THE ANALYSIS OF POLYCHLORINATED BIPHENYLS IN TRANSFORMER FLUID AND WASTE OILS

DRAFT

1. Scope

1.1 This is a gas chromatography (GC) method applicable to the determination of commercial mixtures of polychlorinated biphenyls (PCBs) in transformer fluids and certain other hydrocarbon based waste oils. The method can be used to analyze waste oils for individual PCB isomers or complex mixtures of chlorinated biphenyls from monochlorobiphenyl through decachlorobiphenyl only if they have been previously identified by other methods[1] or by knowledge of the sample history.

1.2 The detection limits are dependent upon the complexity of the sample matrix and the ability of the analyst to properly maintain the analytical system. Using a carefully optimized instrument, this method has been shown to be useful for the determination of commercial PCB mixtures spiked into transformer fluid over a range of 5.0 to 500 mg/Kg. Based upon a statistical calculation at 5 mg/Kg for a simple oil matrix, the method detection limit for Aroclors 1221, 1242, 1254, and 1260 is 1 mg/Kg. The method

U. S. Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Prior to sample analysis, each analyst must demonstrate the ability to generate acceptable results with this method by following the procedures described in Section 10.2.

2. Summary

2.1 The sample is diluted on a weight/volume basis so that the concentrations of each PCB isomer is within capability of the gas chromatographic (GC) system (0.01 to 10 ng/µL).

2.2 The diluted sample is then injected into a gas chromatograph for separation of the PCB isomers. Measurement is accomplished with a halogen specific detector which maximizes baseline stability and minimizes interferences normally encountered with other detectors. The electron capture detector (ECD) can normally be substituted for the halogen specific detector, when samples contain dichloro- through decachlorobiphenyl isomers (Aroclors 1232, 1242, 1016, 1248, 1254, 1260, 1262 and 1268) or when the sample matrix does not interfere with the PCBs. Several cleanup techniques are provided for samples containing interferences. A mass spectrometer operating in the selected ion monitoring mode of data aquisition may also be used as the GC detector, when PCB levels are sufficiently high and the PCB m/e ranges are free from interference. Interfer-

ences may occur in some waste oil samples even after exhaustive cleanup.

2.3 The concentrations of the PCBs are calculated on a mg/Kg basis, using commercial mixtures of PCBs as standards. The analysis time, not including data reduction, is approximately 35 min/sample.

3. Interferences

3.1 Qualitative misidentifications are always a potential problem in GC analysis. The use of a halogen specific detector and the analyst's skill in recognizing chromatographic patterns of commercial PCB mixtures minimizes this possibility.

3.2 Whenever samples are analyzed that do not provide chromatographic patterns which are nearly identical to the standards prepared from commercial PCBs, the analyst must confirm the presence of PCBs by analysis after column cleanup, analysis on dissimilar gas chromatographic columns or by gas chromatography/mass spectrometry (GC/MS).

3.3 During the development and testing of this method, certain analytical parameters and equipment designs were found to affect the validity of the analytical results. Proper use of the method requires that such parameters or designs must be used as specified. These items are identified in the text by the word "must." Anyone wishing to deviate from the method in areas so identified, must demonstrate that the deviation does not affect the validity of the data. Alternative test procedure approval must be obtained through the EMSL-CI Equivalency Program[2]. An experienced analyst may make modifications to parameters or equipment identified by the

term "recommended". Each time such modifications are made to the method, the analyst must repeat the procedure in Section 10.2. In this case, formal approval is not required, but the documented data from 10.2 must be on file as part of the overall quality assurance program.

3.4 Samples diluted 100:1 analyzed by electron capture GC, consistently produce results that are 10 to 20% lower than the true value (Section 12). This is due to quenching of the detector response by high boiling hydrocarbons coeluting with the PCBs. The degree of error is matrix dependent and is not predictable for samples of unknown origin. As the PCB concentration approaches 20 percent of a control level, e.g., 50 mg/kg, the analyst must routinely reanalyze a duplicate spiked sample to determine the actual recovery. Spike the duplicate or diluted sample at 2 times the electron capture observed value and reanalyze according to Section 10.2. Correct the results accordingly.

4. Apparatus

4.1 Gas Chromatograph - The gas chromatograph should be temperature programmable, equipped for on-column injection, and capable of accepting 1/4 inch OD glass columns.

4.2 Gas Chromatographic Detector

4.2.1 A halogen specific detector is used to eliminate interferences causing misidentifications or false-positive values due to non-organohalides which commonly coelute with the PBCs.

a. Electrolytic conductivity detector - the Hall Model 700-A

(HED), available from Tracor, has been found to provide the sensitivity and stability needed for the current PCB Regulations.

b. Other halogen specific detectors, including older model electrolytic conductivity detectors and microcoulometric titration, may be used. However, the stability, sensitivity, and response time of these detectors may raise the method detection limit and adversely affect peak resolution. Each system must be shown to be operating within requirements of the PCB regulations by collecting single laboratory accuracy and precision data and method detection limits on simple spiked samples as described in Section 10.2.

4.2.2 Semi-specific detectors such as ECD may be substituted when sample chromatographic patterns closely match those of the standards. Acid cleanup (Section 8.1) or Florisil slurry cleanup (Section 8.7) should be incorporated routinely when the ECD is used. See Section 3.4 for additional quality control procedures for ECD.

4.2.3 Quantitative GC/MS techniques can be used and the recommended approach is selected ion monitoring (SIM). The GC/MS data system must have a program that supports this method of data acquisition. The program must be capable of monitoring a minimum of eight ions, and it is desirable for the system to have the ability to change the ions monitored as a function of time. For PCB measurements several sets of

ions may be used depending on the objectives of the study and the data system capabilities. The alternatives are as follows:

Single ions for high sensitivity	154, 188, 222, 256, 292, 326, 360, 394
Short mass ranges which may give enhanced sensitivity depending on the data system capabilities	154-156, 188-192, 222-226, 256-260, 290-295, 322-328, 356-364, 390-398
Single ions that give decreased sensitivity but are selective for levels of chlorination (1).	190, 224, 260, 294, 330, 362, 394

The data system must have the capability of integrating the abundances of the selected ions between specified limits, and relating integrated abundances to concentrations using the calibration procedures described in this method.

