Designation: D4059 – 00 (Reapproved 2010)

Standard Test Method for Analysis of Polychlorinated Biphenyls in Insulating Liquids by Gas Chromatography[1]

This standard is issued under the fixed designation D4059; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes a quantitative determination of the concentration of polychlorinated biphenyls (PCBs) in electrical insulating liquids by gas chromatography. It also applies to the determination of PCB present in mixtures known as askarels, used as electrical insulating liquids.

1.2 The PCB mixtures known as Aroclors[2] were used in the formulation of the PCB-containing askarels manufactured in the United States. This test method may be applied to the determination of PCBs in insulating liquids contaminated by either individual Aroclors or mixtures of Aroclors. This technique may not be applicable to the determination of PCBs from other sources of contamination.

1.3 The precision and bias of this test method have been established only for PCB concentrations in electrical insulating mineral oils and silicones. The use of this test method has not been demonstrated for all insulating fluids. Some insulating liquids, such as halogenated hydrocarbons, interfere with the detection of PCBs and cannot be tested without pretreatment.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D923 Practices for Sampling Electrical Insulating Liquids

3. Symbols

3.1 The following symbols are used in this test method:

C —concentration of PCB (ppm by weight) in the insulating test specimen.
C_i —concentration of PCB (ppm by weight) found for the peak, *i*, in the chromatogram of the insulating liquid test specimen.
d —density of the test specimen at 25°C, g/mL.
f_i —relative content of the PCB species associated with each individual peak, *i*, in the chromatogram of the standard Aroclor solution, %.
M —total amount of PCB in the standard test specimen injected into the chromatograph, g.
M_i —amount of PCB represented by peak, *i*, in the chromatogram of the standard Aroclor test specimen, g.
$R_i{}^s$ —response of the detector to PCB components with relative retention time, *i*, in the chromatograms of the standard, *s*, solutions, response may be expressed as peak height, peak area, or integrator counts.
$R_i{}^x$ —response of the detector to PCB components with relative retention time, *i*, in the chromatogram of an unknown test specimen, may be expressed as peak height, peak area, or integrator counts.
$R_p{}^s$ —response of the detector to PCB components in the largest or most cleanly separated peaks, *p*, in chromatograms of standard solutions; may be expressed as peak height, peak area, or integrator counts.
$R_p{}^x$ —response of the detector to PCB components in the largest or most cleanly separated peaks, *p*, in the chromatogram of an unknown test specimen contaminated by a single Aroclor; may be expressed in peak height, peak area, or integrator counts.
ν^s —volume of the standard test specimen injected into the chromatograph, µL.
ν^x —volume of the unknown test specimen injected into the chromatograph, µL.
V —original volume of the test specimen to be analyzed, µL.
V^s —total volume of the diluted standard, mL.
V^x —total volume of the test specimen to be analyzed, µL.
W^x —weight of the test specimen to be analyzed, g.
W^s —weight of the initial standard Aroclor test specimen, g.

4. Summary of Test Method

4.1 The test specimen is diluted with a suitable solvent. The resulting solution is treated by a procedure to remove interfering substances after which a small portion of the resulting solution is injected into a gas chromatographic column. The components are separated as they pass through the column with carrier gas and their presence in the effluent is measured by an electron capture (EC) detector and recorded as a chromatogram. The test method is made quantitative by comparing the sample chromatogram with a chromatogram of a known quantity of one or more standard Aroclors, obtained under the same analytical conditions.

5. Significance and Use

5.1 United States governmental regulations mandate that electrical apparatus and electrical insulating fluids containing

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[1] This test method is under the jurisdiction of Committee D27 onElectrical Insulating Liquids and Gasesand is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

Current edition approved May 15, 2010. Published June 2010. Originally published as a proposal. Last previous edition approved in 2005 as D4059 – 00(2005)$^{\varepsilon1}$. DOI: 10.1520/D4059-00R10.

[2] Registered trademark of Monsanto Co.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

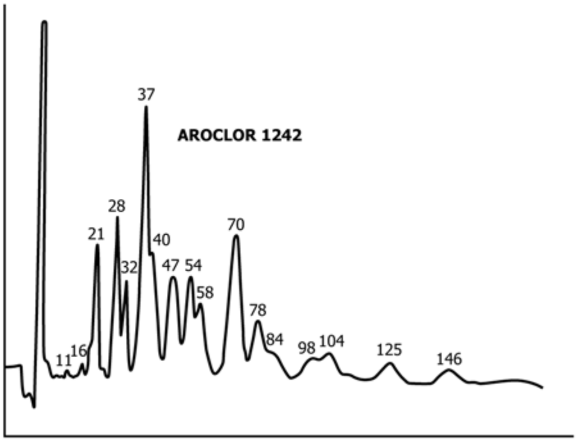

FIG. 1 Column: 3 % OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

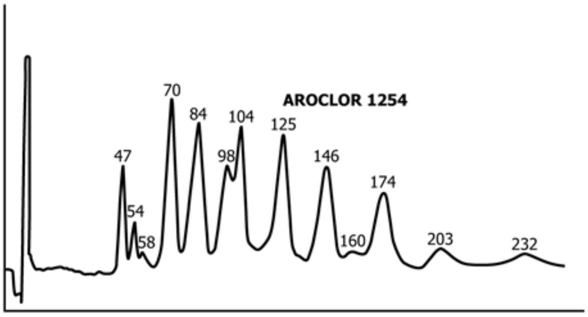

FIG. 2 Column: 3 % OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

PCB be handled and disposed of through specific procedures. The procedure to be used for a particular apparatus or quantity of insulating fluid is determined by the PCB content of the fluid. The results of this analytical technique can be useful in selecting the appropriate handling and disposal procedure.

