Designation: D 5812 – 96 (Reapproved 2002)ε1

An American National Standard

Standard Test Method for Determination of Organochlorine Pesticides in Water by Capillary Column Gas Chromatography[1]

This standard is issued under the fixed designation D 5812; 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.

ε[1] NOTE—Editorial changes were made in July 2002.

1. Scope

1.1 This test method covers the capillary gas chromatographic determination of various organochlorine pesticides, including some of their degradation products and related compounds in finished drinking water. This test method is not limited to this particular aqueous matrix; however, its applicability to other aqueous matrices must be determined. The tested compounds include the following:

Pesticide	Chemical Abstract Service Registry Number [A]
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
γ-BHC	319-86-8
δ-BHC	58-89-9
α-Chlordane	5103-71-9
γ-Chlordane	5103-74-2
Chlorobenzilate	501-15-6
Chloroneb	2675-77-6
Chlorothalonil	2921-88-2
DCPA	1897-45-6
4,4′-DDD	72-54-8
4,4′-DDE	72-55-9
4,4′-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-0708
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Etridiazole	2593-15-9
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Methoxychlor	72-43-5
cis-Permethrin	52645-53-1
trans-Permethrin	52645-53-1
Propachlor	1918-16-7
Trifluralin	1582-09-8

[A] Numbering system of CAS Registry Services, P.O. Box 3343, Columbus, OH 43210-0334.

1.2 Table 1 and Table 2 list the applicable concentration ranges and precision and bias statements for this test method. The applicability of this test method to other compounds must be demonstrated.

1.3 The extract derived from this procedure may be analyzed for these constituents by using the gas chromatography (GC) conditions prescribed in Test Method D 5175 (capillary column). Although the columns used in this test method may be adequate for analyzing PCBs, no data were collected for any multi-congener constituents during methods development.

1.4 This test method is restricted to use by or under the supervision of analysts experienced in the use of GC and interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results using the procedures described in Section 12.

1.5 Analytes that are not separated chromatographically by either the primary or secondary chromatographic columns (for example, analytes having very similar retention times) cannot be identified and measured individually in the same calibration mixture or water sample unless an alternative technique for identification and quantitation exists (see 7.9 and 13.4).

1.6 When this test method is used to analyze unfamiliar samples for any or all of the analytes listed in 1.1, analyte identifications and concentrations should be confirmed by at least one additional technique.

1.7 The values stated in SI units are to be regarded as the standard.

1.8 *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.* Specific hazards statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water

[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.

Current edition approved May 10, 1996. Published July 1996. Originally published as D 5812 – 95. Last previous edition D 5812 – 95.

[2] *Annual Book of ASTM Standards,* Vol 11.01.

TABLE 1 Regression Equations for Method Precision and Mean Recovery for Reagent Water

Compound	Concentration Range,μ g/L	Single-analyst Precision, s_r	Overall Precision, s_R	Mean Recovery, X
Aldrin	0.03–1.38	0.061X + 0.004	0.130X + 0.009	0.909C + 0.007
α-BHC	0.02–1.00	0.059X + 0.001	0.127X + 0.005	1.015C + 0.004
β-BHC	0.02–1.00	0.034X + 0.004	0.148X + 0.005	0.975C + 0.006
γ-BHC	0.03–1.51	0.047X + 0.005	0.147X + 0.007	0.998C + 0.006
δ-BHC	0.02–1.01	0.050X + 0.001	0.119X + 0.002	0.958C + 0.005
α-Chlordane	0.03–1.50	0.062X + 0.000	0.138X + 0.000	1.008C + 0.003
γ-Chlordane	0.03–1.51	0.048X + 0.002	0.129X + 0.001	0.936C + 0.005
Chlorobenzilate	1.00–50.00	0.067X + 0.022	0.178X + 0.117	0.993C + 0.263
Chloroneb	1.00–50.08	0.111X − 0.016	0.159X + 0.275	0.942C + 0.280
Chlorothalonil	0.05–2.51	0.096X + 0.001	0.233X + 0.001	0.955C + 0.001
DCPA	0.05–2.51	0.047X + 0.002	0.161X + 0.002	0.998C + 0.013
4,4′-DDD	0.05–2.50	0.087X − 0.001	0.150X + 0.000	0.970C + 0.006
4,4′-DDE	0.02–1.00	0.093X + 0.001	0.166X + 0.000	0.982C + 0.000
4,4′-DDT	0.12–6.01	0.044X + 0.017	0.140X + 0.002	0.976C + 0.006
Dieldrin	0.04–2.01	0.089X + 0.000	0.150X + 0.009	0.962C + 0.009
Endosulfan I	0.03–1.51	0.070X + 0.000	0.127X + 0.009	0.957C + 0.006
Endosulfan II	0.03–1.49	0.059X + 0.001	0.120X + 0.002	0.974C + 0.003
Endosulfan sulfate	0.03–1.51	0.115X + 0.003	0.158X + 0.007	0.988C + 0.004
Endrin	0.03–1.50	0.108X − 0.002	0.134X + 0.002	0.991C + 0.002
Endrin aldehyde	0.05–2.49	0.105X − 0.004	0.121X + 0.003	0.940C + 0.007
Etridiazole	0.05–2.48	0.049X + 0.002	0.149X + 0.010	0.960C + 0.007
Heptachlor	0.02–1.00	0.068X + 0.001	0.100X + 0.011	0.961C + 0.009
Heptachlor epoxide	0.03–1.50	0.049X + 0.002	0.122X + 0.005	0.950C + 0.006
Hexachlorobenzene	0.01–0.50	0.049X + 0.000	0.124X + 0.003	0.841C + 0.003
Methoxychlor	0.10–5.01	0.108X − 0.004	0.190X − 0.003	1.044C + 0.016
cis-Permethrin	1.00–50.08	0.077X + 0.034	0.138X + 0.204	0.938C + 0.314
trans-Permethrin	1.00–50.12	0.096X − 0.001	0.233X + 0.001	0.955C + 0.001
Propachlor	1.00–50.08	0.052X + 0.098	0.119X + 0.370	0.978C + 0.317
Trifluralin	0.05–2.51	0.064X + 0.003	0.144X + 0.004	0.888C + 0.004