4.3 Gas Chromatographic Columns

4.3.1 The GC columns and conditions listed below are recommended for the analysis of PCB mixtures in oil. If these columns and conditions are not adequate, the analyst may vary the column parameters to improve separations. The columns and conditions selected must be capable of adequately resolving the PCBs in the various Aroclor mixtures so that each Aroclor is identifiable through isomer pattern recognition. See Figures 1 through 6 to establish this. To properly use the calculation procedure described in Section 11.5, the analyst must use the methyl silicone column described in

4.3.2. Capillary columns and their associated specialized injection techniques are acceptable alternatives to the recommended packed columns. Due to problems associated with the use of capillary columns the analyst must demonstrate that the entire system will produce acceptable results by performing the operations described in Section 10.2.

4.3.2 Recommended primary analytical column: Glass, 1/4 inch O.D. (2 mm I.D.) 6 ft (180 cm) long, packed with Gas-Chrom Q (100/120 mesh) coated with 3% OV-1.

Carrier gas: 40 to 60 mL/min (helium, nitrogen or 10% methane in argon).

Temperature Program: 120°C isothermal for 2 minutes, 6°/minute to 220°C and hold until all compounds elute.

Figure 6 shows a chromatogram of the PCB locator mixture (see Section 5.8) analyzed under these conditions. Each PCB peak has been identified by assigning the same relative retention times determined in the isothermal runs Figures 1 through 6.

Isothermal Operation:

Aroclor 1221, 1232, or Cl_1 through Cl_4 isomers 140 to 150°C

Aroclor 1016, 1242, 1254, 1260, 1262, 1268, or Cl_3 through Cl_{10} isomers 170 to 200°C

4.3.3 Recommended confirmatory column: Glass tubing 1/4" O.D., 2 mm I.D. 6 ft (180 cm) long, packed with Gas-Chrom Q 100/120 mesh coated with 1.5% OV-17 + 1.95% OV-210.

Carrier gas: 40 to 60 mL/minute (helium, nitrogen or 10% methane in argon).

Column temperatures:

Aroclor 1221, 1232, or Cl_1 through Cl_4 isomers-170 to 180°C.

Aroclor 1016, 1242, 1254, 1260, 1262, 1268, or Cl_3 through Cl_{10} isomers-200°C.

4.4 Volumetric flasks - 10- 100- 200- and 250-mL

4.5 Pipets - 0.10 mL, 1.0 mL, and 5.0 mL, Mohr delivery (for viscous oils cut off tip of pipet).

4.6 Micro syringes - 10.0 µL

4.7 Sample containers - 20 mL or larger screw-cap bottles with Teflon faced cap liners. (Aluminum foil cap liners can be used for non-corrosive samples).

4.8 Chromatographic column - Chromaflex, 400 mm long x 19 mm ID (Kontes K-420540-9011 or equivalent).

4.9 Gel Permeation Chromatograph - GPC Autoprep 1002 or equivalent, available from Analytical Bio Chemistry Laboratories, Inc.

4.10 Balance - Analytical, capable of accurately weighing 99 ± .0001 grams.

4.11 Kuderna-Danish (K-D) Apparatus

4.10.1 Concentrator tube-10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of solvent.

4.11.2 Evaporative flask - 500 mL (Kontes K-57001-0500 or

equivalent). Attach to concentrator tube with springs (Kontes K-662750-0012).

4.11.3 Snyder column - Three-ball macro (Kontes K503000-0121 or equivalent).

5. Reagents and Materials

5.1 Reagent safety precautions

5.1.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemical sspecified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

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

5.1.3 Diethyl ether should be monitored regularly to determine the peroxide content. Under no circumstances should diethyl ether be used with a peroxide content in excess of 50 ppm as an explosion could result. Peroxide test strips manufactured by EM Laboratories (available from Scientific Products

Co., Cat. No. P1126-8 and other suppliers) are recommended for this test. Procedures for removal of peroxides from diethyl ether are included in the instructions supplied with the peroxide test kit.

5.2 Hexane (mixed hexanes), isooctane, acetonitrile, methylene chloride, cyclohexane, and diethyl ether - Pesticide grade.

5.3 Column packings (recommended)

5.3.1 Gas Chrom Q (100/120 mesh) coated with 3% OV-1.

5.3.2 Gas Chrom Q (100/120 mesh) coated with 1.5% OV-17 + 1.95% OV-210.

5.4 Standards

5.4.1 Aroclors 1221, 1232, 1242, 1016, 1254, 1260, 1262, 1268. Primary dilutions of various Aroclors in isooctane will be available from U.S. EPA, EMSL-Cincinnati Quality Assurance Branch, 26 W. St. Clair Street, Cincinnati, Ohio 45268.

5.4.2 2-Chlorobiphenyl, 3-chlorobiphenyl, and decachlorobiphenyl

5.4.3 Pure individual PCBs as identified in the sample by mass spectrometry or indicated by retention data.

5.4.4 Alumina (Fisher A540 or equivalent).

5.4.5 Silica gel (Davison Grade 950 or equivalent).

5.4.6 Florisil (PR grade or equivalent).

5.4.7 Sulfuric acid A.C.S.

5.4.8 Quality Control Check Sample, Certified Sample of PCBs in oil available from U.S. EPA, EMSL-Cincinnati Quality Assurance Branch, 26 W. St. Clair Street, Cincinnati, Ohio 45268.