5.2 Quantification in this technique requires a peak-by-peak comparison of the chromatogram of an unknown specimen with that of standard Aroclor test specimens obtained under identical conditions. The amount of PCB producing each peak in the standard chromatogram shall be known independently.

5.3 The technique described is based on data for standard chromatograms of Aroclors 1242, 1254, and 1260 obtained using specific chromatographic column packing materials and operating conditions.[4] Relevant chromatograms are reproduced in Fig. 1, Fig. 2, and Fig. 3[5], for isothermal packed columns and in Figs. X4.1 through X4.3) for temperature programmed mega-bore capillary columns. Each peak is identified by its retention time relative to that of a standard. The types and amounts of PCB associated with each peak have been determined by mass spectroscopy and are given in Table 1, Table 2, and Table 3.[4] Other chromatographic operating conditions, and in particular, other column packing materials, may give different separations. The data given in the tables should not be used if chromatograms of the standards differ significantly from those shown in the figures. The peaks in such standard chromatograms shall be independently identified and quantified.

5.4 Different isomers of PCB with the same number of chlorine substituents can cause substantially different responses from EC detectors. Mixtures of PCB containing the same amount of PCB, but with a different ratio of isomers, can give quite different chromatograms. This technique is effective only when the standard PCB mixtures and those found in the

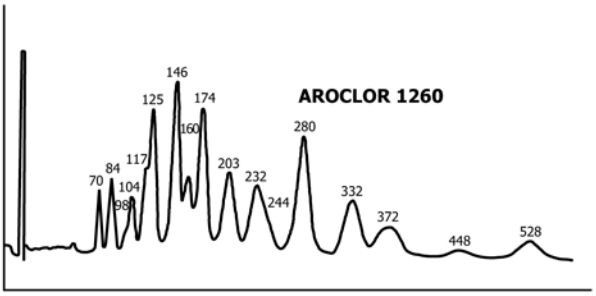

FIG. 3 Column: 3 % OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

TABLE 1 Composition of Aroclor 1242[6]

RRT [A]	Mean Weight, %	Relative Standard Deviation [B]	Number of Chlorines [C]
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	2.3	16.4	5
125	1.6	20.4	5 ⎫ 85 % 6 ⎭ 15 %
146	1.0	19.9	5 ⎫ 75 % 6 ⎭ 25 %
Total	98.5		

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

[B] Standard deviation of six results as a percentage of the mean of the results (*sic* coefficient of variation).

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

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[4] Webb, R. G., and McCall, A. C., *Journal of Chromatographic Science*, Vol 11, 1973, p. 366.

[5] Reproduced from the *Journal of Chromatographic Science* by permission of Preston Publications, Inc.

TABLE 2 Composition of Aroclor 1254[6]

RRT[A]	Mean Weight, %	Relative Standard Deviation[B]	Number of Chlorines[C]
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 % 6 } 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] Retention time relative to *p,p*'-DDE = 100. Measured from first appearance of solvent.

[B] Standard deviation of six results as a percent of the mean of the results (*sic* coefficient of variation).

[C] From GC-MS data. Peaks containing mixtures of isomers are bracketed.

TABLE 3 Composition of Aroclor 1260[6]

RRT [A]	Mean Weight %	Relative Standard Deviation [B]	Number of Chlorines [C]
70	2.7	6.3	5
84	4.7	1.6	5
	3.8	3.5	
98 104			5 } [D] 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 %
232 244	9.8	3.4	6 } [E] 7 } 10 % 90 %
			7
280	11.0	2.4	8
332	4.2	5.0	8
372	4.0	8.6	8
448	0.6	25.3	
528	1.5	10.2	
Total	98.6		

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

[B] Standard deviation of six results as a mean of the results (*sic* coefficient of variation).

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

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

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

unknown test specimen are closely related. Aroclors 1242, 1254, and 1260 are adequate standards because they have been found to be the most common PCB contaminant in electrical insulating oils.

6. Interferences

6.1 Electron capture detectors respond to other chlorine containing compounds and to certain other electrophilic materials containing elements such as other halogens, nitrogen, oxygen, and sulfur. These materials may give peaks with retention times comparable to those of PCBs. Most common interferences will be removed by the simple pre-analysis treatment steps detailed within this test method. The chromatogram of each analyzed test specimen should be carefully compared with those of the standards. The results of an analysis are suspect if major extraneous or unusually large individual peaks are found.

6.1.1 Data acquisition and treatment by electronic integrators or other instrumental means easily permits the unrecognized inclusion of interferences in the quantification of results. Visual examination of chromatograms by those skilled in the method should be made to obtain maximum accuracy.

6.2 The sensitivity of EC detectors is reduced by mineral oils. The same amount of oil must pass through the detector in both calibration and analysis to ensure a meaningful comparison for quantification. Sample, standard dilutions, and injection volumes should be carefully chosen in this test method to match the interference of the oil.

6.2.1 The sensitivity of EC detectors is not significantly affected by silicone liquids. Evaluate the need for matrix matching within your analytical scheme before proceeding. Mineral oil should be absent from standards and dilution solvents used in the analysis of silicone test specimens.

6.3 Residual oxygen in the carrier gas may react with components of test specimens to give oxidation products to which EC detectors will respond. Take care to ensure the purity of the carrier gas.

