40%. If the RPD is more than 40%, then the chromatograms should be evaluated for interferences, baseline stability, etc. If there is not an obvious problem, then the data must be flagged and addressed in the case narrative. The lower result from the two columns is reported.

9.13 Data Assessment

Instrument generated data goes through a series of reviews prior to being submitted to the client. First the analyst reviews the data to ensure method and client requirements are met. Then the instrument data goes through a peer review covering the same items as the analyst. Both reviews are documented on Form QA-020C, provided as Figure 1. The Quality Assurance Manager also reviews a minimum of 10% of data to evaluate the QA process.

9.13.1 Analytical data generated by the instrument software is reviewed and evaluated by the analyst as follows: instrument calibration, calibration verifications, surrogate recoveries, All QC measures are evaluated and the results documented on the separate forms:

9.13.1.1 Generating the average calibration factors and percent relative standard deviations.

9.13.1.2 Generating a report for percent recoveries for the surrogates (e.g., a QA check report using the Agilent ChemStation software).

9.13.1.3 Calculating analyte percent recoveries CCV, LCS, SCV, MS, and RPD for MSD.

9.13.2 In order for the analytical data to be acceptable, the calibration standards and quality control measures must meet the criteria listed in this SOP.

9.13.3 All false positives are deleted ("Q-Deleted" in Agilent's ChemStation software). All positively identified target analytes are reported to LIMS.

9.13.3.1 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples. Please see the Manual Integration SOP.

9.13.3.2 Anytime the analyst alters the instrument generated quantitation report (e.g., manual integration), the hard copies of both reports (original and corrected) must be retained.

9.13.3.3 Discrepancies in the analytical run are described in "QC Summary form" and discussed with the Lead Chemist.

9.13.3.4 Reviewed data is entered into LIMS, hard copies of the LIMS report is printed and compared to the original data.

9.13.4 All records derived from the analytical process are assembled in the analytical sequence data packages. The content and order of these packages and client reports are documented in SOP L-D-102.

9.13.5 Sequence data packages are filed in the PHILIS-2 document storage area at each location. Electronic data, including reports are maintained on servers in multiple locations.

9.13.6 Corrective Actions for Out of Control

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

9.13.7 When an instrument calibration fails to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

9.13.8 Corrective actions for a failing CCV: If the calibration does not meet the ±20% limit on the basis of each compound, check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±20%, then a new initial calibration must be prepared. See Sec. 11.6.6 for a discussion on the effects of a failing calibration verification standard on sample results.

9.13.9 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

9.13.10 The analyst shall report to the Lead Chemist and indicate of the "QC Summary form" any out control event. Such events include:

9.13.10.1 Damage to the sample.

9.13.10.2 Holding time exceeded.

9.13.10.3 Inadequate sample preservation.

9.13.10.4 Sample results exceeds the Agency's action limit

9.13.10.5 Samples do not reflect historical data.

9.13.10.6 Upward trending or sample results approaching interval warning limits.

9.13.11 The Lead Chemist will implement the corrective action plan described in the PHILIS-2 corrective action plan document.

9.13.12 Corrective Action for a Contaminated MB: If a compound fails to meet the criteria in Section 12.4, the lead chemist will be informed. In general, batch samples, other than those that are non-detect for the contaminant compounds will be re-extracted. However, if the analyte in the method blank was not detected in any of the associated samples, the data can still be reported, but flagged accordingly.

9.13.13 MS/MSD Corrective Action: If the recovery or RPD of an analyte is outside of its control limits, or if an RPD fails, then a corrective action must be performed. Typically, if the recoveries of the MS/MSD are similar but not within control limits and the recoveries of the LCS are within control limits, then the analysis can continue. This is documented as matrix interference.

9.13.13.1 If there are recovery failures in the MS/MSD and the LCS, then the batch must be re-extracted and/or re-analyzed. Or, all associated data must be qualified and a reason must be included in the data package detailing the batch was not re-extracted and re-analyzed.

9.13.13.2 If re-extraction is not possible due to limited sample volume, then a duplicate LCS (LCSD) must be run with the re-extraction batch. The RPD of the LCS/LCSD must be less than or equal to the established control limit.

9.13.14 LCS Corrective Action: If any analyte in the LCS is outside the established control limits, a corrective action must be performed.

9.13.14.1 If the batch is not re-extracted or re-analyzed, the reasons for accepting the batch must be clearly presented in the report. An example of acceptable reasons for this might be that the MS/MSD are acceptable and sample surrogate recoveries are within control limits, showing that the problem was just on the LCS. This is also applicable if the analyte that failed is not a target analyte for the project, or if the analyte recovered above the control limit, but was not detected in the associated samples.