5.5 Standard Stock Solutions - Prepare primary dilutions of each of the Aroclors or individual PCBs by weighing approximately 0.01 g of material within ± 0.0001 g. Dissolve and dilute to 10.0 mL with isooctane or hexane. Calculate the concentration in µg/µL. Store the primary dilutions at 4°C in 10 to 15 mL narrow-mouth, screw-cap bottles with Teflon cap liners. Primary dilutions are stable indefinitely if the seals are maintained. The validity of primary and secondary dilutions must be monitored on a quarterly basis by analyzing EMSL-CI Quality Control Check Samples.

5.6 Working Standards - Prepare working standards similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Dilute the mixture to volume with pesticide quality hexane. Calculate the concentration in ng/µL as the individual Aroclors or as the individual PCBs. Store dilutions at 4°C in 10- to 15-mL narrow-mouth, screw-cap bottles with Teflon cap liners. These secondary dilutions can be stored indefinitely if the seals are maintained.

5.7 Laboratory control standard (LCS) - Prepare a LCS by spiking a PCB-free oil, typical of the matrix normally analyzed, at 50.0 mg/Kg (i.e. transformer oil) with a PCB mixture typical of those normally found in the samples (i.e. Aroclor 1260 at 50.0 mg/Kg).

5.8 PCB Locator Mixture - Prepare a PCB locator mixture containing 0.1 ng/µL of 2-chlorobiphenyl, 0.1 ng/µL 3-chlorobiphenyl, 0.5 ng/µL Aroclor 1242, 0.5 ng/µL Aroclor 1260, and 0.2 ng/µL Aroclor 1268 in hexane (0.1 ng/µL of decachlorobiphenyl can be substituted for Aroclor 1268). Use the chromatogram generated by the PCB locator

mixture to help identify the retention times of the various PCB isomers commonly found in commercial PCB mixtures.

6. Sample Collection and Handling

6.1 Sample containers should have a volume of 20 mL or more and have Teflon lined screw caps.

6.2 Sample Bottle Preparation

6.2.1 Wash all sample bottles and seals in detergent solution. Rinse with tap water and then distilled water. Allow the bottles and seals to drain dry in a contaminant free area. Then rinse seals with pesticide grade hexane and allow to air dry.

6.2.2 Heat sample bottles to 400°C for 15 to 20 min or rinse with pesticide grade acetone or hexane and allow to air dry.

6.2.3 Store the clean bottles inverted or sealed until use.

6.2.4 Prior to reuse, rinse the bottles and seals 3 times with hexane, air dry, and then proceed to 6.2.1.

6.3 Sample Preservation - The samples should be stored in a cool, dry, dark area until analysis. Storage times in excess of 4 weeks are not recommended for unknown or undefined sample matrices.

6.4 Sample Collection

6.4.1 Fill a large container (i.e. 500-mL beaker) from a representative area of the sample source (if practical, mix the sample source prior to sampling).

6.4.2 Collect a minimum of two 20-mL samples (Field Sample 1 (FS1) and Field Sample 2 (FS2)) approximately 80% full from the sampling container.

6.4.3 Repeat 6.4.1 and 6.4.2 if there is a need to monitor sampling precision as described in Section 10.6.

7. Dilution and Analysis

7.1 The approximate PCB concentration of the sample may be determined by X-ray fluorescence, microcoulometry, density measurements, or by analyzing a very dilute mixture of the sample (10,000:1) according to 7.4.

7.2 For samples in the 0 to 100 mg/Kg range, dilute 100:1 in hexane.

7.2.1 Pipet 1.0 mL of sample into a 100 mL volumetric flask using a 1.0-mL Mohr pipet (for viscous samples, cut the capillary tip off the pipet). Dilute to volume with hexane. Stopper and mix.

7.2.2 Using the same pipet as in 7.2.1, deliver 1.0-mL of sample into a tared 10-mL beaker weighed to ± .001 g. Reweigh the beaker to ± .001 g to determine the weight of sample used in 7.2.1.

7.2.3 As an alternative to 7.2.1 and 7,2.2, weigh approximately 1 gram to ±.001 g of sample in a volumetric flask and dilute to 100-mL in hexane.

7.2.4 Analyze the diluted sample according to 7.4 or store the diluted sample in a narrow-mouth bottle with a Teflon lined screw-cap.

7.3 For samples above 100 mg/Kg in concentration, dilute 1000:1 in hexane.

7.3.1 Pipet 0.10 mL of sample into a 100-mL volumetric flask using a 0.10 mL Mohr pipet. Dilute to volume with hexane, stopper and mix.

7.3.2 Using the same pipet as in 7.3.1, deliver 0.10 mL of sample into a tared 10 mL beaker to ± .0001 g. Reweigh the beaker to determine the weight of sample used in 7.3.1.

7.3.3 As an alternative to 7.3.1 and 7.3.2, weigh approximately 0.1 gram to ±.0001 g of sample and in a 100 mL volumetric flask dilute to volume with hexane.

7.3.4 Analyze the diluted sample according to 7.4 or store the diluted sample in a narrow-mouth bottle with a Teflon-lined screw-cap.

7.3.5 If the concentration of PCBs is still too high for the chromatographic system, prepare secondary dilutions from 7.3.1 or 7.3.3 until acceptable levels are obtained.

7.4 Analyze the sample by injecting the hexane mixture into the gas chromatograph using auto injectors or the solvent flush technique[3].

Note: When semi-specific detectors are used, cleanup techniques (See Section 4.2.2) should be routinely incorporated into the analysis scheme prior to injection.

7.4.1 Recommended injection volumes: Halogen specific detector - 4 to 5 µL, electron capture detector-2 to 3 µL. Smaller volumes may be injected when auto injectors are used if the resulting method detection limits are acceptable.

