



Standard Test Method for Polychlorinated Biphenyls (PCBs) in Water ¹

This standard is issued under the fixed designation D 3534; 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.

ε¹ NOTE—Section 14 was added editorially in June 1995.

1. Scope

1.1 This test method covers the determination of certain polychlorinated biphenyls (PCBs) including: Aroclors² 1221, 1232, 1242, 1248, 1254, 1260, and 1016.

1.2 The detection limit is in the range from 0.1 to 0.5 µg/L for Aroclor 1254 and 1260 when analyzing 1 L of water using an electron capture detector. The detection limit is compound dependent and is also determined by instrumental sensitivity and interferences present. When using a microcoulometric or conductivity detector, the detection limit is approximately 1.0 µg/L.

1.3 Precision and bias statements reflect recovery of PCB products dosed into water samples. These statements may not apply to environmentally altered PCBs.

1.4 As the precision and bias statements given may apply only to waters used, it is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information only.

1.6 *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.* For a specific hazard statement, see Note 2.

2. Referenced Documents

2.1 ASTM Standards:

D 1129 Terminology Relating to Water³

D 1193 Specification for Reagent Water³

D 3086 Test Method for Organochlorine Pesticides in Water⁴

D 3304 Method for Analysis of Environmental Materials

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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² Aroclor is a registered trademark of Monsanto Co. All Aroclor production was stopped in 1977. For alternate availability, see paragraph 8.4 of this test method.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 11.02.

for Polychlorinated Biphenyls⁵

D 3370 Practices for Sampling Water³

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents⁴

E 355 Practice for Gas Chromatography Terms and Relationships⁶

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Practice E 355.

4. Summary of Test Method

4.1 Polychlorinated biphenyls are extracted by liquid-liquid extraction and are separated from interferences prior to gas chromatographic determination. Sulfuric acid partitioning or a combination of the standard Florisil⁷ column cleanup procedure and a silica gel microcolumn separation procedure (1,2,3)⁸ are employed. Identification is made from gas chromatographic patterns obtained through the use of two or more unlike columns. Detection and measurement is accomplished using an electron capture, microcoulometric, or electrolytic conductivity detector. Techniques for confirming qualitative identification are suggested. The detection limit is approximately 0.1 µg/L for the PCB mixtures (Aroclors) listed in 1.1 when analyzing 1 L of sample using an electron capture detector. When using a microcoulometric or conductivity detector, the detection limit is approximately 1.0 µg/L. Precision and accuracy statements reflect recovery of PCB products dosed into water samples. These statements do not apply to environmentally altered PCBs.

5. Significance and Use

5.1 The extensive and widespread use of PCBs has resulted in their presence in all parts of the environment. Like the organochlorine pesticides, the PCBs are very persistent. While they are generally less toxic than the organochlorine pesticides, they do have adverse effects on mammals, birds, fish, and other

⁵ Annual Book of ASTM Standards, Vol 10.03.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Florisil, a trademark of and available from Floridin Co., Three Penn Center, Pittsburgh, PA 15235, has been found satisfactory for this purpose.

⁸ The boldface numbers in parentheses refer to the list of references at the end of this test method.

aquatic animals. Thus, we must identify and quantitate the PCBs present in the environment. Because of their cumulative nature and level of occurrence, the method for their determination must be capable of measuring quantities less than 1 µg/L in water.

6. Interferences

6.1 Certain phthalate esters, organophosphorus pesticides, and elemental sulfur interfere when using electron capture for detection.

6.2 Organochlorine pesticides and other halogenated compounds constitute interferences in the determination of PCBs. Most of these are separated by the test method described in this standard. However, certain compounds, if present in the sample, will occur with the PCBs. Included are sulfur, heptachlor, aldrin, DDE, chlordane, mirex, and to some extent *o,p'*-DDT and *p,p'*-DDT. Sulfur may be removed by the addition of elemental mercury (4).

7. Apparatus

7.1 *Glassware*, Kuderna-Danish (K-D).

7.1.1 *Snyder Columns*, three-ball (macro).

7.1.2 *Evaporative Flasks*, 500-mL.