TABLE 2 Regression Equations for Method Precision and Mean Recovery for Finished Drinking Water[A]

Compound	Concentration Range,μ g/L	Single-analyst Precision, s_r	Overall Precision, s_R	Mean Recovery, X
Aldrin	0.03–1.49	0.048X + 0.008	0.175X + 0.005	0.826C + 0.008
α-BHC	0.02–1.00	0.094X − 0.000	0.198X + 0.000	0.940C + 0.003
β-BHC	0.02–1.00	0.142X − 0.001	0.227X + 0.003	0.923C + 0.005
γ-BHC	0.03–1.51	0.070X − 0.001	0.138X + 0.006	0.938C + 0.002
δ-BHC	0.02–1.01	0.066X + 0.005	0.133X + 0.004	0.905C + 0.007
α-Chlordane	0.03–1.50	0.070X + 0.000	0.164X + 0.000	0.870C + 0.005
γ-Chlordane	0.03–1.51	0.072X + 0.000	0.138X + 0.001	0.865C + 0.005
Chlorobenzilate	1.00–50.00	0.146X − 0.042	0.243X + 0.292	0.874C + 0.207
Chloroneb	1.00–50.08	0.100X − 0.024	0.185X + 0.110	0.883C + 0.218
Chlorothalonil	0.05–2.51	0.100X + 0.001	0.180X + 0.004	0.920C + 0.000
DCPA	0.05–2.51	0.136X − 0.003	0.224X − 0.003	0.920C + 0.015
4,4′-DDD	0.05–2.50	0.102X + 0.001	0.146X + 0.002	0.908C + 0.008
4,4′-DDE	0.02–1.00	0.081X − 0.001	0.203X − 0.002	0.842C + 0.002
4,4′-DDT	0.12–6.01	0.110X − 0.005	0.162X + 0.012	0.858C + 0.009
Dieldrin	0.04–2.01	0.065X − 0.000	0.140X − 0.000	0.882C + 0.006
Endosulfan I	0.03–1.51	0.072X + 0.001	0.117X + 0.003	0.898C + 0.004
Endosulfan II	0.03–1.49	0.064X − 0.000	0.119X + 0.002	0.901C + 0.002
Endosulfan sulfate	0.03–1.51	0.132X − 0.000	0.233X + 0.007	0.948C + 0.009
Endrin	0.03–1.50	0.062X + 0.001	0.120X + 0.002	0.893C + 0.001
Endrin aldehyde	0.05–2.49	0.076X − 0.001	0.097X + 0.005	0.874C + 0.003
Etridiazole	0.05–2.48	0.074X + 0.001	0.240X − 0.000	0.916C + 0.009
Heptachlor	0.02–1.00	0.072X + 0.001	0.075X + 0.009	0.980C + 0.005
Heptachlor epoxide	0.03–1.50	0.066X + 0.001	0.084X + 0.004	0.944C + 0.006
Hexachlorobenzene	0.01–0.50	0.013X + 0.002	0.097X + 0.005	0.833C + 0.004
Methoxychlor	0.10–5.01	0.142X − 0.004	0.285X − 0.007	0.936C + 0.017
cis-Permethrin	1.00–50.08	0.112X + 0.012	0.161X + 0.292	0.833C + 0.200
trans-Permethrin	1.00–50.12	0.184X − 0.087	0.410X − 0.063	0.814C + 0.287
Propachlor	1.00–50.08	0.087X + 0.061	0.158X + 0.185	0.925C + 0.353
Trifluralin	0.05–2.51	0.066X + 0.002	0.147X + 0.004	0.847C + 0.006

[A] X = mean recovery; C = analyte true concentration.

and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[2]

D 3370 Practices for Sampling Water[2]

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents[3]

[3] *Annual Book of ASTM Standards,* Vol 11.02.

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]
D 4128 Practice for Identification of Organic Compounds in Water by Combined Gas Chromatography and Electron Impact Mass Spectrometry[3]
D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]
D 5175 Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography[3]
D 5810 Guide for Spiking into Aqueous Samples[3]
E 260 Practice for Packed Column Gas Chromatography[4]
E 355 Practice for Gas Chromatography Terms and Relationships[4]
E 697 Practice for Use of Electron-Capture Detectors in Gas Chromatography[4]
E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[4]

2.2 *U.S. EPA Standards:*

Method 508, Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector (Revision 3.0, 1988)[5]
Analytical Methods for Pesticides/Aroclors (February 1991)[6]
Method 680, Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry (Revision 3.0, 1988)[5]

2.3 *AOAC Standard:*

Method 990.06, Organochlorine Pesticides in Water[7]

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *field duplicates (FD 1 and FD 2)*—two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD 1 and FD 2 provide a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.2.2 *field reagent blank (FRB)*—reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The reagent water must be transferred to an empty, clean sample container in the field. The purpose of the FRB is to determine whether analytes or other interferences are present in the field environment.

3.2.3 *instrument performance check (IPC) solution*—a solution of analytes used to evaluate the performance of the instrument system with respect to test method criteria.

3.2.4 *laboratory duplicates (LD 1 and LD 2)*—two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD 1 and LD 2 provide a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2.4.1 *Discussion*—Analysis of laboratory duplicates or spiked samples requires the collection of duplicate 1-L sample bottles or the use of 2-L sample containers.