9.13.14.2 If re-extraction and re-analysis of the batch are not possible due to limited sample volume, the LCS is reported, all associated samples are flagged accordingly, and the appropriate comments are made in the report.

9.13.15 When system performance does not meet the established QC requirements, corrective action is required, and may include one instrument maintenance

9.13.16 Contingencies for handling Out of Control data

See the QAPP under which the samples were analyzed for guidance. The Lead Chemist will implement the corrective actions.

9.14 Relative Error

If the calibration curve is a Response Factor curve, then the Relative Error is the Average Response Factor.

If the calibration curve is Linear Regression or Quadratic Regression, then run the lowest and midpoint calibration points against the curve and calculate the % difference from the true value. These are the Relative Errors.

10.0 Calibration and Standardization

Instruments are calibrated with an ICAL of at least five levels, and confirmed after the analysis of no more than 20 samples (10 recommended) with a continuing calibration standard. Recommended instrument conditions are listed in Table 2.

10.1 Initial Calibration (ICAL)

A minimum five-point calibration curve is prepared for establishing average calibration factors or linear regression curve fitting. Six calibration points are required for quadratic (second-order) curve fits. The low point of the calibration curve must be equal to or less than the reporting limit. The high standard defines the calibration range. See Section 10 preparation of the ICAL levels.

10.1.1 Include a calibration standard after each group of 20 samples (it is recommended that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. Thus, injections of method blank extracts, matrix spike samples, and other non-standards are counted in the total number of samples. Solvent blanks, injected as a check on cross-contamination, need not be counted in the total. The calibration factors for the calibration must be within ±20% of the initial calibration (see Sec. 11.6.2). When this continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

10.1.2 When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts, described below.

10.1.2.1 As noted in Sec. 3.0, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other

seven Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial multi-point calibration is performed using the mixture of Aroclors 1016 and 1260.

10.1.2.2 Standards of the other seven Aroclors are necessary for pattern recognition. When employing the traditional model of a linear calibration through the origin, these standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Sec. 7.2.4.1 has been used to describe the detector response. The standards for these seven Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards in Sec. 7.2.4.1.

10.1.3 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards (from either Sec. 7.2.4.1 or 7.2.4.2) using the equation below.

$$CF = \frac{Peak\ Area\ in\ the\ Standard}{Total\ Mass\ of\ the\ Standard\ Injected\ (in\ ng)}$$

Using the equation above, a calibration factor will be determined for each characteristic peak, using the total mass of the Aroclor injected. These individual calibration factors are used to quantitate sample results by applying the factor for each individual peak to the area of that peak, as described in Sec. 11.9.

For a five-point calibration, five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture, e.g., there will be at least 25 separate calibration factors for the mixture. The single standard for each of the other Aroclors (see Sec. 7.2.4.2) will generate at least three calibration factors, one for each selected peak.

If a non-linear calibration model is employed, as described in Method 8000D, then additional standards containing each Aroclor of interest will be employed, with a corresponding increase in the total number of calibration factors.

The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration, if a linear calibration model is used. This involves the calculation of the mean response or calibration factor, the standard deviation, and the relative standard deviation (RSD) for each Aroclor peak.

When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the linear calibration models must be applied to the other seven Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors (see Sec. 11.4.3.3), use the calibration factors from those standards to evaluate linearity.

In general, non-linear calibrations also will consider each characteristic Aroclor peak separately.

10.1.4 A minimum five-point calibration curve is prepared. This is valid for average calibration factors or linear regression curve fitting. A minimum of six calibration points is required for quadratic curve fits. The low point of the calibration curve must be at or below the reporting limit. The high standard defines the range of the calibration.

10.1.5 In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a multi-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern and linear calibration is employed) and not use the 1016/1260 mixture described in Sec. 10.2.4.1 or the pattern recognition standards described in 10.2.4.2. When non-linear calibration models are employed, more than five standards of each Aroclor of interest will be needed to adequately describe the detector response (see Method 8000D).

10.1.6 Rejection of Calibration Points

10.1.6.1 It is not generally acceptable to remove points from a calibration. Typically, instrument maintenance and the accuracy of the calibration standards should be examined if the calibration acceptance criteria are not met.

10.1.6.2 If no problems are found, then a point can be rejected as long as it meets the following criteria:

A. The rejected point is the highest or lowest point in the ICAL.

B. The lowest remaining calibration point is still at or below the reporting limit. If the calibration point is higher, then the reporting limit must be raised.

C. The highest remaining calibration point defines the upper concentration of the working range, and all samples above this concentration must be diluted and re-analyzed.

D. The calibration must still have the minimum number of calibration levels required by the method. [Five levels for average response

factors and linear curve-fits, six levels for quadratic (second-order) curve-fits].