6.3.1 The use of an oxygen scrubber and a moisture trap on both the carrier gas and the detector makeup gas is recommended to extend the useful column and detector life.

6.4 Trichlorobenzenes (TCBs) are often present with PCBs in insulating oils and will generate a response in the EC detector. These appear earlier than the first chlorinated biphenyl peak ($i = 11$) in most cases and should be neglected in this analysis. Unusually high concentrations of TCBs may be present occasionally and may obscure the lower molecular weight PCB peaks.

6.5 Components of high-molecular weight mineral oils may have longer than normal retention on the chromatography column, resulting in “ghost” peaks or excessive tailing. These conditions interfere with the data system's ability to accurately quantify material at levels approaching the method detection limit. Inject reagent grade solvent blanks until the chromatogram's baseline returns to normal before continuing with the analysis.

7. Apparatus

7.1 *Instruments:*

7.1.1 *Gas Chromatograph,* equipped with oven temperature control reproducible to 1°C and with heated injection port.

7.1.2 *Means to Record the Chromatogram,* such as a pen recorder, preferably coupled to a digital integrator to determine peak areas. An automatic sample injector may be used.

7.1.3 *Injector,* stainless steel construction, equipped with suitable adapters to permit use of direct column injection, packed column injection, or split/splitless capillary injection. All metal surfaces shall be lined with glass.

7.1.3.1 Mega-bore capillary columns may be effectively utilized on a packed column injector by replacing the standard glass liner with a tapered capillary liner. While capillary conversion kits are commercially available, this specialized hardware will not routinely be necessary when working with mega-bore columns.

7.1.4 *Detector*—High-temperature ^{63}Ni electron capture detector with sufficient sensitivity to allow 50 % full-scale recorder deflection with a sample containing 0.6 ng or less of phosphorothioic acid o-(2-chloro-4-nitrophenyl) o,o-dimethylester ("dicapthon"). The detector must be operated within its linear response range and the detector noise level should be less than 2 % of full scale.

NOTE 1—Other detectors may be used. Refer to Appendix X1.

7.2 *Column,* made of glass or fused silica, packed with appropriate materials. A precolumn may be used to extend the analytical column's useful life.

7.2.1 A 1.83-m (6-ft) long, 6.35-mm (0.25-in.) outside diameter, 2 to 4-mm (0.08 to 0.16 in.) inside diameter glass column packed with 3 % OV1[6] on 80/100 mesh Chromosorb [7] has been found useful. Other column lengths may be used, provided they give adequate separation of the PCB components. Packings OV101[6] and DC200[8] on Chromosorb WAW[7] also give separations with which the data in Table 1, Table 2, and Table 3 may be used.

7.2.2 A fused silica wide-bore capillary column such as a 15-m mega-bore (0.53-mm ID) column having a 1.5-µm film of polydimethylsiloxane has been shown to approximate a packed column system and generate chromatograms with similar separations thus allowing the use of the Webb & McCall calibration data.[4]

7.3 *Volumetric Flasks and Pipettes,* appropriate for making dilutions.

7.4 *Precision Syringe,* glass, graduated to 0.1 µL.

7.5 *Vials,* glass, with PTFE-lined aluminum caps.

7.6 *Analytical Balance or Hydrometer,* capable of measuring densities of approximately 0.9 g/mL.

8. Chromatograph Operation Conditions

8.1 *General*—The characteristics of individual chromatographs and columns differ. Particular operating conditions should be chosen so as to give the separations shown in Fig. 1, Fig. 2, and Fig. 3 for Aroclors 1242, 1254, and 1260. Retention times of the peaks should be determined relative to 1,1' bis (4-chlorophenyl) ethane (*p*,*p*'-DDE) to identify the individual peaks with those shown in the chromatograms and listed in the tables. General ranges of temperatures and flow rate with which satisfactory separations have been obtained are listed.

8.2 *Column Temperature*—Isothermal temperatures between 165 and 200°C have been found suitable when using packed column (see Fig. 1). Temperature programming of megabore columns over the range of 165 to 300°C has been found to enhance resolution and decrease the analytical run time, while generating a chromatogram suitable for use with the packed column GC/MS data[4] (see Appendix X4).

NOTE 2—Typical chromatographic conditions for a temperature programmed mega-bore capillary column are included in Appendix X4 with the sample chromatograms.

8.3 *Detector Temperature*—Control the detector isothermally above the maximum oven analysis temperature. A suitable temperature is typically between 280 and 400°C. Follow instrument manufacturer's instructions to prevent exceeding the maximum allowable temperature for the radioactive foil.

8.4 *Injection Port Temperature* —Maintain the injection port isothermally above a minimum of 250°C.

8.5 *Carrier Gas*—Ultrahigh purity 5 % methane-95 % argon mixture (P-5) or nitrogen shall be utilized for packed column chromatography. Optimum performance for mega-bore/capillary columns is achieved with ultrahigh purity hydrogen or helium as the carrier gas and P-5 or nitrogen for detector makeup. A device that will remove oxygen and water vapor from the carrier gas should be used in order to maximize detector sensitivity.

8.6 *Flow Rates*—Column flow rates of 8 to 60 mL/min and, if used, a detector makeup flow of 15 to 30 mL/min have been found satisfactory. When hydrogen or helium are used as a carrier gas, a makeup flow two to three times the carrier flow will be required to obtain sufficient detector sensitivity.