3.2.5 *laboratory fortified blank (LFB)*—an aliquot of reagent water to which known quantities of analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.2.6 *laboratory fortified sample matrix (LFM)*—an aliquot of an environmental sample to which known quantities of analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations (see 3.2.4.1).

3.2.7 *laboratory reagent blank (LRB)*—an aliquot of reagent water that is treated exactly like a sample, including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The LRB is used to determine whether method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.2.8 *quality control sample (QCS)*—a sample containing analytes or a solution of analytes in a water-miscible solvent that is used to fortify reagent water or environmental samples. The QCS must be independent of solutions used to prepare standards and should be obtained from a source external to the laboratory. The QCS is used to check laboratory performance with externally prepared test materials and is analyzed exactly like a sample.

3.2.9 *spike*—an addition of a known quantity of a component of known identity to a known volume of a sample in order to determine the efficiency with which the added component is recovered. Spike components should be prepared from a different source than that used for calibration standards. Refer to Guide D 5810 for guidance on spiking organics into aqueous samples.

3.2.10 *standard solution, secondary dilution*—a solution of several analytes prepared in the laboratory from stock analyte solutions and diluted as necessary to prepare calibration solutions and other needed analyte solutions.

3.2.11 *standard solution, stock*—a concentrated solution containing a single certified standard that is an analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare secondary dilution standards.

[4] *Annual Book of ASTM Standards*, Vol 14.02.
[5] Available from U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH 45268.
[6] U.S. EPA CLP Statement of Work for Organics Analysis, Document OLM01.1.1, Available from U.S. EPA Contracts Management Division (MD33), Administration Building Lobby, Alexander Drive, Research Triangle Park, NC 27711.
[7] Available from Association of Official Analytical Chemists, Suite 400, 2200 Wilson Boulevard, Arlington, VA 22201.

4. Summary of Test Method

4.1 Pesticides in a water sample are extracted with methylene chloride (CH_2Cl_2) using a separatory funnel. The extract is dried, concentrated, exchanged to methyl tert-butyl ether (MTBE), and concentrated to 5 mL. Analysis is performed on a gas chromatograph equipped with an electron capture detector (ECD).

5. Significance and Use

5.1 The extensive and widespread use of organochlorine pesticides and PCBs has resulted in their presence in all parts of the environment. These compounds are persistent and may have adverse effects on the environment. Thus, there is a need to identify and quantitate these compounds in water samples.

6. Interferences

6.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running LRBs in accordance with 12.2.

6.1.1 Glassware must be cleaned scrupulously as soon as possible after use. Rinse thoroughly with the last solvent used, and then wash with hot tap water and detergent. Rinse thoroughly with tap water followed by reagent water. Drain to dryness, and heat in an oven or muffle furnace at 400°C for 1 h. Do not heat volumetric glassware. Thermally stable materials might not be eliminated by this treatment. A thorough rinse with acetone may be substituted for heating. After drying and cooling, store sealed glassware in a clean environment to prevent any accumulation of dust or other contaminants. Seal the glassware by capping it with aluminum foil.

6.1.2 The use of high-purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

6.2 Phthalate esters, found frequently in plastics, paints, and other common laboratory items, produce a positive response on an electron capture detector. Samples and solvents should therefore come into contact with only those materials specified in this test method.

6.3 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sampling rinsing of the sample syringe and associated equipment with solvent can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of a solvent blank should be made to ensure that accurate values are obtained for the next sample. Continue the injection of blanks until analyses demonstrate that reportable values in the next sample could not have been caused by contamination.

6.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all of the analytes listed in the Scope are not resolved from each other on any one column; that is, one analyte of interest may be an interferant for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending on the water sampled. Cleanup of sample extracts may be necessary. Positive identifications should be confirmed (see 13.4).

6.5 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. The chromatographic comparability of standards to sample may be affected if this is not the case.

6.6 Caution must be taken in the determination of endrin since it has been reported that the splitless injector may cause endrin degradation **(1)**.[8] The analyst should be alerted to this possible interference resulting in an erratic response for endrin.

6.7 Variable amounts of pesticides and PCBs from aqueous solutions may adhere to glass surfaces. It is recommended that sample transfers and glass surface contacts be minimized to the extent possible.

6.8 Aldrin and methoxychlor are oxidized by chlorine rapidly. Dechlorination with sodium thiosulfate at the time of collection will retard further oxidation of these compounds.

6.9 An interfering, erratic peak has been observed with the retention window of heptachlor during many analyses of reagent, tap, and groundwater. It appears to be related to dibutyl phthalate; however, the specific source has not yet been determined. The observed magnitude and character of this peak vary randomly in numerical value from successive injections made from the same vial. This type of outlying observation is normally recognized. If encountered, additional analyses will be necessary.

7. Apparatus

7.1 *Separatory Funnel*, 2000-mL capacity, with a TFE-fluorocarbon stopcock.

7.2 *Boiling Chips*, silicon carbide or TFE-fluorocarbon. Solvent rinse before use.

7.3 *Kuderna-Danish Concentrator*, 500 mL, with a receiver tube, 3-ball macro Snyder column, and 2-ball micro Snyder column.

7.4 *Water Bath*, heated, with a concentric ring cover, capable of temperature control (±5°C).

7.5 *Vials*, auto sampler with septa and caps. Vials should be compatible with the automatic sample injector and should have an internal volume not greater than 2 mL.

7.6 *Automatic Sample Injector*, for the gas chromatograph, which must not require more than 0.5 mL of solution per injection, including rinsing and flushing.

7.7 *Micro Syringe*, 10 and 100 µL.

7.8 *Standard Solution Storage Containers*, 15-mL bottles with TFE-fluorocarbon lined screw caps.