10.1.6.3 Interior calibration points may be rejected if there is an obvious reason such as poor injection, no surrogates added, standard made wrong or wrong standard. All analytes must be removed in these cases.

10.1.7 Weighting of Calibration Data Points.

In a linear regression curve-fit, the lower points of the ICAL have a significant bias over the higher points in determining the generated curve. This is not seen in quadratic regression. However, in environmental analysis, accuracy at the low end is very important. For this reason, it is preferred that the weighting of the lower concentrations is increased. 1/Concentration^2 or 1/Concentration weighting will improve accuracy at the low end of the ICAL and should be used for curve-fits. All compounds using linear or quadratic regression must have the low point quantitated against the curve and the resulting value must be within 30% of the true concentration.

Quantitation is performed using the calibration curve or average calibration factor from the initial curve, not the continuing calibration.

10.2 Initial Calibration Verification (SCV)

An initial calibration verification (SCV) made from a different source than the ICAL (an alternate vendor or a unique lot from the same vendor) must be analyzed immediately after the calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those Aroclors that fail the second source standard initial calibration verification. However, analyses may continue for those Aroclors that fail the criteria with an understanding that these results could be used for screening purposes and would be considered estimated values.

10.3 Continuing Calibration Verification (CCV)

10.3.1 The continuing calibration verification (CCV) is analyzed before and after each 20 samples or less, when an initial calibration is not analyzed. A CCV must bracket all samples to be reported. The CCV standard must contain the 1016 and 1260 Aroclors and surrogates to be reported or contain the Aroclor of interest and surrogates. The level for the CCV should be near the middle of the ICAL.

10.3.2 The percent difference/drift for each Aroclor must be less than or equal to 20%. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values. If the CCV fails, the system should be evaluated for obvious problems, correct method used, or minor maintenance. After performing these evaluations, etc. a second CCV may be injected. If this CCV also fails, then a new calibration curve must be performed.

10.3.3 Sample analysis may begin if the CCV passes the above criteria. If the CCV fails, see Section 10.3.2.

11.0 Procedure

11.1 Sample Extraction

11.1.1 Batch up to 20 samples for extraction.

11.1.2 At least one MB and one LCS are required in each extraction batch.

11.1.3 For samples to be analyzed as MS/MSD, the client must provide enough volume for a parent sample and the MS/MSD. If performing a 1-L extraction, this means the client must provide 3L of sample. If an MS/MSD pair cannot be prepared due to insufficient sample amounts, then an LCS/LCSD (LCS duplicate) pair must be prepared.

11.1.4 For the MS/MSD samples, transfer the samples into their appropriately marked containers (1-L bottles, 40-mL VOA vials, or PSE metal tubes). Spike the MS/MSD with the appropriate amount of surrogates and spikes.

11.1.5 See specific extraction and cleanup SOPs for the preparation procedures.

11.2 Sample Preparation

11.2.1 Remove samples from the laboratory refrigerator.

11.2.2 Verify that the samples have been logged into LIMS, and are within holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.

11.3 Analysis of Standards and Calibration Procedure

11.3.1 Allow all standards and sample extracts to warm to room temperature prior to injection. Calibrate the instrument as described in Section 10.

11.3.2 Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

11.3.3 To start an analytical batch, analyze a set of IC standards or a CCV (Section 10) using the conditions given in Section 10.3.2.

11.3.4 Dual-column analysis conditions

11.3.4.1 A 1-µL injection of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest. All calibration standards, quality control standards, and samples must be injected at the same volume.

11.3.4.2 GC Parameters

A. Table 2 lists suggested GC operating conditions for the analysis of PCBs as Aroclors for the dual-column analysis. Use the conditions in these tables as guidance and establish the GC temperature program and flow rate necessary to separate the analytes of interest.

B. When determining PCBs as Aroclors, chromatographic conditions should be adjusted to give adequate separation of the characteristic peaks in each Aroclor.

C. Tables 4 and 5 summarize example retention times of 5 Aroclor peaks determined during dual-column analysis using the operating conditions listed in Table 2. These retention times are provided as guidance as to what may be achieved using the GC columns, temperature programs, and flow rates described in this method.

D. Once established, the same operating conditions must be used for the analysis of samples and standards.

11.3.5 In ChemStation (or Gerstel software), load the sequence from the previous run and enter in the sequence information for the day. A typical sequence will have one or two rinses, the CCV, an instrument blank, the QC from the batch, then the samples. If the samples being analyzed are suspicious or possibly high in non-target analytes, running hexane blanks during the sequence will help maintain the quality of your instrument.

11.3.6 Record the peak area (or height) for each congener or each characteristic Aroclor peak to be used for quantitation.