7.5 If the resulting chromatogram shows evidence of column flooding or nonlinear responses due to excess sample, further dilute the sample according to 7.3.5.

7.6 Determine whether or not PCBs are present in the sample by

comparing the sample chromatogram to that of the PCB locator mixture Section 5.8.

7.6.1 If a series of peaks in the sample match some of the retention times of PCBs in the PCB locater mixture, attempt to identify the source by comparing chromatograms of each standard prepared from commercial mixtures of PCBs (See Section 5.6). Proceed to Section 11.4 if the source of PCBs is identified.

7.6.2 If the sample contains a complex mixture of PCBs, proceed to Section 11.5.

7.6.3 If a 1000:1 or higher dilution ratio sample was analyzed and no measurable PCB peaks were detected, analyze an aliquot of sample diluted to 100:1.

7.6.4 If several PCB interference problems are encountered or if PCB ratios do not match standards, proceed to Section 8, use alternate columns, or use GC/MS to verify whether or not the nonrepresentative patterns are due to PCBs.

8. Cleanup - Several tested cleanup techniques are described. Depending upon the complexity of the sample, one or all of the techniques may be required to resolve the PCBs from interferences.

8.1 Acid Cleanup

8.1.1 Place 5.0 mL of concentrated sulfuric acid into a 40-mL narrow-mouth screw-cap bottle. Add 10.0 mL of the diluted sample. Seal the bottle with a Teflon-lined screw-cap and shake for 1 minute.

8.1.2 Allow the phases to separate, transfer the sample (upper

phase) to a clean narrow-mouth screw-cap bottle. Seal with a Teflon-lined cap.

8.1.3 Analyze according to Section 7.4.

8.1.4 If the sample is highly contaminated, a second or third acid cleanup may be employed.

NOTE: This cleanup technique was tested over a period of about 6 months using both electron capture and electrolytic conductivity detectors. Care was taken to exclude any samples that formed an emulsion with the acid. The sample was withdrawn well above the sample-acid interface. Under these conditions no adverse effects associated with column performance and detector sensitivity to PCBs were noted. This cleanup technique could adversely affect the chromatographic column performance for future acid degradable samples.

8.2 Florisil Column Cleanup

8.2.1 Variances between batches of Florisil may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.

8.2.2 Place a 20.0 g charge of Florisil, activated at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70 to 80 mL of hexane. Just before the exposure of the sodium

sulfate layer to air, stop the flow. Discard the eluate.

8.2.3 Add 2.0 mL of the undiluted sample to the column with a 2- mL Mohr pipet. (For viscous samples, cut the capillary tip off the pipet.) Add 225 mL of hexane to the column. Carefully wash down the inner wall of the column with a small amount of the hexane prior to adding the total volume. Collect and discard the first 25.0 mL.

8.2.4 Collect exactly 200 mL of hexane eluate in a 200-mL volumetric flask. All of the PCBs must be in this fraction.

8.2.5 Using the same pipet as in 8.2.2, deliver 2.0 mL of sample into a tared 10 mL beaker weighed to ± 0.001 g. Reweigh the beaker to determine the weight of the sample diluted to 200 mL.

8.2.6 Analyze the sample according to Section 7.4.

8.3 Alumina Column Cleanup

8.3.1 Adjust the activity of the alumina by heating to 200°C for 2 to 4 hours. When cool, add 3% water (wt:wt) and mix until uniform. Store in a tightly sealed bottle. Allow the deactivated alumina to equilibrate at least 1/2 hr before use. Reactivate weekly.

8.3.2 Variances between batches of alumina may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of Alumina can then be adjusted accordingly.

8.3.3 Place a 50.0 g charge of alumina into a Chromaflex column.

Settle the alumina by tapping. Add about 1 cm of anhydrous sodium sulfate. Pre-elute the column with 70 to 80 mL of hexane. Just before exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

8.3.4 Add 2.5 mL of the undiluted sample to the column with a 5-mL Mohr pipet. (For viscous samples, cut the capillary end off the pipet.) Add 300 mL of hexane to the column. Carefully wash down the inner walls of the column with a small volume of hexane prior to adding the total volume. Collect and discard the 0 to 50 mL fraction.

8.3.5 Collect exactly 250 mL of the hexane in a 250-mL volumetric flask. All of the PCBs must be in this fraction.

8.3.6 Using the same pipet as in 8.3.4, deliver 2.5 mL of sample into a tared 10-mL beaker ± 0.001 g. Reweigh the beaker to determine weight of sample diluted to 250 mL.

8.3.6 Analyze the sample according to Section 7.4.

8.4 Silica Gel Column Cleanup.

8.4.1 Activate silica gel at 135°C overnight.

8.4.2 Variances between batches of silica gel may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of silica gel can then be adjusted accordingly.

8.4.3 Place a 25 g charge of activated silica gel into a Chromaflex column. Settle the silica gel by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the silica gel.

8.4.4 Preelute the column with about 70 to 80 mL of hexane. Discard the eluate. Just before the exposure of the sodium sulfate layer to air, stop the flow.

8.4.5 Add 2.0 mL of the undiluted sample to the column with a 2-mL Mohr pipet. (For viscous samples, cut the capillary tip off the pipet.)

8.4.6 Wash down the inner wall of the column with 5 mL of hexane.

8.4.6 Elute the PCBs with 195 mL of 10% diethylether in hexane V:V.

8.4.8 Collect exactly 200 mL of the eluate in a 200-mL volumetric flask. All of the PCBs must be in this fraction.

8.4.9 Using the same pipet as in 8.4.5, deliver 2.0 mL of sample into a tared 10-mL beaker (± 0.001 g). Reweigh to determine the weight of sample diluted to 200 mL.