7.9 *Gas Chromatograph*—Analytical system equipped with a temperature programming capability, splitless injector (0.5 min splitless mode), capillary column, and linearized ECD. (Alternate detectors, including electrolytic conductivity detector/halogen mode, may be used in accordance with 12.4 and if detection levels are adequate.) A computer data system

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

TABLE 3 Relative Retention Times for Method Analytes

Analyte	Relative Retention Time, [A] [B] min	
	Primary	Alternative
Etridiazole	0.69	0.67
Chloroneb	0.75	0.77
Propachlor	0.85	0.91
Trifluralin	0.93	[C]
Hexachlorobenzene	0.94	[C]
α-BHC	0.93	0.97
β-BHC	0.98	1.18
γ-BHC (Lindane)	0.99	1.04
δ-BHC	1.03	1.22
Chlorothalonil	1.04	1.17
Heptachlor	1.11	1.08
Aldrin	1.18	1.12
DCPA	1.21	1.21
Heptachlor epoxide	1.24	1.24
γ-Chlordane	1.28	1.29
Endosulfan I	1.30	1.28
α-Chlordane	1.31	1.31
Dieldrin	1.35	1.35
4,4′-DDE	1.35	1.32
Endrin	1.38	1.38
Endosulfan II	1.40	1.45
Chlorobenzilate	1.41	1.42
4,4′-DDD	1.42	1.38
Endrin aldehyde	1.43	1.52
Endosulfan sulfate	1.47	[C]
4,4′-DDT	1.48	1.48
Methoxychlor	1.57	1.58
cis-Permethrin	1.72	[C]
trans-Permethrin	1.73	[C]

[A] Columns and analytical conditions are described in 7.9.2 and 7.9.3.
[B] Retention time relative to pentachloronitrobenzene (IS) = 1.00.
[C] Data not available.

is recommended for measuring peak areas. Table 3 lists retention times observed using the columns and conditions described as follows.

7.9.1 Two gas chromatographic columns are recommended. Either column may be used as the primary analytical column unless routinely occurring analytes are not resolved adequately. Column 1 is designated as the primary column in Table 3. Alternative columns may be used in accordance with the provisions described in 12.4. Alternative columns may use a different inside diameter or film thickness.

7.9.2 *Column 1 (Primary Column)*—0.25-mm inside diameter by 30-m long fused silica capillary, with a chemically bonded phenylmethyl polysiloxane phase.[9] Helium carrier gas flow is established at 30 cm/s linear velocity. The injection volume is 2-µL splitless mode with a 45 s delay. The oven temperature is programmed from 60 to 300°C at 4°C/min. The injector temperature is 250°C. The detector temperature is 320°C.

7.9.3 *Column 2 (Alternative Column)*—0.25-mm inside diameter by 30-m long fused silica capillary, with a chemically bonded cyanopropylphenlylmethyl polysiloxane phase.[10] The conditions are as described for Column 1 in 7.9.2.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[11] 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, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193 and shown to contain no interfering compounds at concentrations sufficient to interfere with the analytes listed in Table 1.

8.3 *Methylene Chloride, n-Hexane, Acetone, MTBE, Methanol, and Toluene*, pesticide grade or equivalent.

8.4 *Sodium Sulfate and Sodium Chloride*, for treatment before use, pulverize a batch and place it in a muffle furnace at room temperature. Increase the temperature to 400°C and hold for 30 min. Cool and place in a bottle and cap.

8.5 *Sodium Hydroxide Solution, 400 g/L*—Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.

8.6 *Sulfuric Acid Solution, 1 + 1*—Slowly add 50 mL of concentrated H_2SO_4(sp gr 1.84) to 50 mL of reagent water.

8.7 *Sodium Thiosulfate Solution*—Mix 1 g of sodium thiosulfate ($Na_2S_2O_3$) with water and bring to 25-mL volume in a volumetric flask.

8.8 *Mercury*.

8.9 *Phosphate Buffer, pH 7*—Mix 29.6 mL of 0.1-N HCI and 50 mL of 0.1-M dipotassium phosphate.

8.10 *Mercuric Chloride Solution, 10 mg/mL*—Dissolve 100 mg of $HgCl_2$ in reagent water and dilute to 10 mL.

8.11 *Standard Solutions, Stock*—These solutions may be obtained as certified solutions or prepared from pure standard materials using the following procedure (depending on the compound solubility, alternate solvents, such as hexane or toluene, may be used):

8.11.1 Prepare stock standard solutions (1000 µg/mL) by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE, and dilute to volume with MTBE in a 10-mL volumetric flask. Larger volumes may be made at the convenience of the analyst. When the compound purity is assayed to be 96 % or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or an independent source.

8.11.2 Transfer the stock standard solutions into TFE-fluorocarbon sealed screw-cap bottles. Store at 4 ± 2°C, and protect from light. Stock analyte solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

[9] DB-5, 0.25-µm film, available from J. and W. Scientific, Rancho Cordova, CA, or equivalent, has been found to be suitable for this purpose.

[10] DB-1701, 0.25-µm film, available from J. and W. Scientific, Rancho Cordova, CA, or equivalent, has been found to be suitable for this purpose.

[11] 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 Analar 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.

8.11.3 Stock standard solutions must be replaced after two months, or sooner, if a comparison with check standards indicates a problem. Check standards should be from different sources. Corrective actions are required if standard solutions do not agree. This may include re-preparation of the standards or obtaining additional standard reference materials.

8.12 *Standard Solutions, Secondary Dilution*—Use stock standard solutions to prepare secondary dilution standard solutions that contain the analytes in MTBE.

NOTE 1—Spiking solutions must be in a water-soluble solvent (such as MTBE). Calibration standards must be in the same solvent as the sample extracts (MTBE). The secondary dilution standards should be prepared at concentrations that can be diluted easily to prepare calibration standards that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace, and check frequently for signs of deterioration or evaporation, especially just before preparing the calibration standards. The storage time described for stock analyte solutions in 8.11.3 also applies to secondary dilution standard solutions.