9. Reagents and Materials

9.1 *Standards*—Sample quantities, or analyzed solutions, of Aroclors 1242, 1254, and 1260.[9]

9.2 *Insulating Oil,* fresh unused, of the type being analyzed, PCB-free.

NOTE 3—Mineral insulating oils with a viscosity approximately 10 cSt at 40°C are produced by a number of petroleum companies and have been found suitable for this purpose.

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[6] Registered trademark of Ohio Valley Specialty Co.

[7] Registered trademark of Johns-Manville Product Corp.

[8] Registered trademark of Dow-Corning Co.

[9] Available from the Floridin Co., Three Penn Center, Pittsburgh, PA 15235, or from chromatographic material supply companies.

9.3 *Solvent—n-Hexane*, Heptane or 2,2,4-trimethylpentane (*iso*octane), pesticide grade.

9.4 *Sulfuric Acid,* concentrated, AR grade.

9.5 *Adsorbent* for polar, electrophilic impurities.

NOTE 4—Florisil® (60/100 mesh)[9] has been found suitable for this purpose. Before use, activate each batch by heating overnight at 130°C in a foil-covered glass container. Florisil® heated to appreciably higher temperatures can absorb some PCB. Test the effect of each activated batch on a standard Aroclor solution.

9.6 *Dicapthon* [phosphorothioic acid-O(2-chloro-4-nitrephenyl)-O,O-dimethylester] to determine detector sensitivity.

9.7 *p, p'-DDE* [1,1'-bis(4-chlorophenyl)ethane] to establish relative retention times.

NOTE 5—Mixtures of Aroclors 1242, 1254, and 1260 may be used conveniently for standards.

10. Sampling

10.1 Obtain the test specimen of oil in accordance with Practices D923.

11. Calibration

11.1 Chromatograms of Aroclors 1242, 1254, and 1260 together contain all the peaks normally found in Aroclor mixtures.[4] These three materials may, therefore, be used as standards for routine quantitative analysis of PCB contamination of insulating fluids. Other Aroclors (for example 1016, 1248, etc.) standards may be useful for identification purposes, but are not needed in quantifying the results.

11.2 Aroclor 1242 contains virtually no PCB substituted with seven or eight chlorines and Aroclor 1260 contains virtually no mono-, di-, tri-, or tetrachlorobiphenyls. Analysis of mixtures of the total range of mono- to octa-substituted biphenyls requires calibration based on standard test specimens of Aroclor 1242, Aroclor 1254, and Aroclor 1260.

11.3 Dissolve a carefully weighed amount of a standard Aroclor in a measured amount of solvent (see 11.3.1 and 11.3.2) to give a solution containing approximately 1 mg/mL. Additional dilutions may be required to obtain a working stock solution for preparation of working standards. The exact weight of the Aroclor and the total volume of the final solution should be recorded as W^s, g and V^s, mL.

11.3.1 *Mineral Insulating Oil Test Specimens*—Use a stock solution of mineral oil in solvent to prepare standards for analysis of mineral oil test specimens, made by dissolving 10 to 20 g of the appropriate mineral insulating oil per 1 L of pesticide-grade solvent. The precise amount of oil should be chosen to give the same solvent-to-oil ratio in standards as that to be obtained on diluting test specimens to be analyzed (see 12.3). The ratio of solvent-to-oil should not be less than 50:1.

11.3.2 *Silicone Insulating Liquid Test Specimens*—Use pesticide-grade solvent alone to prepare standards for analysis of silicone liquid test specimens.

11.3.2.1 The most convenient method of preparing the standard for injection is to dilute a commercially available solution of known concentration. Otherwise, it is necessary to prepare the standard by progressive dilutions. The amount of oil in the stock solution may require adjustment if the commercial standard solution is very dilute.

11.4 Inject a volume, v^s , µL, of the diluted Aroclor standard into the chromatograph. Recommended injection volumes range from 1 to 5 µL, depending on individual detector response and anticipated sample injection volume (12.5). The quantity of PCB injected, M, g, is as follows:

$$M = \frac{W^s}{V^s} \times v^s \, 10^{-3} \text{ g} \tag{1}$$

Identify each peak by comparison with the relative retention times given in Table 1, Table 2, and Table 3 or by comparison with the chromatograms in Fig. 1, Fig. 2, and Fig. 3. The quantity of PCB represented by each peak, M_i, g, is

$$M_i = M \times f_i \times 10^{-2} \tag{2}$$

11.4.1 Values of f_i are given in Table 1, Table 2, and Table 3.

11.4.2 Values of M should be less than 10 ng to avoid overloading the detector with a resulting loss in sensitivity.

12. Procedure

12.1 *Preparation*—Equilibrate the chromatograph to the conditions recommended in Section 8. Clean all glassware and syringes by repeated rinsing in pesticide grade solvent. Ensure that a satisfactory level of cleanliness has been obtained by injecting aliquots of the solvent washings into the chromatograph. A solvent peak will be recorded, but the chromatogram should not contain any peaks with a retention time greater than 1 min.

12.2 *Standardization*—Use the standard solution of Aroclor(s) as prepared in 11.3 to obtain standard chromatograms. Measure and record values of the detector response, $R_i^{\,s}$, and calculate the values for M_i (11.4).

12.3 *Sample Preparation*—Weigh 0.1 to 0.2 gm of the test specimen into a volumetric flask and dilute to volume with solvent (9.3). Dilute the test specimen by a minimum solvent-to-sample ratio of 50:1. Record the weight, W^x g, of the test specimen. Record the total volume of the diluted test specimen, V^x, mL.