11.3.7 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

11.3.8 The laboratory must determine retention times and retention time windows for their specific application of the method. Absolute retention times are generally used for compound identification. When absolute retention times are used, retention time windows are crucial to the identification of target compounds and should be established by one of the approaches described in Method 8000D.

Retention Time windows are set by injecting a calibration standard. Using ChemStation, evaluate the chromatogram and set the retention times for the 3-5 peaks that identify the aroclor and you want to use for the calibration. Evaluate the peaks in the calibration standards to make sure the correct peaks are being chosen. Save the calibration that includes the proper retention times.

11.3.9 When conducting either Aroclor or congener analysis, it is important to determine that common single-component pesticides such as DDT, DDD, and DDE do not elute at the same retention times as the target congeners. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples. Therefore, in conjunction with determining the retention time windows of the congeners, the analyst should analyze a standard containing the DDT analogs. This standard need only be analyzed when the retention time windows are determined. It is not considered part of the routine initial calibration or calibration verification steps in the method. There is also no performance criteria associated with the analysis of this standard.

11.3.10 If Aroclor analysis is performed and any of the DDT analogs elute at the same retention time as an Aroclor peak that was chosen for use in quantitation (see Sec. 11.4.6), then the analyst must either adjust the GC conditions to achieve better resolution, or choose another peak that is characteristic of that Aroclor and does not correspond to a peak from a DDT analog.

11.4 Method Blank

11.4.1 Analyze a method blank immediately after the CCV or the last standard in the IC. If a MB is unavailable, then use an instrument blank (IB).

11.4.2 Evaluate the method blank according to the criteria given in Section 9.4. If the method blank passes the criteria, the analysis of samples may start.

11.5 Sample Analysis

11.5.1 Analyses of extracts are performed using an automated injection GC/ECD instrument with the same parameters as those used for the standards.

11.5.2 Inject 1µL of the extract using the sample injection technique as used for the standards.

11.6 Identification and Quantitation of Aroclors

11.6.1 The data system will determine the concentration of each analyte in the extract using calculations in Section 12. Quantitation is based on the initial calibration, not the continuing calibration verification.

11.6.2 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst. The minimum documentation required is a hard copy of the original data peak integration and a copy showing the manual integration with the analyst initials and date and explanation of the reason for the manual integration.

11.7 Dilutions

11.7.1 Guidance for Dilutions Due to Matrix

11.7.2 If the response for any compound exceeds the current calibration range, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initially diluted extract has no hits or hits below 20% of the calibration range and the matrix allows for an analysis at a lesser dilution, the sample should be re-analyzed at a dilution to bring the most abundant analyte above 50% of the calibration range.

11.7.3 Once surrogates are diluted to a level where accurate quantitation is not possible (i.e., at a dilution of 4 or greater) then surrogates should be reported as diluted out.

11.7.4 Reporting Dilutions

The least dilute sample with no target analytes above the calibration range will be reported. Other dilutions will be reported only at the client's request.

11.8 Percent Moisture of Solid Samples

Analytical results of soil or solid samples may be reported as a dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as a dry weight.

11.9 Confirmation

Tentative identification of an analyte occurs when the Aroclor peak pattern from a sample matches that found in the associated calibration or pattern standard. Confirmation is necessary using gas chromatography with a dissimilar column or a mass spectrometer.

11.9.1 When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. The lower quantitated result should be reported. If the RPD between the two results is greater than 40%, then the lower quantitated result must also be flagged.

11.9.2 GC/MS confirmation

GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection by GC/MS.

11.9.2.1 Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10 ng/µL in the final extract, while SIM may only be a concentration of 1 ng/µL.

11.9.2.2 The GC/MS must be calibrated for the target analytes when it is used for quantitative analysis. If GC/MS is used only for confirmation of the identification of the target analytes, then the analyst must demonstrate that those PCBs identified by GC/ECD can be confirmed by GC/MS. This demonstration may be accomplished by analyzing a single-point standard containing the analytes of interest at or below the concentrations reported in the GC/ECD analysis. When using SIM techniques, the ions and retention times should be characteristic of the Aroclors to be confirmed.

11.9.2.3 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the extract of the associated blank.

11.10 Identification of Aroclors

11.10.1 The qualitative identification of compounds determined by this method is based on retention time and visual comparison to a chromatograph of an Aroclor standard analyzed under the same conditions.

11.10.2 All congeners and surrogates are identified when the retention time (RT) of the Aroclor sample is within ± 0.03 minutes of the RT of the initial daily calibration standard or at the midpoint of the calibration curve if the sequence starts with an initial calibration. The ± 0.03 minutes is a default value and other times may be established by performing

a retention time window study. The Aroclor is confirmed on the second column with an RPD less than 40%, and visual comparison to the Aroclor standard. If there is an obvious interference causing the second column RPD to be greater than 40%, the problem can be documented in LIMS and explained in the Case Narrative. The data must be flagged.