8.13 *Surrogate Solution*—Prepare a surrogate spike solution, using the procedures described in 8.11 and 8.12 of 4,4′-dichlorobiphenyl (DCB) at 500 µg/mL in MTBE. Check frequently for stability. The addition of 0.050 mL surrogate solution to a 1-L water sample results in a surrogate standard concentration of 25µ g/L.

NOTE 2—All spiking solutions must equilibrate to room temperature prior to use. Other surrogate spikes (such as tetrachloro-m-xylene and decachlorobiphenyl) and spike concentrations may be used.

8.14 *Internal Standard Solution (Optional)*—Prepare an internal standard solution, using the procedures described in 8.11 and 8.12, of pentachloronitrobenzene (PCNB) at 100 µg/mL in MTBE (or the same solvent as that used for the calibration standards). The addition of 5 µL of the internal standard solution to 5.0 mL of sample extract should result in a final internal standard concentration of 0.1 µg/mL (in sample extract). Octachloronaphthalene and decachlorobiphenyl are alternate internal standards; other compounds and concentrations may be used.

8.15 *Instrument Performance Check (IPC) Solution*—This is prepared by combining microlitre aliquots of appropriate secondary dilution standard solutions in MTBE. Recommended IPC analytes and final concentrations are as follows:

	µg/mL
Chlorpyrifos	0.002
DCPA	0.05
Chlorothalonil	0.05
δ-BHC	0.04
Endrin	0.05
4,4′-DDT	0.1

9. Hazards

9.1 **Warning**—The toxicity and carcinogenicity of chemicals used in this test method have not been defined precisely; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding the safe handling of chemicals used in this test method. Additional references to laboratory safety are available **(2–4)** for the information of the analyst.

9.2 **Warning**—The following organohalides have been classified tentatively as known or suspected human or mammalian carcinogens; aldrin, PCBs, chlordane, dieldrin, heptachlor, hexachlorobenzene, and toxaphene. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox.

10. Sampling

10.1 *Sample Collection*:

10.1.1 Collect the sample in accordance with either Specification D 1192 or Practices D 3370, whichever is applicable.

10.1.2 Glass bottles (1-L recommended) equipped with TFE-fluorocarbon or aluminum foil-lined screw caps, prepared in accordance with Practices D 3694, are used for sample collection. Fill a sufficient number of sample bottles with sample to permit the running of duplicates, spikes, and reanalyses.

10.2 *Sample Preservation*:

10.2.1 The samples must be chilled to 4°C at the time of collection and maintained at that temperature until the sample is prepared for the extraction procedure. Field samples must be packed with sufficient ice to ensure that they will be maintained at 4 ± 2°C until arrival at the laboratory.

10.2.2 If residual chlorine is present, add 2-mL of sodium thiosulfate solution per litre of sample to the sample bottle prior to collecting the sample.

10.2.3 Mercuric chloride (1 mL of a 10 mg/mL mercuric chloride solution) should be added to a 1-L sample bottle prior to sample collection if biological degradation of the target analytes may occur. Mercuric chloride is a highly toxic chemical and must be handled with caution. Samples containing mercuric chloride must be disposed of properly.

10.2.4 After adding the sample to the bottle containing preservative(s), seal the sample bottle and shake vigorously for 1 min.

10.3 *Sample and Extract Storage*:

10.3.1 Store samples and extracts at 4 ± 2°C, away from light, until the analyses have been completed.

10.3.2 Extract all samples as soon as possible after collection and within 7 days of sample collection (refer to 13.1).

10.3.3 Analyze all samples as soon as possible after extraction and within 14 days of sample extraction. Longer storage times may be permitted based on the information given in 10.3.4.

10.3.4 Analyte stability may be affected by the matrix; the analyst should therefore verify that the preservation techniques and storage times are applicable to the samples under study.

11. Calibration and Standardization

11.1 Refer to Practices E 260, E 697, and E 1510 for general guidance on GC and ECD analysis. U.S. EPA Method 508, Analytical Methods for Pesticides/Aroclors, and AOAC Method 990.06 are also established methods for GC/ECD analysis.

11.2 Establish GC operating parameters equivalent to those indicated in 7.9.

11.3 *Instrument Performance*—Check the performance of the equipment daily using the IPC solution.

11.3.1 IPC components and performance criteria are listed in Table 4. The sensitivity requirements are set based on the tested concentration range in the test method. Concentrations

TABLE 4 Instrument Performance Check Solution

Test	Analyte	Concentration, µg/mL	Requirements
Sensitivity	chlorpyrifos	0.0020	detection of analyte; S/N > 3
Chromatographic performance	DCPA	0.0500	PSF between 0.80 and 1.15 [A] PGF between 0.80 and 1.15 [B]
Column performance	chlorothalonil δ-BHC	0.0500 0.0400	resolution > 0.50 [C]
Endrin degradation	endrin	0.05	endrin breakdown < 20 % [D]
4,4′-DDT degradation	4,4′-DDT	0.10	4,4′-DDT breakdown < 20 % [D]

[A] PSF (Peak Symmetry Factor)—Calculated using the following equation: PSF = $W(Fh)/[0.5 \times W(th)]$, where $W(Fh)$ = width of the peak front at half height, assuming the peak is split at its highest point, and $W(th)$ = total peak width at half height.

[B] PGF (Peak Gaussian Factor)—Calculated using the following equation: PGF = $[1.83 \times W (1/2)]/W (1/10)$, where $W (1/2)$ = peak width at half height and $W (1/10)$ = peak width at tenth height.