12.3.1 It may be necessary to further dilute specimens containing large amounts of PCB to ensure that the EC detector remains within its linear response range. Adjust the solvent-to-oil ratio for mineral oil test specimens to match the solvent-to-oil ratio of the standard. This can be done conveniently by using the stock oil-solvent solution in making further secondary dilutions.

12.3.2 Prior approximate analysis to estimate PCB content is helpful at this stage in deciding the appropriate dilution.

12.3.3 Alternatively, the volume, V , mL, and density, d(g/mL), of the test specimen may be measured and recorded. Measure the volume by a properly calibrated pipet or syringe. The density at room temperature of mineral oils in current use may be assumed to be 0.89 g/mL in routine analysis with a loss in accuracy of 2 to 3 %, at most. The typical density of silicone insulating liquid has been found to be 0.96 g/mL.

12.4 *Removal of Interferences:*

12.4.1 *Adsorbent Treatment*—Place approximately 0.25 g of adsorbent in a clean glass vial. Pour the solution prepared in 12.3 into the vial and seal the vial with the lined cup. Shake thoroughly. Allow the adsorbent to settle and decant the treated solution into a second vial. Use this solution for analysis.

12.4.2 *Acid Treatment*—Carefully place a volume of concentrated sulfuric acid approximately equal to one half of that of the diluted test specimen into a clean glass vial. Pour the solution prepared in 12.3 in the vial and seal the vial with the lined cap. Shake thoroughly. Allow the sulfuric acid phase to separate and settle and decant the upper sample phase into a second vial. Use this solution for analysis.

12.4.3 Acid treatment alone has been found to be effective for silicone test specimens and for most mineral oil test specimens. Machine shaking for 10 min, followed by standing for 15 min to allow the phases to separate in the vial is often adequate. Separation of the acid and test specimen can be enhanced by centrifuging. Treatment with adsorbent, alone or following treatment with acid, is effective in removal of interferences from some mineral oil test specimens. Interferences can also be removed by other treatments. Refer to Appendix X2.

12.5 *GC Analysis*—Inject 1 to 5 µL (v^x) of the diluted sample into the chromatograph. Record the chromatogram at the same attenuation setting and chart speed as used in the standardization procedure. Additional dilutions may be necessary to bring the chromatogram on scale.

12.5.1 The volume ν^x for mineral oil test specimens should be the same as the volume ν^s used for calibration in 11.4, so that the EC detector responds to the same volume of oil with both injections.

13. Calculations

13.1 Measure the response, R_i^x (peak height or area, integrator counts), for each peak common to both the chromatogram of the test specimen being analyzed and that of the relevant standard obtained under the same chromatographic conditions. Calculate the concentration of PCB resulting in each peak, *i*, in the chromatogram of the sample being analyzed from the following equation.

$$C_i = M_i \times \frac{R_i^x}{R_i^s} \times \frac{1}{v^x} \times \frac{V^x}{W^x} \times 10^6\text{, ppm} \quad (3)$$

Calculate the total PCB content, *C*, by summing the concentrations associated with each peak in the chromatogram, as follows:

$$C = \sum_i C_i \quad (4)$$

13.1.1 Standard and appropriate ranges of peak retention times ($a \leq i \leq b$) are described in 13.2 and 13.3.

NOTE 6—($V \times d$) may be used in place of W^x. See 12.3.3.

13.2 When the chromatogram of a test specimen being analyzed clearly shows it to contain only a single Aroclor (1242 or 1254, or 1260), calculate the PCB content using the response, R_i^s, found in the chromatogram of a comparable single Aroclor standard and the values of PCB content associated with the same peaks in the chromatogram of that standard (Table 1, Table 2, or Table 3). The relevant peaks for Aroclor 1242 have relative response times of $11 \leq i \leq 146$; for Aroclor 1254, $47 \leq i \leq 232$, and for Aroclor 1260, $70 \leq i \leq 528$.

13.2.1 The higher resolving power of mega-bore columns may result in additional peaks beyond those identified within the Webb & McCall paper.[4] Except in those specific instances where an identified peak is obviously resolved into two similarly sized peaks requiring grouping together to address the entire assigned mass, daughter or satellite peaks may be ignored without significant impact on the final calculated value. The assumption is made that by assigning the entire mass to the major or parent peak and ignoring smaller peaks, a multi-level calibration will generate more consistent results.

13.2.2 A simplified, but more approximate calculation may be made when the test specimen contains only a single Aroclor. Calculate PCB content as follows:

$$C = M \times \frac{R_p^x}{R_p^s} \times \frac{1}{\nu^x} \times \frac{V^x}{W^x} \times 10^6\text{ ppm} \quad (5)$$

where R_p^x and R_p^s are the responses of the larger or more cleanly separated of the peaks in the chromatograms of the test specimen being analyzed and of the standard. The total PCB content calculated in this way may be incorrect, because the PCB content reflected by any individual peak has been reduced or relatively enhanced by specific PCB removal processes. The response of that particular peak may have been enhanced by unremoved impurity, or the response of that particular peak may have been affected by some instrumental anomaly. The reported result should be the average of that calculated for a minimum of three peaks in the chromatogram of the test specimen being analyzed. This simplified calculation should not be used in circumstances where maximum accuracy is required.