8.4.10 Analyze the sample according to Section 7.4.

8.5 Gel Permeation Cleanup

8.5.1 Set up and calibrate the gel permeation chromatograph with an SX-3 column according to the instruction manual. Use 15% methylene chloride in cyclohexane (V:V) as the mobil phase.

8.5.2 Place 1.0 mL of sample into a 100-mL volumetric flask, using a 1-mL Mohr pipet. (For viscous samples, cut the capillary tip off the pipet.)

8.5.3 Dilute the sample to volume, using 15% methylene chloride in cyclohexane (V:V).

8.5.4 Using the same pipet as in 8.5.2 deliver 1.0 mL of sample into a tared 10-mL beaker ± 0.001 g. Reweigh the beaker ± 0.001 g to determine the weight of sample used in 8.5.2.

8.5.5 As an alternative to 8.5.2 and 8.5.3 weigh approximately 1 gram ± 0.001 g of sample and dilute to 100.0 mL in 15% methylene chloride in cyclohexane (V:V).

8.5.6 Inject 5.0 mL of the diluted sample into the instrument. Collect the fraction containing the Cl_1 through Cl_{10} PCBs (see operator's manual) in a K-D flask equipped with a 10-mL ampul.

8.5.7 Concentrate the 8.5.4 fraction down to less than 5 mL. Using K-D evaporative concentration techniques.

8.5.8 Dilute to 5.0 mL with hexane, then analyze according to Section 7.4. Be sure to use 100 mL as the dilution volume for the final calculation.

8.6 Acetonitrile Partition

8.6.1 Place 10.0 mL of the previously diluted sample into a 125-mL separatory funnel with enough hexane to bring the final volume to 15 mL. Extract the sample four times by shaking vigorously for one minute with 30-mL portions of hexane-saturated acetonitrile.

8.6.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 mL of distilled water and 40 mL of saturated sodium chloride solution. Mix thoroughly for 30 to 35 seconds. Extract with two 100 mL portions of hexane by vigorously shaking about 15 seconds.

8.6.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100-mL portions of distilled water. Discard the water layer and pour the hexane layer through a

3 to 4 inch anhydrous sodium sulfate column into a 500-mL K-D flask equipped with a 10 mL ampul. Rinse the separatory funnel and column with three 10 mL portions of hexane.

8.6.4 Concentrate the extracts to 6 to 10 mL in the K-D evaporator in a hot water bath, then adjust the volume to 10.0 mL. Be sure to use the correct dilution volume (8.6.1) for the final calculation.

8.6.5 Analyze according to Section 7.4.

8.7 Florisil Slurry Cleanup

8.7.1 Place 10 mL of the diluted sample into a 20-mL narrow-mouth screw cap container. Add 0.25 g of Florisil. Seal with a Teflon lined screw cap and shake for 1 minute.

8.7.2 Allow the Florisil to settle then decant the treated solution into a second container. Analyze according to Section 7.4.

9. Calibration

9.1 Single Point Calibrations - Prepare calibration standards from standard stock solutions in hexane that are close to the unknown in composition and in concentration. When using an electrolytic conductivity detector, if the sample response is in the low level nonlinear detection area, then the calibration point must be within 20% of the sample. The ECD must be operated only within its linear response range.

9.2 As an alternative to 9.1, prepare a calibration curve for each Aroclor or PCB detected in the sample. The standard curve must

contain at least 3 points, two of which must bracket the sample concentration. When using an electrolytic conductivity detector, if the sample response is in a low level nonlinear area of the calibration curve, two of the calibration points must be within 20% of the unknown. The calibration curve must be checked daily, using the Quality Check Sample Section 5.7. If the calibration curve is not within 15 percent of the Quality Check Sample, recalibrate the instrument. It will be necessary to correct electron capture data for recovery (See Section 3.4). Use the recovery value determined the same day the calibration curve was generated. The corrected value must be within 15% of the spike value, otherwise the instrument must be recalibrated.

10. Quality Control

10.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consists of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. After January 1, 1982, ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

10.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 10.2.

10.1.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 10.2.

10.1.3 The laboratory must spike and analyze a minimum of 10 percent of all samples to monitor continuing laboratory performance. This procedure is described in Section 10.4.

10.2 To establish the ability to generate acceptable accuracy and precision in the use of this method, the analyst must perform the following operations.

10.2.1 For each commercial PCB mixture or individual PCB normally measured, select a spike concentration representative of high interest levels in the samples (25 to 75 mg/kg). Using stock standards, prepare a quality control check sample concentrate in issoctane 1000 times more concentrated than the selected concentrations.

10.2.2 Using a microsyringe, add 100 uL of the check sample concentrate to each of a minimum of four 100-mL aliquots of PCB-free oil. A representative waste oil may be used in place of the clean oil, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 7.

10.2.3 Calculate the average percent recovery, (R), and the

relative standard deviation of the concentration found. Waste oil background corrections must be made before R calculations are performed.

10.2.4 Using the appropriate data from Tables 7, 8, and 9, determine the recovery and single operator precision expected for the method and compare these results to the values calculated in Section 10.2.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

10.2.5 After January 1, 1982, the values for R and s must meet method performance criteria provided by the U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, before any samples may be analyzed.

10.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

10.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3 s

Lower Control Limit (LCL) = R - 3 s

where R and s are calculated as in Section 10.2.3. The UCL and LCL can be used to construct control charts[4] that are useful in observing trends in performance. After January 1, 1982, the control limits above must be replaced by method performance criteria provided by the U.S. Environmental Protection Agency.

10.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for waste oil samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of waste oil as described in Section 10.2.2, followed by the calculation of R and s. Alternately, the analyst may use four waste oil data points gathered through the requirement for continuing quality control in Section 10.4. The accuracy statements should be updated regularly.

10.4 The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 10.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for the parameter in all samples processed as part of the same set must be qualified as described in Section 11.9. The laboratory should monitoring the frequency of data so qualified to ensure that it remains at or below 5%.