[C] Resolution between the two peaks as defined by the following equation: $R_s = 2(t_{Rj} - t_{Ri})/(W_{bi} + W_{bj})$, where t_{Rj} and t_{Ri} = retention times of peaks ($t_{Rj} > t_{Ri}$), and w_{bi} and w_{bj} = width of peaks at base. Refer to Practice E 355.

[D] See 11.3.4.

in the IPC must be adjusted if laboratory concentration ranges differ from those in this test method.

11.3.2 Significant peak tailing must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or operation of the detector.

11.3.3 Check the precision between replicate injections. Poor precision is generally traceable to pneumatic leaks, especially the injection port. If the precision is good but the GC system exhibits decreased sensitivity, it may be necessary to generate a new curve or set of calibration factors to verify the decreased responses before searching for the source of the problem.

11.3.4 Observed relative area responses of endrin (see 6.6) and 4,4′-DDT in the IPC must meet the following general criteria if endrin and 4,4′-DDT are compounds of interest:

11.3.4.1 The breakdown of endrin into its aldehyde and ketone forms must be consistent (±10 % relative standard deviation) during a period of sample analysis. Demonstrate equivalent breakdown in the IPC, LFB, LFM, and QCS. Consistent breakdown in these analyses would suggest that the methodology is in control.

11.3.4.2 The total percent breakdown for either endrin or 4,4′-DDT must not exceed 20 %. If the breakdown exceeds 20 % in the IPC, LFB, and LFM, the problem is probably in the instrument or a bad stock solution. Correct the problem before proceeding. If breakdown exceeds 20 % only in the LFM, note this when reporting the sample results.

$$\%\ \text{breakdown endrin} = \frac{(EA + EK)\ 100}{E} \quad (1)$$

where:
EA = endrin aldehyde area,
EK = endrin ketone area, and
E = total endrin area (endrin + EA + EK).

$$\%\text{breakdown } 4,4'-DDT = \frac{(DDE + DDD)\ 100}{DDT} \quad (2)$$

where:
DDE = 4,4′-DDE area,
DDD = 4,4′-DDD area, and
DDT = total DDT area (4,4′-DDT + DDE + DDD).

11.4 *Calibration*—At least three calibration standards are needed; five are recommended. One should contain analytes at a concentration at or below the lowest reporting value for each compound. The other levels should be at concentrations that bracket the range expected in samples. For example, if the lowest reporting value is 0.02 µg/L, prepare calibration standards at concentrations of 0.002, 0.01, 0.02, 0.1, and 0.2 µg/mL for a sample with an expected concentration of 0.02 to 1.0 µg/L (0.004 to 0.2 µg/mL in extract).

11.4.1 Starting with the standard of lowest concentration, analyze each calibration standard beginning with 13.3, and tabulate the peak height or area response versus the concentration in the standard. Use the results to prepare a calibration curve for each compound by plotting the peak height or area response versus the concentration. Alternatively, if the ratio of concentration to response (calibration factor) is a constant over the working range (10 % relative standard deviation (RSD) or less), the average ratio or response factor (RF) can be used in place of a calibration curve.

11.4.1.1 For internal standard calibration, select an internal standard that is similar in analytical behavior to the pesticides of interest. Calculate the relative response factor (RRF) as follows:

$$RRF = \frac{(C_i)(A_{is})}{(A_i)(C_{is})} \quad (3)$$

where:
C_i = concentration of pesticide,µ g/mL,
C_{is} = concentration of internal standard, µg/mL,
A_i = area of pesticide, and
A_{is} = area of internal standard.

Calculate the average RRF or prepare a calibration curve.

11.4.1.2 Internal standard calibration is recommended. Use external standard calibration if internal is not applicable. Calculate the RF as follows for external standard calibration:

$$RF = \frac{C_i}{A_i} \quad (4)$$

where:
C_i = concentration of pesticide,µ g/mL, and
A_i = area of pesticide.

Calculate the average RF or prepare a calibration curve.

11.4.2 If initial calibration is not performed daily, verify the working calibration curve or RF on each working day by the measurement of one or more calibration standards prior to the analysis of samples. Additional calibration checks, such as one every ten samples, or at the end of an analytical sequence, are good laboratory practice. If the RF or calculated amount for any analyte varies from the predicted response by more than

±20 %, repeat the test using a fresh calibration standard. Generate a new calibration curve if the results still do not agree.

NOTE 3—Based on the data quality objectives of the program, other calibration criteria may be established.

11.5 *Assessing the Internal Standard*—When using the internal standard calibration procedure, the analyst is expected to monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standards IS response by more than 30 %.

11.5.1 If greater than 30 % deviation occurs with an individual extract, optimize the instrument performance and inject a second aliquot of that extract.

11.5.1.1 If the reinjected aliquot produces an acceptable internal standard response, report the results for that aliquot.

11.5.1.2 If a deviation of greater than 30 % is obtained for the reinjected extract, check the instrument performance as described in 11.5.2. If acceptable, report the results obtained from the reinjected extract, but annotate them as suspect.

11.5.1.3 Alternately, analysis of the sample may be repeated beginning with Section 13, provided that the sample is still available.

11.5.2 If consecutive samples fail the IS response acceptance criterion, analyze a calibration check standard immediately.

11.5.2.1 If the check standard provides a RF within 20 % of the predicted value and meets the IS criteria given in 11.5, follow the procedures itemized in 11.5.1 for each sample failing the IS response criterion.

11.5.2.2 If the check standard provides a RF that deviates more than 20 % of the predicted value, the analyst must recalibrate, as specified in 11.4. All samples analyzed since the last successful calibration must be reanalyzed.

11.6 Verify the calibration standards periodically, recommending at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. The results from these analyses must be within the limits used to check the calibration routinely.

12. Quality Control

12.1 Minimum quality control requirements are the initial demonstration of laboratory capability and the analysis of IPC, LRBs, LFBs, LFM, and, if available, QCSs. See Guide D 3856 and Practice D 4210 for a general discussion of good laboratory practices.