13.3 The PCB content of test specimens containing mixtures of Aroclors should be calculated using standards of all three Aroclors. The PCB concentrations measured by peaks $i = 11$ through 78 should be calculated in accordance with 13.2 using values of M_i and R_i^s derived from an Aroclor 1242 standard; those measured by peaks $i = 84$ through 174 using values derived from an Aroclor 1254 standard; and those measured by peaks $i = 203$ through 528 using values derived from an Aroclor 1260 standard. The total PCB content is the summation of the concentrations measured by all the peaks in the chromatogram as follows:

$$C = \sum_i C_i \quad (6)$$

where:

i = 11 to 78 + 84 to 174 + 203 to 528.

13.3.1 The retention-time windows are convenient for the purpose of quantifying total PCB content in mixtures. Peaks in the chromatogram of the unknown test specimen are then compared with comparable peaks in the most relevant standard chromatogram. However, the PCB content in the window $i = 11$ to 78 is not the total content of Aroclor 1242 because Aroclor 1242 also contains PCBs having longer retention times. Similarly, the Aroclor 1254 and 1260 concentrations are not defined by the PCB contents resulting from the two longer retention-time windows. More complex proportionating procedures are needed to calculate individual Aroclor concentrations in test specimens containing mixtures. This method is directed toward determining the total PCB content.

13.3.2 A skilled analyst may readily recognize the components of a mixture of Aroclors found in an oil test specimen. However, calculation of the individual concentrations of the components is inherently somewhat imprecise because of the overlap of peaks in the chromatograms of the several Aroclors. It is recommended that the total PCB content be calculated to the nearest part per million and the relative ratios (1:1, 3:1, 1:2, etc.) of the individual Aroclors present be noted. An impression of undue accuracy in the determination of individual Aroclors is avoided.

NOTE 7—The response factors (M_i/R_i^s) for peaks with $i = 117$, 146, and 174 in the chromatograms of Aroclor 1254 and 1260 are somewhat different. Calculation of the concentrations of peaks $84 \leq i \leq 174$ should be based on the use of Aroclor 1260 as the standard if Aroclor 1254 is clearly a minority component (that is, if peak (shoulder) 117 is distinct; if peak 98 is indistinct; if the height of peak 104 is distinctly less than that of peak 84, etc.) and if maximum accuracy is required.

NOTE 8—Calculation of PCB content based on a mixed standard (11.2 (Note 7)) is useful in the routine analysis of mixtures containing Aroclor 1254 and 1260. The differences due to different response factors are minimized using the mixed standard.

14. Report

14.1 Report the following information:

14.1.1 The results in parts per million (by weight) of PCB in the insulating fluid.

14.1.2 The Aroclor(s) used as the standards.

14.1.3 Indicate the type of Aroclor(s) present if possible and desired.

15. Precision and Bias

15.1 The precision, bias, and lower limit of detection have been evaluated by a statistical examination of the results of separate interlaboratory tests of mineral oil and silicone test specimens. The data was generated using packed column chromatography under isothermal conditions on mineral oil[10] and silicone liquid.[11] Additional data was obtained using megabore column chromatography with temperature programming on mineral oil.[12]

15.2 *Repeatability*—the difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, with normal and correct operation of the test method, was found to vary with PCB level. The repeatability interval at the 95 % confidence level, $I(r)_{0.95}$, can be represented by:

$$I(r)_{0.95} = k(r) \times (X_{\text{mean}})^{0.75} \tag{7}$$

where *k(r)* for mineral oil is 0.32 using packed columns and 0.35 using megabore columns; and 0.64 for silicone liquids using packed columns. The repeatability interval of the results of the round robin tests can be typified as follows:

PCB Level, ppm	Repeatability Interval-$I(r)_{0.950}$, ppm Oil-packed	 Oil-megabore	 Silicone-packed
5	1	1	2
50	6	7	12
500	34	37	68

15.3 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, with normal and correct operation of the test method, was found to vary with PCB level. The reproducibility interval at the 95 % confidence level, $I(R)_{0.95}$, can be represented by

$$I(R)_{0.95} = k(R) \times (X_{\text{mean}})^{0.75} \tag{8}$$

where *k(R)* for mineral oil is 1.03 for packed columns and 0.79 for megabore columns; and 1.34 for silicone liquids using packed columns. The reproducibility interval of the results of these round robin tests can be typified as follows:

PCB Level, ppm	Reproducibility Interval-$I(R)_{0.95}$, ppm Oil-packed	 Oil-megabore	 Silicone-packed
5	3	3	4
50	19	15	25
500	109	84	142

15.4 *Bias*—The bias of this test method was evaluated by comparing the mean value found for each test specimen by several laboratories with the known amount added to that test specimen.

15.4.1 For packed columns, the average bias for oil test specimens was as follows:

PCB Level, ppm	Bias, ppm
0–10	0
35–75	–1
380–500	–4

15.4.2 For packed columns, the average bias for silicone test specimens was as follows:

PCB Level, ppm	Bias, ppm
0–10	1
35–100	2
440	8

15.4.3 The bias when using megabore columns could not be determined from the data of the interlaboratory round robin because the“ true values” of the spiked additions were questionable.

15.5 *Method Detection Limit*—MDL is defined here as the minimum concentration of an analyte that can be reported with 95 % confidence that the value is above zero. The MDL was determined to be 2 ppm PCB in both mineral oil and silicone liquids when using packed columns, and 1 ppm PCB in mineral oil when using megabore columns.

15.5.1 The MDL values have been determined from the reproducibility results of the interlaboratory study on test specimens containing less than 10 ppm PCB. It should be noted that a value of the MDL for an individual laboratory may be calculated from the results of *n* replicate analyses on a test specimen containing about 5 ppm PCB using the following equation:[13]

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[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:D27-1004.

