

En Chem, Inc.

Quality Assurance Document

En Chem SOP
K-SVO-77
REV. NO. 2
Effective Date: June 25, 2003
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Standard Operating Procedure Analytical Method

TITLE: Extraction and Analysis of Polychlorinated Biphenyls (PCB's) in Soils and Sediments from the Fox River.

DEPARTMENT: Semivolatile Organics

APPLICATION: This method is used to determine the concentration of PCB's in soils and sediments related to work on the Fox River and Green Bay. Historically, Aroclor 1242 and Aroclor 1254 have been the predominant PCBs found in the Fox River system. The following PCB Aroclors are routinely analyzed using this method:

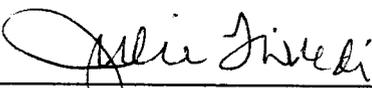
Aroclor 1016 Aroclor 1232 Aroclor 1248 Aroclor 1260
Aroclor 1221 Aroclor 1242 Aroclor 1254

REFERENCES: Test Methods for Evaluating Solid Waste, 3rd. Ed.
SW846 Method 8000B, December 1996
SW846 Method 8082, December 1996

PROCEDURE SUMMARY:

Soil and sediment samples are analyzed for moisture content and then air dried. The dried sample is homogenized and the moisture content analyzed again. The prepared sample is Soxhlet extracted. Contaminants may be removed from the extract using column chromatography with Florisil. Sulfur is removed by mixing the extract with elemental mercury or copper or by gel permeation chromatography. A sulfuric acid cleanup may also be required if contaminants persist. A volume of sample extract is injected into a gas chromatograph (GC) and PCB Aroclors are detected by an electron capture detector (ECD). Results are reported in parts per billion ($\mu\text{g}/\text{kg}$). Soil and sediment sample results are corrected for moisture after air drying and reported on a dry weight basis.

REVIEWED BY:


Julie Trivedi
Quality Assurance Officer

6/25/03

Date

APPROVED BY:


Glen A. Coder
Laboratory Manager

6/25/03

Date

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SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

PCBs have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood.

APPARATUS AND MATERIALS:

Note: Apparatus and materials equivalent to those listed may be used.

Glass wool or extraction thimbles

Aluminum foil or aluminum pie pans

Beakers, 250, 400 ml Pyrex glass

Pyrex glass wool

Balance, analytical to +/- 0.0001 g

Muffle furnace capable of operating at 400°C.

Soxhlet extraction apparatus, manual or automated, including condenser, heater, and solvent collection flasks.

Kuderna Danish (K-D) apparatus consisting of: 10 ml graduated concentrator tubes, 500 ml evaporative flask, and three-ball macro Snyder columns.

Teflon boiling chips, approximately 10/40 mesh

Chromatography column, 20 mm ID with stopcock and 300 ml solvent reservoir.

Water bath, heated with concentric ring cover. Capable of temperature control. The bath should operate in a hood.

TurboVap

Nitrogen evaporator device for concentrating solvent to final volume in KD tubes.

Copper filings and/or elemental mercury for the removal of sulfur.

Gas Chromatograph: Hewlett Packard (HP) 5890 or HP 6890 Micro equipped with Electron Capture Detectors (ECD)

GC Autosampler: HP7673A.

Data Processor: TurboChrom IV.

Printer: HP laserjet 4M/Plus.

Syringes: 10-1000 µL Gastight syringes (Hamilton series 1000).

Autosampler Vials: 2 mL with crimp top caps.

Detector: ECD (HP).

GC Columns: Column 1 - DB-17 Capillary column, 30 m x 0.32 mm I.D. (J&W Scientific).

Column 2 - DB-1701 Capillary column, 30 m x 0.32 mm I.D. (J&W Scientific).

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Column 3 - DB-5 Capillary column, 30 m x 0.32 mm I.D. (J&W Scientific).

Column 4 - STX-CLP Capillary column, 30 m x 0.32 mm I.D. (Restek).

Column 5 - STX-CLP2 Capillary column, 30 m x 0.25 mm I.D. (Restek).

Recommended GC Column Conditions:

Carrier gas - Helium
Flow rate - 2.0 mL/min.
Make-up gas - Nitrogen
Flow rate - 65 mL/min.
Detector temp. - 350° C
Injector temp. - 205° C
Splitless injection

GC Temperature Program:

Initial temp. - 110° C
Initial time - 0.5 min.
Rate (1) - 20° C/min.
Hold Time (1) - 0.0 min.
Rate (2) - 11° C/min.
Final temp. - 280° C
Final time - 10 min.