11.10.3 Identification is hampered when sample components are not resolved chromatographically. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate adjustments of GC parameters may be necessary.

11.11 Sample cleanup

Chromatographic analysis or sample appearance may indicate the need for sample cleanup and or dilution. When sample cleanup is necessary (yellow or dark color extract), it is required that the Method Blank, the Blank Spike, the sample, and the sample associated QC must also go through the cleanup process. Cleanups available are L-P-108 (Acid Cleanup), L-P-109 (Sulfur Cleanup), and L-P-110 (Florisil Cleanup). Analyst experience will aid in determining which cleanups will be required.

12.0 Data Analysis and Calculations

12.1 The concentration of each Aroclor is calculated using Agilent ChemStation software using the multipoint average calibration factor method established in Section 13 of this SOP. Calibration factors and analyte concentrations are calculated by the equations below:

12.2 RL's are established by the lowest point in the calibration curve.

12.3 When PCBs are to be determined as Aroclors, external standard calibration is used.

12.4 The same GC operating conditions used for the initial calibration must be employed for the analysis of samples.

12.5 The calibration factor for each analyte calculated from the calibration verification standard (CFv) should not exceed a difference of more than 20% when compared to the mean calibration factor from the initial calibration curve. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.), consult Method 8000D for the specifics of calibration verification.

$$\%\, Difference = \frac{\overline{CF} - CF_V}{\overline{CF}}\ x\ 100$$

12.6 When internal standard calibration is used for PCB congeners, the calibration factor calculated from the calibration verification standard (RF_V) should not exceed a ±20% difference when compared to the mean calibration factor from the initial calibration. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.), consult Method 8000D for the specifics of calibration verification.

12.7 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Sec. 11.

12.8 Quantitative results are determined for each identified analyte (Aroclors or congeners), using an external calibration procedure. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

12.9 Each sample analysis employing external standard calibration must be bracketed with an acceptable initial calibration, calibration verification standard(s) (every 20 samples or less). The results from these bracketing standards must meet the calibration verification criteria in Sec. 11.

12.10 When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that met the QC criteria must be evaluated to prevent misquantitations and possible false negative results. Reinjection of the sample extracts may be required. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

12.11 However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >20%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, since the verification standard has demonstrated that the analyte would have been detected if it were present. In contrast, if an analyte above the QC limits was detected in a sample extract, then reinjection is necessary to ensure accurate quantitation.

12.12 If an analyte was not detected in the sample and the standard response is more than 20% below the initial calibration response, then reinjection is necessary. The purpose of this reinjection is to ensure that the analyte could be detected, if present, despite the change in the detector response, e.g., to protect against a false negative result.

12.13 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every

20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

12.14 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

12.15 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

12.16 If compound identification or quantitation is precluded due to interferences (e.g., broad, rounded peaks or ill-defined baselines are present), corrective action is warranted. Cleanup of the extract or replacement of the capillary column or detector may be necessary. The analyst may begin by rerunning the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

12.17 Qualitative identification

The identification of PCBs as Aroclors using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. See Method 8000D for information on the establishment of retention time windows.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Confirmation is necessary when the sample composition is not well characterized. See Method 8000D for information on confirmation of tentative identifications. See Sec. 14 of this procedure for information on the use of GC/MS as a confirmation technique.

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative result on both columns once the identification has been confirmed. See Method 8000D for a discussion of such a comparison and appropriate data reporting approaches.

12.17.1 When simultaneous analyses are performed from a single injection (the dual-column GC configuration described in Sec. 6.3), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, both columns must meet the calibration acceptance criteria, including RPD between columns. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

12.17.2 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:

12.17.2.1 The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.

12.17.2.2 The absence of major peaks representing any other Aroclor.

12.17.2.3 The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.).

This information should either be provided to the data user or maintained by the laboratory.

12.18 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

In a typical dual column analysis, the column giving the lower result will be reported.