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:D27-1005.

[12] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:D27-1013.

[13] Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L.,“ Trace Analysis for Wastewaters,” *Environmental Science and Technology*, Vol 15, pp. 1426–1435 (1981).

$$MDL_{0.95} = t_{(n-1,\ 0.95)} \times S \quad (9)$$

where:

$t_{(n\text{-}1,\ 0.95)}$ = student's t value for n-1 and a confidence level of 95 %,
n = number of replicates, and
S = standard deviation of n replicate analyses. A value of the MDL for an individual laboratory may differ from the MDL values reported in these collaborative studies.

16. Keywords

16.1 gas chromatography; PCBs; polychlorinated biphenyls; transformer insulating liquids; transformer mineral oils; transformer silicone liquids

APPENDIXES

(Nonmandatory Information)

X1. OTHER DETECTORS

X1.1 Halogen-specific electrolytic conductivity (HE) detectors are available and have been found to be useful. Their use is not affected by the presence of oil or nonhalogen-containing interferences. Differing isomer responses are reduced. It is difficult to maintain reliable response and sensitivity of HE detectors. General experience has shown that the EC detector is more easily optimized, more reliable, and more sensitive. Therefore, the EC detector is the detector of choice in this method for the routine analysis of PCB in transformer oils. The HE detectors should be considered in other circumstances.

X2. ALTERNATIVE PROCEDURES FOR REMOVAL OF INTERFERENCES

X2.1 Interferences may be removed by shaking the diluted test specimen with a volume of concentrated sulfuric acid equal to one half of the volume of the diluted test specimen. The acid phase is then allowed to separate, and the oil-solvent phase analyzed in accordance with the procedure described in 12.5. Treatment with Florisil® is a part of the method chosen because the solid is noncorrosive and may be more easily handled and its disposal is more convenient. Sulfuric acid may react with components of the oil to give interfering substances. A combination of treatment with solid adsorbent and acid may be beneficial in some cases.

X2.2 Removal of interferences using a Florisil® packed microcolumn has been found to be effective as an alternative to the shaking procedure. Insert a glass wool plug into the wide end of a heavy glass wall Pasteur pipette (146 mm long and 7 mm in outside diameter). Tamp down the glass wool to the narrow end of the pipette and add Florisil® to form a 35-mm high column. A second glass wool plug is tamped down on the top of the column. Activate the adsorbent by heating the pipette at 130°C overnight (the activated column store at 130°C for prolonged periods before use). Elute the microcolumn with 2 mL of oil-solvent standard solution immediately before use. Fifty to one hundred microlitres of test specimen are transferred quantitatively to the top of the column. The column is then eluted with 5 to 8 mL of the oil-solvent standard solution which is collected. The eluant is diluted with oil-solvent standard solution to at least a 50:1 solvent-to-oil ratio. The diluted test specimen is analyzed in accordance with 12.5.

X3. ALTERNATIVE METHODS FOR QUANTIFYING PCBs

X3.1 Many other methods are available for quantifying PCBs in a variety of background matrices. Some of these methods may be appropriate for determining PCBs in petroleum-based insulating liquids and synthetics, while others are suited for other test specimen backgrounds. Three alternative methods are compared with this test method for sample matrix, clean-up, chromatographic column, detector type, detection limits, baseline quench correction, and a comments section in Table X3.1.

TABLE X3.1 Comparison of Alternate Methods

Category	ASTM D4059	EPA[A]	NIST[B]	AOAC[C]
Sample Matrix	insulating liquids	transformer and waste oil	hydrocarbons	food products, paper agricultural materials
Sample Clean-up	Florisil, acid	acid, Florisil, silica gel	high pressure liq chrom	solvent partition, Florisil
Column	packed	packed	capillary	packed
Detector	ECD	ECD or HECD	ECD	ECD
Detection Limits, ppm	2[D]	1	1[E]	unknown
Baseline Quench	addition of sample matrix	no provision	clean-up removes quench	no provision
Comments	lacks quality control provision	quality control provision	exten-clean-up provision	not specific for insulating liquids

[A] Method 600⁄4-81-045, US Environmental Protection Agency.

[B] Method for Standard Reference Materials (SRM), National Bureau of Standards.

[C] Official Methods of Analysis of Association of Official Analytical Chemists (AOAC), Section 29.

[D] See Note 22.

[E] Based on detector signal-to-noise ratio.

X4. MEGABORE CHROMATOGRAMS

X4.1 Chromatograms presented (See Figs. X4.1-X4.3) are examples obtained from a mega-bore capillary column optimized to simulate packed column resolution. Actual chromatograms were obtained from a Perkin Elmer Autosystem Gas Chromatograph equipped with an autosampler, packed column injector, mega-bore column adapter, a mega-bore column liner, and an EC detector. A helium flow of 12 mL/min was utilized as the carrier gas with a nitrogen makeup of 32 mL/min to the ECD detector.

X4.2 Temperature profile was set as detector zone 400°C, injector zone 275°C, initial oven 190°C hold for 1 min, ramped to 225 at 11°C/min hold for 1 min, and then ramp to 290°C at 17°C/min and hold for 1 min. Peak identifiers have been added to the chromatographs to aid in the comparison to the referenced document.[4] These labels are not true relative retention values and the actual retention times will vary with instrument conditions. Complete references for this work may be found within the research report.