REAGENTS:

Solvents:

Hexane, acetone, dichloromethane, and isooctane (2,2,4-trimethylpentane) pesticide grade.

Stock Standards Solutions:

Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf-life of standard solutions is 1 year from the date of preparation.

Calibration Standards:

Prepare a five point curve for Aroclor 1242 and Aroclor 1254. Recommended concentrations are 0.1, 0.3, 0.5, 0.8, and 1.0 ug/mL. Prepare solutions of the remaining Aroclors at the mid-point concentration of the curve. Aroclors 1016 and 1260 may be combined in the same solution (AR1660). Shelf-life of the calibration solutions is one year from the date of preparation.

Surrogate Standards:

Commercially prepared standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf-life of standard solutions is one year from the date of receipt.

QUALITY ASSURANCE - Extraction:

Samples are extracted in sets of 20 samples or less. Each set must contain a method blank and a laboratory control spike. A matrix spike and matrix spike duplicate (MS/MSD) will be prepared and analyzed with each set of samples.

Method Blank: A method blank consisting of an amount of sodium sulfate or blank sand, equivalent to the typical sample extraction weight (10 or 20 grams), which is extracted and analyzed with every set of 20 samples or less.

Surrogate Spike: Tetrachloro-m-xylene (TMX) and Decachlorobiphenyl (DCB) are added as surrogate compounds to all samples prior to extraction. The recovery of the surrogates provides and indication of the method efficiency for each sample. Recoveries should be between 60% and 140%.

Control Spike (LCS): A laboratory control spike consisting of 10 or 20 grams of sodium sulfate or blank sand fortified with about five times the reporting limit of Aroclor 1242 or Aroclor 1254 is extracted and analyzed with each set of samples. The recovery of the Aroclor 1242 or Aroclor 1254 should be between 65% and 135%.

Matrix Spikes (MS/MSD): A matrix spike consists of an aliquot of one of the field sample fortified with Aroclor 1242 or Aroclor 1254 at 10 to 100 times the reporting limit. The matrix spike is then extracted and analyzed with each set of samples. The recovery of the Aroclor 1242 or Aroclor 1254 should be between 65% and 135%.

Recoveries of the control spikes and matrix spikes are calculated using the following equation:

$$\text{Control/matrix spike percent recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

Where: SSR = Spike sample results
 SR = Sample results
 SA = Spike amount added

The surrogate recoveries are calculated using the same equation without the sample result (SR) factor.

SAMPLE PREPARATION:

Samples must be dried within 14 days of collection and analyzed within 40 days from the date of extraction. The hold time may be suspended by freezing the samples. The holding time begins when the samples are thawed. The dried samples are considered dormant, the hold time is suspended, and the samples may be stored at room temperature.

Prior to extraction the sample must be removed from the jar and placed in an aluminum pan or on a large piece of aluminum foil and allowed to air dry to about 10% moisture or less. Stirring the samples occasionally and maintaining an airflow over them will aid in the drying process. Analyze a portion of the sample for moisture content before and after drying (EnChem SOP LAB16). The

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dried sample should be ground with a mortar and pestle to homogenize it. Remove large rocks, sticks and other large foreign debris prior to grinding.

SAMPLE EXTRACTION:

Dried and homogenized samples must be soxhlet extracted. The procedure may follow EPA SW846 Method 3540 for soxhlet extraction as described below, or Method 3541, automated soxhlet extraction (En Chem SOP K-SVO-79).

Soxhlet rinsing: Set up soxhlet extractors and place two plugs of glass wool or an extraction thimble in each. Add about 300 ml of dichloromethane and boiling chips or copper filings to the Erlenmeyer flask. Copper filings will allow for sulfur precipitation during extraction. Turn on the heaters and allow the soxhlet to cycle for a couple hours. Turn off the heaters, allow to cool, then dismantle the soxhlet and drain the dichloromethane.

Weigh 20 grams of the dried soil/sediment into a 250 ml beaker. Use 20 grams of sodium sulfate or blank sand for the method blank and control spike. Add surrogate spiking solution to each sample and QC sample. Add Aroclor 1242 or 1254 spiking solution to the control spike and matrix spikes.

Place the sample into the pre-rinsed soxhlet extractor between the two plugs of glass wool or in the extraction thimble topped with a plug of glass wool. Turn on the heat and allow the extractors to cycle a minimum of 16 hours.

Turn off the heat and allow to cool. Remove the soxhlet extractors together with the Erlenmeyers from the heaters and add about 30 ml of dichloromethane to the soxhlet to rinse it. Drain the solvent into the Erlenmeyer and remove the soxhlet.

