



Standard Test Method for Analysis of Polychlorinated Biphenyls in Insulating Liquids by Gas Chromatography¹

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 Aroclors² 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

¹ This test method is under the jurisdiction of Committee D27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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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.

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 clearly 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 clearly 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.
v^s	—volume of the standard test specimen injected into the chromatograph, μL .
v^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

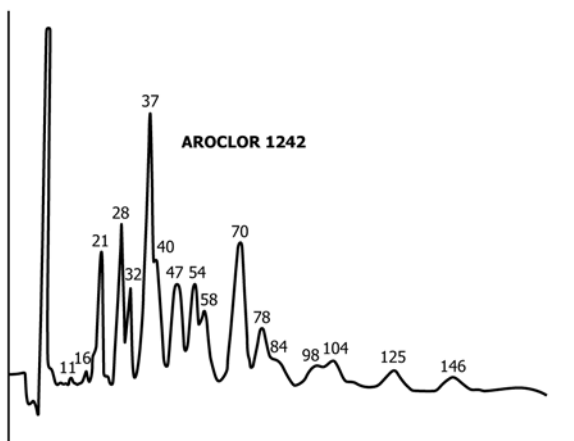


FIG. 1 Column: 3 % OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

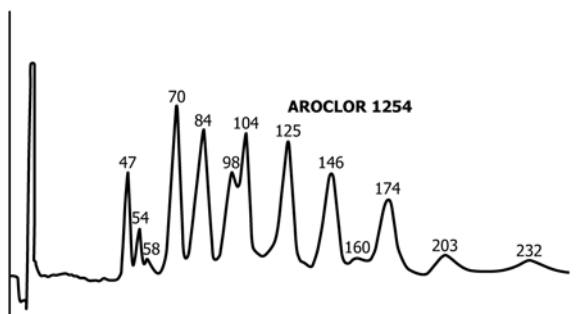


FIG. 2 Column: 3 % OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

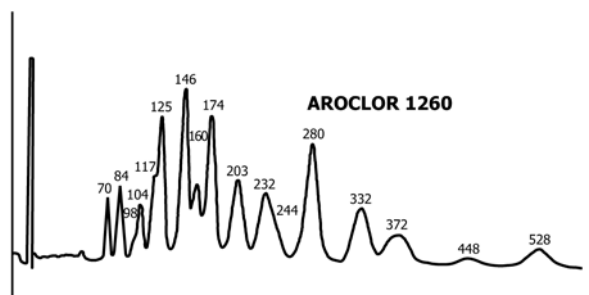


FIG. 3 Column: 3 % OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

TABLE 1 Composition of Aroclor 1242⁶

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.

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. 3⁵, 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 differ-

ent 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

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 1254⁶

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.

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.

TABLE 3 Composition of Aroclor 1260⁶

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			5 } ^D 60 %
{ 104			6 } 40 % 6
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	9.8	3.4	6 } ^E 10 % 7 } 90 %
{ 244			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.

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