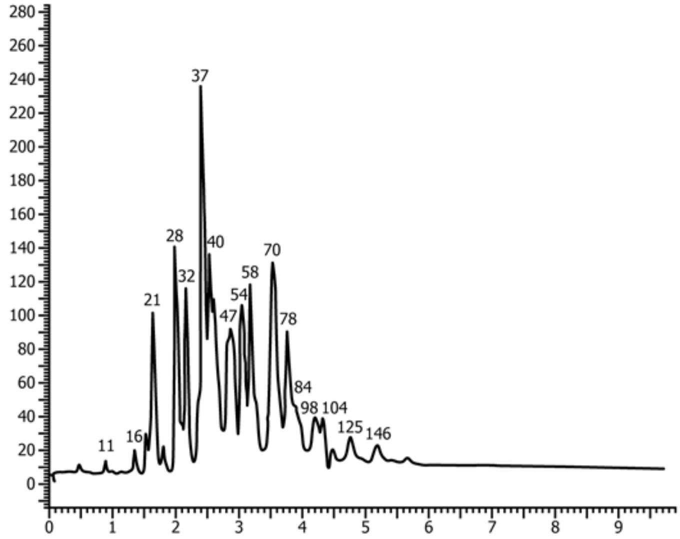

FIG. X4.1 Aroclor 1242

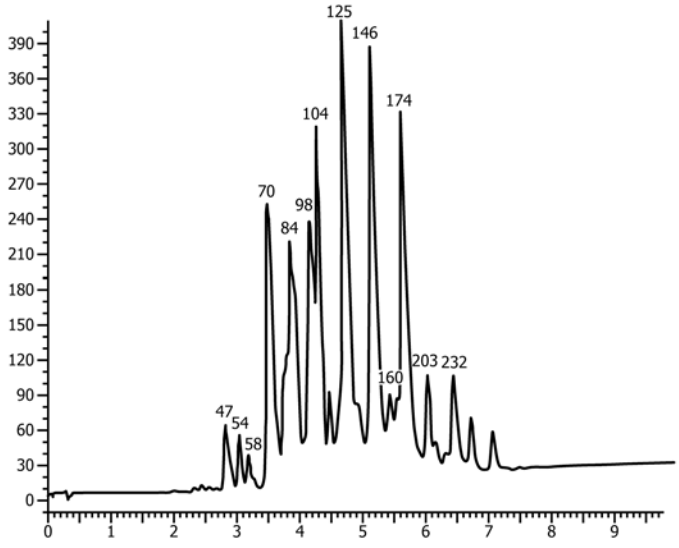

FIG. X4.2 Aroclor 1254

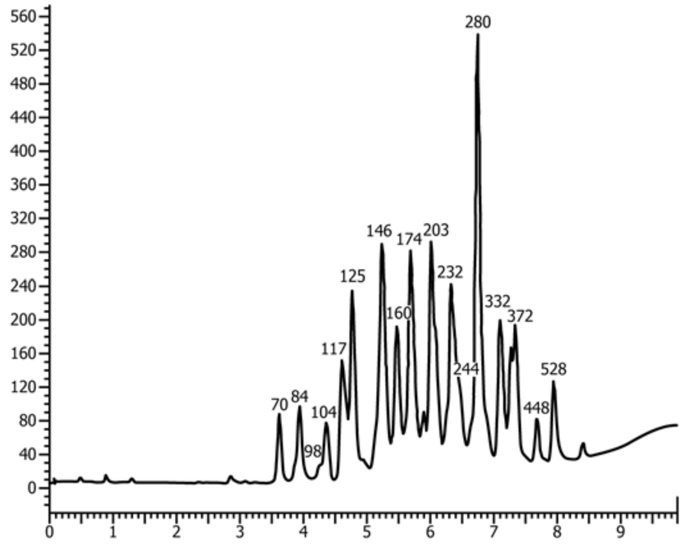

FIG. X4.3 Aroclor 1260

X5. MEGABORE COLUMN DECONTAMINATION[14]

X5.1 One of the most common causes of column performance degradation is contamination resulting from residue left on the column from dirty test specimens. This degradation can result in loss of resolution, peak shape problems, or baseline disturbances resembling excessive bleed. Solvent rinsing a capillary column will remove most contaminates and restore column performance. The following procedure has been shown to restore efficiency on bonded and cross-linked columns such as the polydimethylsiloxane fused silica column utilized within this procedure.

X5.2 Cool down the GC and remove the capillary column. Before rinsing the column remove approximately 0.5 m from the injection end and the thermally degraded section from the detector end.

NOTE X5.1—Solvent-rinse kits are commercially available from chromatography specialty houses and column manufacturers.

X5.3 Since the identity of the contaminate residue is unknown, it is essential that the solvents selected to rinse the column include a polar and a nonpolar solvent. Start with a polar solvent such as methanol, utilize acetone as an intermediary, and finish with the hexane or the injection solvent. The rinsing is accomplished by utilizing gas pressure to fill the column from the end with the appropriate solvent and allow the solvent to soak for approximately 10 min. Use the compressed gas source to remove the majority of the rinse solvent before starting the next rinse solvent. After the last solvent has been dispensed from the column, allow the carrier

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[14] J & W Scientific GC reference notes, *Column Contamination*, 1992–1993 Catalog, p. 249.

gas to flow through the column for 5 to 10 min to dry the column. Install the column into the GC injector and again allow gas to flow for 5 to 10 min. Install the column into the detector and check for leaks. Heat the column at 2 to 3°C/min until the normal conditioning temperature has been reached. Condition the column as usual.

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