Pour the extract into a 500 ml KD flask fitted with a 10 ml concentrator KD tube. Attach a three ball snyder column to the KD flask and concentrate the extract on a hot water bath. When the volume reaches about 5.0 ml add about 50 ml of hexane and concentrate again to about 5.0 ml. Remove the concentrator from the water bath and cool. Remove the KD apparatus and bring the volume of the extract in the KD tube to 10 ml with hexane.

EXTRACT CLEANUP:

A variety of cleanups may be performed as determined necessary on extracts from the manual or automated soxhlet extraction. A column chromatography cleanup using Florisil (En Chem Method SVO-57) separates the Aroclors from most other typical environmental interference's. Soil and sediment samples typically need to have sulfur removed using elemental mercury (En Chem Method SVO-27), copper filings (En Chem Method K-SVO-78) or by gel permeation chromatography (En Chem Method SVO-26). A sulfuric acid cleanup may be used, as required, to further remove contaminants (En Chem Method SVO-28).

SAMPLE EXTRACT HANDLING AND STORAGE

The extracts must be analyzed within 40 days of extraction. The extracts may be screened ahead of time to determine if dilutions would be required.

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INITIAL CALIBRATION:

Primary Column

The initial calibration includes an analysis of a five point calibration curve of Aroclors 1242 and 1254 at concentrations of 0.1, 0.3, 0.5, 0.8, and 1.0 µg/mL. The calibration curve will also include TMX and DCB at concentrations of 0.01, 0.02, 0.05, 0.1, and 0.15 µg/mL. Inject a single point standard of Aroclors 1016, 1221, 1232, 1248, and 1260 at 0.5 µg/mL. Five or more peaks are selected for each Aroclor, 1242 and 1254. The calibration factor for each of the five peaks is calculated, as shown below, for each of the five levels. Calculate the %RSD for each Aroclor peak using all five calibration points. See Calibration Curve Criteria below.

Other calibration ranges may be substituted to meet expected concentrations of samples being analyzed. If other Aroclors are found to be present in the samples then a five point calibration of those Aroclors must be analyzed along with the sample extracts.

The analyst will pick at least five (three for Aroclor-1221) of the largest peaks for each Aroclor for use in quantifying the samples. The peaks chosen for quantitation should have minimal co-elution with peaks of other Aroclors. Fewer than five peaks may be used to determine the concentration of an Aroclor if a mixture of Aroclors limits available peaks.

Confirmation Column

Confirmation is generally required using a second GC column of dissimilar stationary phase. When simultaneous analysis is performed for confirmation, the same initial and continuing calibration criteria apply.

Since Aroclors provide distinct multiple peak patterns which may be identified by an experienced analyst, and because the identification of an Aroclor is based primarily on this pattern recognition, the need for second column confirmation is not required for sites having a **single** Aroclor. In this case the analyst must document in the raw data the absence of major peaks representing any other Aroclor.

Calibration Curve Criteria: **All initial calibration and calibration verification criteria apply to both analytical columns.**

1. Linear Calibration using Average Calibration Factors.

$$CF = \frac{\text{Peak Area}}{\text{Std. Concentration in ug/mL}}$$

The percent relative standard deviation (%RSD) of the five calibration factors for each peak, in each Aroclor, must be less than or equal to 20%. If this is the case then linearity can be assumed, and the average calibration factor can be used in place of the calibration curve.

RETENTION TIME WINDOWS:

Retention time windows are generally not applicable to Aroclor analysis since pattern recognition is used to identify the types of Aroclors present

Establish the center of the RT window for each Aroclor peak and surrogate using the absolute RT from the calibration verification standard at the beginning of the analytical shift. The retention time window should be +/-0.03 minutes. The Initial Calibration RT windows may continue to be used as long as method criteria are met. For samples run during the same shift as an initial calibration, use the RT of the mid-point standard in the Initial calibration.

Continuing Calibration Verification Standard

All samples must be bracketed by acceptable calibration verifications.

A midpoint calibration check standard is injected following every ten sample injections for calibration verification. If the average response factor (area/concentration) of the five or more peaks in the check standard deviates by more than 15% of the initial average response factor, the calibration is considered out of control and analysis must be stopped.

If the ending calibration verification standard exceeds the 15% criteria on the high side (i.e. an increase in sensitivity) samples which had no Aroclors detected do not need to be reanalyzed. If the continuing calibration standard criteria is exceeded on the low side (i.e. a drop in sensitivity), then the non-positive samples must be re-analyzed because the ability to meet the detection limit is in question. **Any samples injected prior to the failing calibration which do exhibit an Aroclor pattern must be reinjected under a valid calibration.**

Perform corrective action such as injection port or column maintenance. Prior to the analysis of any subsequent samples an acceptable calibration verification must be analyzed. In the event that this cannot be achieved a new initial calibration must be performed.