10.5 Before processing any samples, the analyst should demonstrate through the analysis of a PCB-free oil sample, that all glassware and reagent interferences are under control. Each time a set of samples is analyzed or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against contamination.

10.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogarm, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

10.7 Analyze the quality control check sample Section 5.7 daily before any samples are analyzed. Instrument status checks, calibration curve validation and long term precision are obtained from these data. In addition, response data obtained from the quality control check standard can be used to estimate the concentration of the unknowns. From this information, the appropriate standard dilutions can be determined for single point calibrations.

10.8 Quarterly, analyze an EMSL-Cincinnati Quality Control Sample (Section 5.4.8) of PCBs in oil or whenever new standard dilutions are prepared.

10.8.1 The results of the EMSL Quality Control Sample should agree within 20% of the true value. If they do not, the analyst must check each step in the standard preparation procedure to solve the problem.

11. Calculations

11.1 Locate each PCB in the sample chromatogram by comparing the retention time of the suspect peak to the retention data gathered from analyzing standards and interference free Quality Control Samples. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for each PCB can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.2 If the response for the peak exceeds the working range of the system, dilute according to Section 7.3.5.

11.3 If the measurment of the peak response is prevented by the presence of interferences, further cleanup is required.

11.4 If the parent Aroclor(s) or PCB(s) are identified in the sample, calibrate according to Section 9. The concentration of the PCBs in the sample are calculated by comparing the sum of the responses for each PCB in the standard to the sum of all of the PCBs in the sample. This is particularly important as sample concentrations approach within 20 percent of 50 mg/kg or any other EPA regulated concentration. If calculations are based upon a single PCB peak or upon a small percentage of the total PCB peaks, serious errors may result. Peaks comprising less than 50% of the total can be disregarded only if 1) interference problems persist after cleanup, 2) when the source of PCBs is obvious 3) when the concentration of PCBs are not within ± 20% of an EPA controlled value i.e., 50 mg/kg.

11.4.1 Measure the peak height or peak area of each peak identified as a PCB in 11.1 in both the sample and the standard.

11.4.2 Use the following formula to calculate the concentration of PCBs in the sample:

$$\text{Concentration} \quad \text{mg/Kg} = \frac{B \times V_t}{A \times W}$$

$$A = \frac{\text{Sum of standard Peak Heights (areas)}}{\text{ng of standard injected}} = \text{mm/ng}$$

$$B = \frac{\text{Sum of sample Peak Heights (areas)}}{\mu\text{L injected}} = \text{mm/}\mu\text{L}$$

V_t = dilution volume of sample in mL

W = weight of the sample in grams

11.5 If the parent Aroclor(s) or source of PCBs is not apparent, calculate the concentration according to the procedure of Webb and McCall (5). The concentration of each PCB is determined individually then added together to determine the total PCB content of the sample. Each PCB identified in the sample must be included in these calculations.

11.5.1 Small variations between Aroclor batches make it necessary to obtain standards prepared from a specific source of Aroclors. Primary dilutions of these reference Aroclors will be available in 1981 from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Cincinnati, Ohio 45268.

11.5.2 Analyze a standard mixture of Aroclors 1242, 1254 and 1260 under the conditions shown in Figures 3, 5, and 6. Analyze the sample under the same conditions. Compare the resulting

standard chromatograms to those shown in Figures 3, 5, and 6. Each PCB peak must be resolved as well or better than those shown in the figures. Determine the relative retention time (RRT) of each peak in the standards with respect to p,p'-DDE or assign the RRT shown in the figures to the corresponding peak in the standard. Identify the RRT of each PCB in the sample by comparing the sample chromatogram to the standard chromatograms.

11.5.3 Identify the most likely Aroclor(s) present in the sample, using the Identification Flow Chart Figure 7.

11.5.4 Analyze standards according to Section 9, using the appropriate Aroclors.

11.5.5 Determine the instrument response factor (A) for each individual PCB, using the following formula:

$$A = \frac{\text{Peak Height (area)}}{Ng_1 \times \frac{\text{mean weight \%}}{100}}$$

Ng_1 = Ng of Aroclor standard injected
Obtain mean weight percent from Tables 1 through 6.

11.5.6 Calculate the concentration of each PCB in the sample using the following formula:

$$\text{Concentration mg/Kg} = \frac{B \times V_t}{A \times W}$$

A = Response factor from 11.4.5

B = $\frac{\text{Peak Height (areas) of sample mm/µl}}{\text{µL injected}}$

V_t = dilution volume of sample in mL

W = weight of sample in grams

The concentration of each PCB must be calculated and added together to obtain the total amount of PCBs present.

11.6 Report all data in mg/Kg.

11.7 Round off all data to 2 significant figures.

11.8 Sum all Aroclors and report what was used as the standard. For example, 57 mg/Kg measured as Aroclor 1260 or 57 mg/Kg measured as Aroclors 1242 and 1260.

11.9 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 10.4, data for the affected parameters must be labeled as suspect.

11.10 For electron capture analyses determine the actual recovery for each sample in the uncorrected 40 to 50 mg/kg concentration range (see Section 3.4). Report the corrected value and the recovery.

12. Single Laboratory Accuracy and Precision

12.1 The single laboratory data shown in Tables 7 through 9 were generated using the recommended procedures described in this method to analyze both spiked and nonspiked oil samples of varying degrees of complexity using a halogen specific detector and an electron capture detector. These data were generated by the Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

References

1. Eichelberger, J. W., L.E. Harris, and W. L. Budde, Anal. Chem., 46, 227 (1974).
2. Federal Register, Vol. 41, No. 232, Wednesday, December 1, 1976.
3. White, L. D., et al., AIHA Journal, 31, 225, (1970).
4. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
5. Webb, R.G., and A.C. McCall, J. Chrom. Sci., 11, 366 (1973).