12.2 *Laboratory Reagent Blanks*—The analyst must demonstrate that all glassware and reagent interferences are under control before processing any samples. Analyze an LRB each time a set of samples is extracted or reagents are changed. If within the retention time window of any analyte, the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination, and eliminate the interference before processing samples.

12.3 *Initial Demonstration of Capability*:

12.3.1 Select a representative spike concentration (at the midpoint of the concentration range or the regulatory maximum contaminant level, whichever is lower) for each analyte. If detection monitoring is the primary objective, the spike level may be at the low end of the concentration range. Add spike concentrate to each of at least four 1-L aliquots of water with a syringe, and analyze each aliquot according to the procedures beginning in Section 13.

12.3.2 For all four aliquots analyzed, the recovery value for each analyte should fall in the range from 70 to 130 %. The relative standard deviation of the four replicates should be <20 %. Consider the performance acceptable and begin the sample analysis for those compounds that meet the acceptance criteria. Repeat the initial demonstration procedures for those compounds that fail these criteria. The regression equations given in Table 1 and Table 2 may also be used to develop acceptance criteria for specific spike levels.

12.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples prior to obtaining experience with the test method. It is expected that, as laboratory personnel gain experience with this test method, the quality of data will improve beyond those required here.

12.4 The analyst is permitted to modify GC columns, GC conditions, or detectors to improve separations or lower analytical costs. Alternative extraction procedures, such as solid phase extraction, may be used. Alternative final solvents, such as hexane, may be used if all required analytes are sufficiently soluble in the alternative solvent. The analyst must repeat the procedures described in 12.3 each time such method modifications are made.

12.5 *Assessing Laboratory Performance—Laboratory Fortified Blank*:

12.5.1 The laboratory must analyze at least one LFB per sample set (all samples extracted within a 24-h period). The spiking concentration of each analyte in the LFB sample should be known accurately and approximately equal to the spike level given in 12.3.1. Calculate the accuracy as percent recovery (X_j). The analyte is judged out of control if the recovery of any analyte falls outside the control limits (see 12.3.2), and the source of the problem should be identified and corrected before continuing analyses.

NOTE 4—The spike used here and in 12.6.1 should contain each single-component analyte of interest. However, the number of analytes in a single spike may be limited by the inability of the test method to resolve completely all analytes of interest (see 1.5 and 13.4.3). Additional spike mixes and QC samples may be required based on the data quality objectives of the program.

12.5.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory may assess laboratory performance against the control limits given in 12.3.2. When sufficient internal performance data become available, develop control limits from the mean percent recovery (X) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{upper control limit} = X + 3S$$

$$\text{lower control limit} = X - 3S$$

NOTE 5—Specific recovery limits may be required based on the data quality objectives of the program.

12.5.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for the analytes of interest.

NOTE 6—No attempts to establish low detection limits should be made before instrument optimization and adequate conditioning of both the column and the GC system. Conditioning includes the processing of LFB and LFM samples containing moderate concentration levels of these analytes.

12.5.4 The laboratory should analyze QCSs from an independent source at least every three months. Corrective action shall be taken and documented if the criteria provided with the QCSs are not met.

12.6 *Assessing Analyte Recovery—Laboratory-Fortified Sample Matrix*:

12.6.1 The laboratory shall add a known spike of each analyte of interest to a minimum of 10 % of the routine samples or one sample spike per aqueous matrix type, whichever is greater. An alternate frequency for spiked samples, or matrix spike/matrix spike duplicate pairs, may be used based on the data quality objectives of the program. The spike concentration should not be less than the background concentration of the sample selected for spiking. The spike should ideally be the same as that used for the LFB in 12.5. Samples from all routine sample sources should be spiked periodically.

12.6.2 Calculate the percent recovery (R_i) for each analyte using the following equation:

$$R_i = \left(C_{LFM} - \frac{C_{NS}}{C_A} \right) 100 \quad (5)$$

where:

C_{LFM} = concentration measured in LFM, µg/L,
C_{NS} = concentration measured in nonspiked sample, µg/L, and
C_A = concentration added to LFM, µg/L.

Since both the native and spiked concentration contribute to the error in R_i, the recovery from matrix spikes will generally be more variable than the recovery from reagent water. The laboratory should establish limits as in 12.5.2 for the various aqueous matrix types analyzed (see Note 5 in 12.5.2).

13. Procedure

13.1 *Extraction of Sample*:

13.1.1 The following procedure uses a separatory funnel liquid-liquid extraction. Other extraction techniques may be used, if equivalent results are demonstrated in the matrix of interest. Other extraction techniques include continuous liquid-liquid extraction and solid phase extraction.

13.1.2 Mark the sample bottle for the later determination of sample volume, or determine the sample volume gravimetrically, assuming a density of 1 g/mL. Fortify the sample with the surrogate standard solution. Fortify the control samples with the standard spike solutions. Transfer the entire contents of the 1-L sample bottle to a 2-L separatory funnel, equipped with a TFE-fluorocarbon stopcock.

13.1.3 Add 50 mL of phosphate buffer. Check the sample pH, and add H_2SO_4(1 + 1) or NaOH solution (400 g/L) to adjust the sample to pH 7 if necessary.

13.1.4 Add 100 g of NaCl to the sample, seal, and shake to dissolve the salt.

13.1.5 Rinse the sample bottle and cup liner with 60 mL of methylene chloride, and pour the solvent into the separatory funnel. Extract the water sample by shaking the separatory funnel vigorously for 2 min. Allow the phases to separate; if an emulsion forms that is greater than one third of the solvent layer, it may possibly be broken by stirring, filtration of the emulsion through glass, wool, or cotton, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. Repeat this entire extraction procedure two more times with fresh solvent, and combine the extracts.