CALIBRATION VERIFICATION ACCEPTANCE CRITERIA:

1. The percent difference (%D) is determined for all analytes. The %D must be within $\pm 15\%$ of the calibration curve. (see below)

$$\%D = \frac{R_2 - R_1}{R_1} \times 100$$

where: R_1 = True value of standard.

R_2 = Calculated amount from succeeding analyses using the \overline{CF} .

The analyst should verify that the software is using appropriate values for calculations.

SAMPLE ANALYSIS

Once the Aroclor pattern has been identified, compare the responses of 3 to 10 major peaks in the calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor (single point) for each of the 3 to 10 characteristic peaks chosen for that specific Aroclor.

A concentration is determined using each of the characteristic peaks and then those 3 to 10 concentrations are averaged to determine the concentration of that Aroclor.

1. Calculations:

Soil/Sediment samples

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(A_x)(V_t)(D)}{(Cf)(W)(S)}$$

- where:
- A_x = Area for selected peak.
 - V_t = Final volume of extract in mL (adjusting for GPC cleanup if necessary)
 - D = Dilution factor
 - Cf = calibration factor *
 - V_i = Initial sample volume (L)
 - W = Initial sample weight (kg)
 - S = % Solids/100 (from the dried sample)

* Note: If Aroclor 1242 or 1254 is being quantified use the average calibration factor from the calibration curve.

2. The method blank and LCS extracted along with the samples should be analyzed on the same instrument and the same analytical sequence as the samples.
3. Surrogate recoveries must be evaluated using laboratory control limits (see appendix B). If **both** surrogate recoveries fail this criteria, re-extract the sample. One surrogate is allowed to be outside of the control limits. For instance, if an interfering peak obscures one surrogate, then that one surrogate may be excluded. In the case of a dilution, the analysts discretion should be used.

QUALITY CONTROL

1. The method blank must meet the surrogate limits (see appendix B). If the blank fails this criteria, all of the associated samples, matrix spikes and laboratory control spikes will be evaluated and a corrective action will be determined.
2. If the blank contains any analyte of interest above the reporting limit (see appendix A), all of the associated samples, matrix spikes, and laboratory control spikes **must** be re-extracted unless the sample concentration is greater than 20X the amount found in the blank or the analyte is not detected in an associated sample.

3. If the laboratory control spike does not meet the recovery criteria specified in Appendix B, the results of all QC performed with the samples will be evaluated by the analyst. Corrective actions may include re-extraction of the samples or reanalysis of the extracts.

4. Sample matrix spike recoveries should fall within the Laboratory Control limits (see appendix B). If a matrix spike recovery fails this criteria, the recovery of the other spiked sample in the MS/MSD pair should be evaluated. If recovery failures are duplicated then the sample matrix is suspected as the problem and the data should be flagged and the failures discussed in the sample narrative. The LCS recoveries can be used to verify that the method was acceptable for the analysis in a clean matrix.

Note: The Aroclor(s) spiked and/or spike amounts may be adjusted when prior knowledge of the type or concentration of Aroclor(s) present in the sample matrix is known, or to comply with project workplans.

The quality control criteria regarding this method may be adjusted to meet specific quality assurance project plans or work plans incorporating or referencing this document.

Appendix A
MDL and Reporting Limits For PCBs

<u>Aroclor</u>	Method 3540 MDL ^A (<u>µg/kg</u>)	Method 3540 Reporting Limit (<u>µg/kg</u>)	Method 3541 Reporting Limit (<u>µg/kg</u>)
AR1016	22	50	100
AR1221	22	50	100
AR1232	22	50	100
AR1242	22	50	100
AR1248	22	50	100
AR1254	22	50	100
AR1260	22	50	100

^A Method Detection Limit determination, USEPA 40CFR Pt.136, App.B, 1988. Method detection limits are updated periodically, the values currently in use may differ slightly from those published.

Note: A Method Detection Limit study utilizing extraction Method 3541 in conjunction with this analytical method has not been performed as of this printing.

Appendix B

LCS/MS/MSD
QUALITY CONTROL LIMITS
for PCB's

Soil
% Rec.

AR1242 or 1254 (65-135)

SURROGATE
LABORATORY CONTROL LIMITS
for PCB's

Soil
% Rec.

Surrogates

Decachlorobiphenyl	(60-140)
Tetrachloro-m-xylene	(60-140)