7.1.3 *Receiver Ampuls*, 10-mL, graduated.

7.1.4 *Ampul Stoppers*.

7.2 *Chromatographic Column*, Chromaflex⁹ (400 mm long by 19-mm inside diameter) with coarse-fritted plate on bottom and TFE-fluorocarbon stopcock; 250-mL reservoir bulb at top of column with flared out funnel shape at top of bulb.

7.3 *Chromatographic Column*, borosilicate glass (approximately 400 mm long by 20-mm inside diameter) with a coarse-fritted plate.

7.4 *Microcolumn*, borosilicate glass, constructed in accordance with Fig. 1.

7.5 *Capillary Pipets*, disposable, 5¾-in. (146 mm), with rubber bulb.

7.6 *Low-Pressure Regulator*, 0 to 5 psig (0 to 34 kPa), with low-flow needle valve.

7.7 *Beaker*, 100-mL.

7.8 *Micro Syringe*, 10-µL.

7.9 *Separatory Funnel*, 2000-mL with TFE-fluorocarbon stopcock.

7.10 *Centrifuge Tubes*, borosilicate glass, calibrated (15-mL).

7.11 *Gas Chromatograph* (GC), equipped with an on-column or glass-lined injection port and an electron capture, microcoulometric, or electrolytic conductivity detector. As an option, a capillary column GC with a split, splitless, or on-column injection system (depending on sensitivity required) and one of the above detectors may be used.

7.12 *Sample Container*, 1000-mL glass (amber glass preferred) bottle with TFE-fluorocarbon-lined screw cap. Clean by washing with warm soapy water, remove soap by rinsing with tap water then reagent water, rinse with methylene chloride, final rinse with reagent water followed by heating at 180°C for

a minimum of 4 h. Caps and liners should be cleaned similarly without heating. Alternatively, clean bottles following the procedure in Practices D 3694.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.¹⁰ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water should be understood to mean reagent water conforming to Specification D 1193, Type II.

8.3 *Antistatic Solution*.¹¹

8.4 *PCB Standards*¹²—Aroclors 1221, 1232, 1242, 1248, 1254, 1260, and 1016.

NOTE 1—Polychlorinated biphenyls and their concentrated solutions should be handled so as to avoid contact to the analyst.

8.5 *Diethyl Ether*—Pesticide quality, redistilled in glass, if necessary, and containing 2 % (volume per volume) ethanol.

8.5.1 Ether must be free of peroxides according to the following test: to 10 mL of ether in a glass-stoppered cylinder previously rinsed with ether, add 1 mL of freshly prepared 10 % KI solution. Shake and let stand 1 min. No yellow color should be observed in the ether layer. As an alternative, test strips¹³ may be used.

8.5.2 Decompose ether peroxides by adding 40 g of a solution of 30 % (weight per volume) ferrous sulfate solution per litre of solvent.

NOTE 2—**Warning:** Reaction may be vigorous if the solvent contains a high concentration of peroxides.

8.5.3 Distill peroxide-free ether in glass and add 2 % (volume per volume) ethanol.

8.6 *Florisil*, PR grade 60 to 100 mesh; purchase activated at 1250°F (675°C) and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130°C in foil-covered glass container. Determine lauric acid value (see Annex A1).

8.7 *Ferrous Sulfate Solution* (30 %)—Dissolve 30 g of ferrous sulfate (FeSO₄) in water and dilute to 100 mL.

8.8 *Gas Chromatographic Materials:*

¹⁰ *Reagent Chemicals*, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Anal. Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

¹¹ Stanul, trademark of, and available from Daystrom Inc., Weston Instrument Div., Newark, NJ 07112, has been found satisfactory for this purpose.

¹² The proportions of individual PCB isomers may vary from one lot to another and from one manufacturer to another. Standard solutions are available from US EPA, 26 W. Martin L. King St., Cincinnati, OH 45219.

¹³ EM Quant test strips, trademark of, and available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, NY 10523, have been found satisfactory for this purpose. An equivalent may also be used.

⁹ Chromaflex, trademark of Kontes Glass Co., [as a special order (Kontes 42540-9011)], Vineland, NJ 08360, has been found satisfactory for this purpose.