12.18.1 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, 1254, 1262, and 1268. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

12.18.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. Non-linear calibration may result in different models for each selected peak. A concentration is determined using each of the characteristic peaks, using the individual calibration factor calculated for that peak, and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

12.18.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor concentrations, then it may be more appropriate to perform the analyses

using the PCB congener approach described in this method. If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

12.19 Calibration factor (CF):

$$CF = \frac{(A_x)}{mass\ of\ std}$$

where:
A_x =Area of the Arolcor or surrogate peak being measured.
Mass of std = Total mass of standard injected in nanograms

Average CF ($\overline{CF}$): $\overline{CF} = \frac{\sum_1^n CF}{n}$

where
n = number of initial calibration standards

12.20 Percent relative standard deviation (%RSD):

$$\%RSD = (^{S}/_{\overline{x}})100$$

where:
$\overline{x} = \overline{CF}$: $\overline{CF} = \frac{\sum_1^n CF}{n}$

where:
s = standard deviation: $= \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$

12.21 Sample concentration using CF:

$$\text{Conc.}\left(\frac{\mu g}{L}\right) = \frac{(A_x)(V_T)(D)}{(\overline{CF})(V_i)(V_o)}$$

where :

A_x =	peak area for compound being measured
V_T =	volume of extract
V_i =	injection volume (1 µL)
$\overline{CF}$ =	mean calibration factor for compound being measured
V_o =	volume of water extracted (mL)
D =	Dilution Factor

12.22 Percent recovery for CCV, SCV, LCS, and MS are performed using the following equation:

$$\%R = \left[\frac{(C_{spk-} C_x)}{C_t}\right] \times 100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample; (C_x = 0 for CCV, LCS and SCV.)
C_t = the theoretical spike concentration.

12.23 Relative percent difference for duplicate is calculated using the following equation:

$$RPD = \left[\frac{|C_1 - C_2|}{(C_1 + C_2)/_2}\right] 100$$

where:
C_1 = concentration of the first sample
C_2 = concentration of the second sample

13.0 Method Performance

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

13.3 Demonstration of laboratory accuracy, precision, and MDLs are presented in Tables 6 and 7.

13.4 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant 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 PHILIS-2 Chemical Hygiene Plan.

14.3 The waste produced from EPA Method 8082A consist of waste collected from the extraction process, extracts, excess sample, standards (stock mixes, PDS), methylene chloride, hexane, and methanol.

14.4 Excess reagents are disposed in accordance with MSDS and laboratory waste management plan requirements.

14.5 Glass pipettes are disposed in the glassware waste container.

14.6 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 St., N.W. Washington, D.C. 20036.

14.7 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA 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, the Agency recommends recycling as the next best option.

14.8 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, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036, http://www.acs.org.

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan.

16.0 References

16.1 EPA Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 1, February 2007; U.S. EPA Office of Solid Waste.

16.2 Method 8000D, Determinative Chromatographic Separations

17.0 Tables, Figures, and Attachments

Table 1. Example Extraction and Analyte Range

Soil Sample Type	Analytical Range	RL Range	Sample Mass	Extract Final Volume
Trace analysis of clean soil sample; clean conformational analysis	Low Level	0.0083 – 0.5 mg/kg	30 grams	5 mL
Moderate soil contamination; extent of contamination evaluation project	Medium Level	0.10 – 6.0 mg/kg	5 grams	10 mL
Heavy contamination of soil, waste characterization	High Level	0.50 – 30 mg/kg	1 gram	10 mL

Table 2. Suggested GC/ECD Operating Conditions for PCBs as Aroclors for the Dual-Column Method of Analysis Using an Agilent 6890 Plus GC with a Micro ECD

Column 1 – Restek RTX-CLPesticide, 30 m x 0.25 mm, 0.25 µm film thickness	
Column 2 – Restek RTX-CLPesticide2, 30 m x 0.25 mm, 0.20 µm film thickness	
Carrier gas (He) flow rate	2.2 mL/min (constant flow)
Makeup gas (N2)	30.0 mL/min
GC Oven Temperature Program	Initial temp = 120 °C (no initial hold) 120 °C to 220°C at 30 °C/min, no hold 220 °C to 240°C at 4 °C/min, no hold 240 °C to 300°C at 10 °C/min, final hold = 4 min
Equilibration time	0.5 min
Post run time	0 min
Total run time	18.33 min
Injector temperature	250 °C
Injection mode	Splitless
Purge flow/time	60.0 mL/min at 0.30 min
Gas saver	Off
Detector temperature	300 °C
Injection volume	1 µL
Solvent	Hexane
Type of Injector	Flash vaporization; 4-mm ID splitless liner
Detector type	Dual µECD
Attenuation	0
Type of splitter	Glass Y-shaped splitter
Range	0

Table 3. Example of Retention Times of Aroclors on the Restek RTX-ClPesticide Column

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1	4.23	3.18	3.92	4.24	4.66	5.74	7.50
2	4.69	3.76	4.24	4.69	5.01	6.01	8.04
3	4.83	3.89	4.69	4.82	5.27	6.50	8.80
4	5.02	3.92	4.82	5.27	5.37	6.69	9.46
5	5.27	4.36	5.27	5.79	5.79	7.16	10.05

Notes:
GC operating conditions are given in Table 2. All retention times in minutes and are provided for illustrative purposes only.
The peaks listed in this table are sequentially numbered in elution order for illustrative purposed only and are not isomer numbers.