TABLE 1

Composition of Aroclor 1221[a]

RRT[b]	Mean Weight Percent	Relative Std. Dev. [c]	Number of Chlorines [d]	
11	31.8	15.8	1	
14	19.3	9.1	1	
16	10.1	9.7	2	
19	2.8	9.7	2	
21	20.8	9.3	2	
28	5.4	13.9	2	85%
			3	15%
32	1.4	30.1	2	10%
			3	90%
37	1.7	48.8	3	
40			3	
Total	93.3			

[a] Data obtained from (5).

[b] Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[c] Standard deviation of seventeen results as a percentage of the mean of the results

[d] From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 2

Composition of Aroclor 1232[a]

RRT[b]	Mean Weight Percent	Relative Std. Dev. [c]	Number of Chlorines [d]	
11	16.2	3.4	1	
14	9.9	2.5	1	
16	17.8	2.4	2	
20	17.8	2.4	2	
21			2	
28	9.6	3.4	2	40%
			3	60%
32	3.9	4.7	3	
37	6.8	2.5	3	
40	6.4	2.7	3	
47	4.2	4.1	4	
54	3.4	3.4	3	33%
			5	67%
58	2.6	3.7	4	
70	4.6	3.1	4	90%
			5	10%
78	1.7	7.5	4	
Total	94.2			

[a] Data obtained from (5).

[b] Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[c] Standard deviation of four results as a mean of the results.

[d] From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 3

Composition of Aroclor 1242[a]

RRT[b]	Mean Weight Percent	Relative Std. Dev. [c]	Number of Chlorines [d]
11	1.1	35.7	1
16	2.9	4.2	2
21	11.3	3.0	2
28	11.0	5.0	2 25% 3 75%
32	6.1	4.7	3
37	11.5	5.7	3
40	11.1	6.2	3
47	8.8	4.3	4
54	6.8	2.9	3 33% 4 67%
58	5.6	3.3	4
70	10.3	2.8	4 90% 5 10%
78	3.6	4.2	4
84	2.7	9.7	5
98	1.5	9.4	5
104	1.6	20.4	5 85% 6 15%
146	1.0	19.9	5 75% 6 25%
Total	98.5		

[a] Data obtained from (5).

[b] Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[c] Standard deviation of six results as a percentage of the mean of the results.

[d] From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 4

Composition of Aroclor 1248[a]

RRT[b]	Mean Weight Percent	Relative Std. Dev. [c]	Number of Chlorines [d]	
21	1.2	23.9	2	
28	5.2	3.3	3	
32	3.2	3.8	3	
47	8.3	3.6	3	
40	8.3	3.9	3	85%
			4	15%
47	15.6	1.1	4	
54	9.7	6.0	3	10%
			4	90%
58	9.3	5.8	4	
70	19.0	1.4	4	80%
			5	20%
78	6.6	2.7	4	
84	4.9	2.6	5	
98	3.2	3.2	5	
104	3.3	3.6	4	10%
			5	90%
112	1.2	6.6	5	
125	2.6	5.9	5	90%
			6	10%
146	1.5	10.0	5	85%
			6	15%
Total	103.1			

[a] Data obtained from (5).

[b] Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[c] Standard deviation of six results as a percentage of the mean of the results.

[d] From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 5

Composition of Aroclor 1254[a]

RRT[b]	Mean Weight Percent	Relative Std. Dev. [c]	Number of Chlorines [d]
47	6.2	3.7	4
54	2.9	2.6	4
58	1.4	2.8	4
70	13.2	2.7	4 25%
			5 75%
84	17.3	1.9	5
98	7.5	5.3	5
104	13.6	3.8	5
125	15.0	2.4	5 70%
			5 30%
146	10.4	2.7	5 30%
			6 70%
160	1.3	8.4	6
174	8.4	5.5	6
203	1.8	18.6	6
232	1.0	26.1	7
Total	100.0		

[a] Data obtained from (5).

[b] Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[c] Standard deviation of six results as a percentage of the mean of the results.

[d] From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 6

Composition of Aroclor 1260[a]

RRT[b]	Mean Weight Percent	Relative Std. Dev. [c]	Number of Chlorines [d]
70	2.7	6.3	5
84	4.7	1.6	5
98	3.8	3.5	[e]
104			5 60%
			6 40%
117	3.3	6.7	6
125	12.3	3.3	5 15%
			6 85%
146	14.1	3.6	6
160	4.9	2.2	6 50%
			7 50%
174	12.4	2.7	6
203	9.3	4.0	6 10%
			7 90%
232			[f]
244	9.8	3.4	6 10%
			7 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	.6	25.3	8
528	1.5	10.2	8
Total	98.6		

[a] Data obtained from (5).

[b] Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[c] Standard deviation of six results as a mean of the results.

[d] From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[e] Composition determined at the center of peak 104.

[f] Composition determined at the center of peak 232.