Table 4. Example of Retention Times of Aroclors on the Restek RTX-ClPesticide2 Column

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1	4.94	3.59	4.50	4.94	5.47	6.98	9.24
2	5.51	4.29	4.94	5.50	5.94	7.40	10.02
3	5.69	4.44	5.50	5.68	6.36	8.11	10.83
4	5.96	4.50	5.68	6.36	6.56	8.36	11.35
5	6.37	5.01	6.36	6.98	6.98	8.84	12.10

Notes:
GC operating conditions are given in Table 2. All retention times in minutes and are provided for illustrative purposes only.
The peaks listed in this table are sequentially numbered in elution order for illustrative purposed only and are not isomer numbers.

Table 5. Specific PCB Congeners that are Major Components in Common Aroclors

Congener	IUPAC Number	Aroclors						
		1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
2,3-DCB	5	X	X	X	X	X		
3,4-DCB	12	X		X	X	X		
2,4,4'-TCB	28*	X		X	X	X	X	
2,2',3,5'-TCB	44			X	X	X	X	X
2,3',4,4'-TCB	66*					X	X	X
2,3,3',4',6-PCB	110						X	
2,3',4,4',5-PCB	118*						X	X
2,2',4,4',5,5'-HCB	153							X
2,2',3,4,4',5'-HCB	138							X
2,2',3,4,4',5,5'-HpCB	180							X
2,2',3,3',4,4',5-HpCB	170							X

Notes
*Apparent co-elution of: 28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

This table is not intended to illustrate all of the congeners that may be present in a given Aroclor, but rather to illustrate the major congener components.

Table 6. Analytes Determined by 8082A
Example Detection Limits and Precision & Accuracy (P&A)

8082A Method List		MDL	Control Limits	RPD	MDL	Control Limits	RPD
Compound	CAS No.	SPE µg/L	SPE % Recovery	SPE %	Soil µg/kg	Soil % Recovery	Soil (%)
Aroclor 1016	12674-11-2	0.02	55-137	30	4.01	59-125	30
Aroclor 1221	11104-28-2	0.05	60-140	30	8.3	60-140	30
Aroclor 1232	11141-16-5	0.05	60-140	30	8.3	60-140	30
Aroclor 1242	53469-21-9	0.05	60-140	30	8.3	60-140	30
Aroclor 1248	12672-29-6	0.05	60-140	30	8.3	60-140	30
Aroclor 1254	11097-69-1	0.05	60-140	30	8.3	60-140	30
Aroclor 1260	11096-82-5	0.045	60-141	30	1.84	57-127	30
Aroclor 1262	37324-23-5	0.05	60-140	30	8.3	60-140	30
Aroclor 1268	11100-14-4	0.05	60-140	30	8.3	60-140	30
TCMX (surr)			60-140	30		60-140	30
DCB (surr)			60-140	30		60-140	30

Notes:
*To be determined based on project requirements.

Table 7. 8082A Method Criteria

Item	Measure	Action
Initial Calibration (ICAL)	Average Response Factor >20.0 % RSD.	Evaluate points in the curve for use of linear or quadratic regression (r2 must be ≥0.990). Also evaluate upper and lower points for removal. Criteria still not met, recalibrate if compound is an analyte of interest.
ICAL Low Point Eval. for compounds using linear or quadratic regression	Low Point or Mid Point Not within ±30% of True Value	Evaluate calibration points. Recalibrate if not problem is found and % deviation or drift is not met and compound is an analyte of interest.
Initial Calibration Verification (SCV)	Not within ±30% of true value for deviation or drift.	Recalibrate if % deviation is not met and the compound is an analyte of interest.
Method Blank	Analyte(s) of interest at or above reporting limit.	If the associated samples are non-detect, no action is required. If the analyte(s) is/are detected in the sample, flag with a "b" or reanalyze. If the analyte level in the sample is 10 times greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% recovery outside laboratory acceptance criteria	If the LCS % recovery is high and the sample is non-detect, no action is required. If the LCS is high and the sample(s) have detects, reanalyze the sample. If the LCS is low, the samples should be reanalyzed. Flag data that does not meet laboratory acceptance criteria
Laboratory Control Spike Duplicate. (LCSD)	% Recovery outside laboratory acceptance criteria. RPD acceptance criteria is 30%.	% recovery same as the LCS. If the RPD value is above the acceptance criteria in the LIMS, then evaluate the system for possible problems. Reprep and reanalyze samples as necessary and if possible. Flag data that does not meet laboratory acceptance criteria
Matrix Spike (MS)	% Recovery outside laboratory acceptance criteria.	If the % Recovery is outside laboratory acceptance criteria, evaluate the LCS. If the LCS is in control, then there is the possibility of matrix effect. The sample should be flagged appropriately.
Matrix Spike Duplicate (MSD)	% Recovery outside laboratory acceptance criteria. RPD acceptance criteria is 30%.	% recovery same as the MS. If the RPD value is above the acceptance criteria in the LIMS, then evaluate the system for possible problems. Reanalyze samples if possible or flag results.
Surrogate(S)	% Recovery outside laboratory acceptance criteria.	If the % recovery is outside laboratory acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary. If the % recovery is on a client sample, re-prep and reanalyze if possible. If the % recovery is within criteria, report the sample within limits. If % recovery is outside criteria and is confirmed, then there is a matrix effect. Flag the results as estimated and report the initial result.
CCV	% difference/drift for each Aroclor is > 20%	Check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±20%, then a new initial calibration must be prepared. See Sec. 11.6.6 for a discussion on the effects of a failing calibration verification standard on sample results.
Samples	% RPD between columns outside lab recovery limit of 40 %.	Check the chromatograms for obvious interferences or improper integration. Check the instrument operating conditions. If there is no obvious problem, then flag the data and report the lower concentration to the client. Address this in the case narrative.

Figure 1. Example PCB Data Review Form

PHILIS Program

CSS

DATA REVIEW FORM – GC/ECD

Instrument and Date: _____ **Sequence #:** _____

Analysis: ☐ PCBs ☐ Pesticides ☐ Other _____

	Yes	No	Peer Rvw	QA Rvw	Comments
Analyst Report					
PHILIS narrative is complete	☐	☐	☐	☐	
Reported data matches the raw data	☐	☐	☐	☐	
Reporting limits and qualifiers are correct	☐	☐	☐	☐	
Sample Receiving					
Samples received in acceptable condition and compliant with COC	☐	☐	☐	☐	
Samples properly preserved	☐	☐	☐	☐	
Sample receipt checklist filled out	☐	☐	☐	☐	
Instrument Calibration					
A minimum 5 point calibration curve is generated for linear (quadratic curve requires 6 points)	☐	☐	☐	☐	
The %RSD of Response Factors is ≤ 20% or curve fit meets criteria	☐	☐	☐	☐	
ICAL points within 30% of known values except 50% of known value for the lowest level	☐	☐	☐	☐	
Single point standard used for other Aroclors/Toxaphene mixtures with RT Windows of ± 0.07 minutes	☐	☐	☐	☐	
DDT and Endrin degradation each below 15% for Pesticides in PEM check	☐	☐	☐	☐	
RT Window is ± 0.05 minutes for TCMX and ± 0.10 minutes for DCB	☐	☐	☐	☐	
SCV is within 30% of true values for deviation or drift	☐	☐	☐	☐	
CCV %D of the CF for each of the 3 to 5 peaks is ± 20%	☐	☐	☐	☐	
Appropriate number of samples between CCVs	☐	☐	☐	☐	
CCV compounds meet acceptance criteria	☐	☐	☐	☐	
Method Blank					
Analytes detected at or above their reporting limits are flagged	☐	☐	☐	☐	
Samples					
Samples prepared and extracts analyzed within holding time limits	☐	☐	☐	☐	
Target compound report included and Chromatograms provided	☐	☐	☐	☐	
Manual integration/Q-Deletion initialed and dated by analyst and reviewer	☐	☐	☐	☐	
Verify all Aroclor/Toxaphene spectral identifications	☐	☐	☐	☐	
Primary column and confirmation column are within 40% agreement	☐	☐	☐	☐	
Calculations have been verified—see calculations sheet	☐	☐	☐	☐	
Surrogate Standard recovery report					
Surrogate recovery meets acceptance criteria	☐	☐	☐	☐	
Sample results are properly flagged	☐	☐	☐	☐	
Preparation batch summary					
All samples are accounted for	☐	☐	☐	☐	
Results reflect sample mass/volume prepared	☐	☐	☐	☐	
Solid results are provided dry weight basis	☐	☐	☐	☐	
Matrix spike/matrix spike duplicate					
MS/MSD percent recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Sample results been flagged appropriately	☐	☐	☐	☐	
Laboratory control spike/laboratory control spike duplicate					
LCS/LCSD recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Have sample results been flagged appropriately	☐	☐	☐	☐	

Analyst review signature Date | Peer review signature Date | QA review signature Date

PHILIS2 Form ID#: QA-019 / Release Date: 09/18/2023

****** This Page Intentionally Blank ******