TABLE 7
ACCURACY AND PRECISION USING
SPIKED MOTOR OIL

Dilution Ratio	Detector	Method Clean-up	Spike mg/Kg	Aroclor Spike	Ave. Conc. Found mg/Kg	(Precision) Rel. Std. Deviation %	(Accuracy) Percent Recovered	Number of Dilution
00:1	HED	None	30.3	1242	28.2	4.2	93.1	5
00:1	ECD	None	30.3	1242	26.7[a]	5.7	88.1	3
00:1	HED	None	31.1	1260	27.2	2.0	87.5	5
00:1	ECD	None	31.1	1260	23.9	2.2	76.8	3
00:1	HED	8.1	30.3	1242	28.4	11.5	93.7	3
00:1	ECD	8.1	30.3	1242	25.4[a]	6.1	83.8	3
00:1	HED	8.1	31.1	1260	28.1	8.0	90.3	3
00:1	ECD	8.1	31.1	1260	24.3	7.8	78.1	3
00:1	HED	8.2	30.3	1242	30.7	2.4	101	4
00:1	ECD	8.2	30.3	1242	27.3[a]	10.2	90.1	4
00:1	HED	8.2	31.1	1260	30.9	3.6	99.4	4
00:1	ECD	8.2	31.1	1260	31.0	8.6	99.7	4
00:1	HED	8.3	30.3	1242	30.3	8.6	100	3
00:1	ECD	8.3	30.3	1242	28.9[a]	5.0	96.4	3
00:1	HED	8.3	31.1	1260	29.8	4.7	95.8	3
00:1	ECD	8.3	31.1	1260	30.8	6.5	99.0	3
00:1	HED	8.4	30.3	1242	29.4	5.8	97.0	3
00:1	ECD	8.4	30.3	1242	26.4[a]	5.3	87.1	3
00:1	HED	8.4	31.1	1260	29.4	5.2	94.5	3
00:1	ECD	8.4	31.1	1260	23.6	4.5	75.9	3
00:1	HED	8.5	30.3	1242	31.9	8.5	105	3
00:1	ECD	8.5	30.3	1242	23.4[a]	3.0	77.2	2
00:1	HED	8.5	31.1	1260	33.6	9.2	108	3
00:1	ECD	8.5	31.1	1260	30.9	5.5	99.4	3
00:1	HED	8.6	30.3	1242	34.4	3.8	107	4
00:1	ECD	8.6	31.1	1242	23.4[a]	4.4	77.2	4
00:1	HED	8.6	30.3	1260	29.1	4.2	96.7	4
00:1	ECD	8.6	31.1	1260	27.0	4.6	86.7	4

Severe interference problems in elution area of 1242. Measurement based upon only 3 of the 10 normally resolved major peaks. Clean-up techniques 8.1, 8.2, 8.3, 8.4, 8.5, and 8.6 did not improve the quality of the 1242 chromatogram. If this were an unknown sample, it would be impossible to qualitatively identify the presence of Aroclor 1242 using ECD. The HED provided an interference-free chromatogram.

TABLE 8
ACCURACY AND PRECISION USING
WASTE TRANSFORMER FLUIDS

Sample	Dilution Ratio	Detector	Method Clean-up	1260 Spike mg/Kg	Ave.[D] Conc. Found	(Precision) Rel. Std. Deviation %	(Accuracy) Percent Recovered	Number of Dilution
A	100:1	ECD	None	--	22.6	3.6	--	7[B]
A	"	HED	None	--	27.0	1.7	--	7[B]
A	"	ECD	8.1	--	22.8	2.5	--	7[B]
A	"	HED	8.1	--	29.7	1.4	--	7
A	"	ECD	8.2	--	22.4	1.0	--	3[B]
A	"	HED	8.2	--	28.2	2.2	--	3[B]
A	"	ECD	8.3	--	22.7	1.3	--	3[B]
A	"	HED	8.3	--	27.8	2.8	--	3[B]
A	"	ECD	8.4	--	20.9	--	--	1
A	"	HED	8.4	--	30.2	--	--	1
A	"	ECD	8.5	--	23.8	0.3	--	7[B]
A	"	HED	8.5	--	28.6	4.1	--	7[B]
A	"	ECD	None	27.0	45.0	3.3	91	7[B]
A	"	HED	None	27.0	55.2	1.5	102	7[B]
B	1000:1	ECD	None	--	452	0.8	--	7[B]
B	"	HED	"	--	471	1.2	--	7
B	"	ECD	"	455	875	0.5	96	7[B]
B	"	HED	"	455	916	2.0	99	7[B]
C	1000:1	ECD	None	--	284	1.2	--	7
C	"	HED	"	--	300	1.4	--	7
C	"	ECD	"	300	607	3.6	104	7[B]
C	"	HED	"	300	686	3.9	114	7

- dark waste oil
- black waste oil with suspended solids
- clear waste oil
- all samples contained Aroclor 1260
- duplicate analyses made at each dilution

TABLE 9
Accuracy and Precision and Limit of Detection Data
Results of Analyses of Shell Transformer Fluid
Spiked with PCBs at 5.0 and 27 mg/Kg

Electron Capture Method
(100:1 Dilution)

Aroclor	Spike (mg/kg)	Number of Analyses	Avg (mg/kg)	Standard Deviation	% Recovery	MDL[a] (mg/kg)
1221	5.0	7	7.5	0.43	150	1.4
1242	5.0	14	3.8	0.18	76	0.5
1254	5.0	7	4.1	0.08	82	0.2
1260	5.0	14	4.7	0.18	94	0.5

Hall Method
(100:1 Dilution)

Aroclor	Spike (mg/kg)	Number of Analyses	Avg (mg/kg)	Standard Deviation	% Recovery	MDL[a] (mg/kg)
1221	5.0	6	7.5	0.23	150	0.7
1242	5.0	7	5.9	0.17	118	0.5
1254	5.0	6	5.8	0.16	116	0.5
1260	5.0	7	5.4	0.10	108	0.3

Shell Transformer Oil + 27 ppm Aroclor 1260
(100:1 Dilution)

Method	Spike (mg/kg)	Number of Analyses	Avg (mg/kg)	Rel. Std. Deviation %	% Recovery
Electron Capture	27	14	24.0	.70	89
Hall 700-A	27	7	28.3	2.1	105

[a]MDL = Method Detection Limit at 99% confidence that the value is not zero. Note: At these values it would be impossible to identify Aroclor patterns with any degree of confidence. 1 mg/Kg appears to be a reasonable MDL.

$$MDL = t_{(n-1,.99)}(S)$$

where:

MDL = the method detection limit

$t_{(n-1,.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

S = standard deviation of the replicate analyses