13.1.6 Dry the combined extracts by pouring through a drying column containing a 10-cm column of anhydrous sodium sulfate (previously rinsed with methylene chloride), and collect in a 400 mL K-D concentrator flask fitted with a calibrated 10-mL concentrator tube. Rinse the column with several small portions of methylene chloride, and collect in the K-D flask. Other concentration devices or techniques may be used if the requirements of 12.3 are met.

13.1.7 Add one or two boiling chips to the concentrator, and attach a three-ball Snyder column. Place the K-D apparatus in a hot water bath (65 to 70°C), and concentrate until the apparent volume of liquid reaches 2 mL. Remove the apparatus and allow it to drain and cool.

13.1.8 Remove the Snyder column, and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of MTBE. Add 5 to 10 mL of MTBE and a new boiling chip, and attach a micro-Snyder column. Pre-wet the Snyder column by adding approximately 1 mL of MTBE to the top. Concentrate the extract as before. Remove the apparatus and allow it to drain and cool. Rinse the walls of the concentrator tube, and bring the extract to a final volume of 5 mL with MTBE.

13.2 *Cleanup*:

13.2.1 Interferences in the form of distinct peaks or high background, or both, in the initial gas chromatographic analysis, along with the physical characteristics of the extract (color, cloudiness, and viscosity), may indicate whether cleanup is required. Sulfur cleanup is detailed below. Other cleanup options, included in the references, are partitioning with acetonitrile **(5)**, Florisil column adsorption chromatography **(6)**, and gel permeation chromatography (see U.S. EPA *Analytical Methods for Pesticides/Aroclors*).

NOTE 7—Cleanup techniques were not evaluated as part of the test method evaluation. All cleanup techniques must be validated according to 12.3.

13.2.2 *Sulfur Cleanup*—To remove sulfur interference from the original extract, pipet 1 mL of the concentrated extract into a clean concentrator tube or TFE-fluorocarbon sealed vial. Add one to three drops of mercury and seal. Agitate the contents of the vial for 15 to 30 s. Prolonged shaking (2 h) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal.

13.3 *Gas Chromatography Analysis*:

13.3.1 Paragraph 7.9 summarizes the recommended operating conditions for the gas chromatograph. Table 3 lists retention times using the conditions given in 7.9. Other GC

columns, conditions, or detectors may be used if the requirements of 12.4 are met.

13.3.2 Calibrate the system daily, as described in Section 11. The standards and extracts must be in the same solvent.

13.3.3 If internal standard calibration is used, add the internal standard solution to the sample extract, seal the vial, and shake.

13.3.4 Inject 2 µL of the sample extract (the injection volume depends on the capacity of the column).

13.3.5 Dilute and reanalyze if the response for any compound exceeds the working range of the system.

13.4 *Identification of Analytes*:

13.4.1 Identify a sample component by comparison of its retention time to that of a reference chromatogram. Consider the identification positive if the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound. Take additional steps to confirm the identity of the analyte(s) (see 13.4.3) if unfamiliar samples are analyzed.

13.4.2 Base the width of the retention time window used to make identifications on measurements of actual retention time variations of standards over the course of a day. Use three times the standard deviation of a retention time to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

13.4.3 Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more than one sample component (that is, a broadened peak with shoulder(s) or a valley between two or more maxima), or any time doubt exists regarding the identification of a peak on a chromatogram, use appropriate alternative techniques to help confirm peak identification. For example, more positive identification may be made by the use of a different chromatography column or alternate detector, or by the use of a mass spectrometer as a GC detector (if the analyte concentration is adequate). Procedures for compound identification by gas chromatography/mass spectrometry can be found in Practice D 4128 and U.S. EPA Method 680.

13.4.4 If interfering compounds are present, or if PCBs are present along with various chlorinated pesticides, a chemical cleanup procedure may permit the compounds of interest to be identified and quantitated. If any of these procedures are used, it is the responsibility of the analyst to analyze the LFMs and demonstrate that the procedure does not affect the performance of the test method significantly.

13.4.5 If mixtures of multicomponent materials (PCBs, toxaphene, and chlordane) are present, or if "weathering" has altered a material so that it no longer resembles the original product, more advanced data analysis techniques may be required **(7)** (see U.S. EPA Method 680).

14. Calculation

14.1 Identify the organohalides in the sample chromatogram by comparing the retention time of the suspect peak to those generated by the calibration standards and LFBs (see 13.4).

14.1.1 If analyzing for multicomponent pesticides/PCBs, identify the multicomponent compounds using all peaks that are characteristic of the specific compound from chromatograms generated with individual standards. Select the most sensitive and reproducible peaks for calculation purposes. Use the sum of the instrument response for selected peaks in the calculations.

14.2 Calculate the analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Section 11.

14.3 If the internal standard calibration procedure is used, calculate the concentration (*C*) in the sample using the calibration curve or RRF determined in 11.4.1.1 and (Eq 6).

$$C(\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RRF)(V_o)} \quad (6)$$

where:

A_s = response for the parameter to be measured,
A_{is} = response for the internal standard,
I_s = amount of internal standard added to each extract, µg, and
V_o = volume of water extracted, L.

14.4 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or RF determined in 11.4.1.2. The concentration (C) in the sample can be calculated from (Eq 7).

$$C(\mu g/L) = \frac{(A_s)(RF)}{(V_o)} \quad (7)$$

where:

A_s and V_o are defined as in (Eq 6).

14.5 The results should be reported with an appropriate number of significant figures (two are recommended).

15. Precision and Bias

15.1 This test method has been tested by eleven laboratories using reagent water and finished drinking water **(8)**. The study was in accordance with Practice D 2777. The waters were spiked with 29 pesticides (separated into two spiking groups) at six concentration levels, as three Youden pairs. Linear equations for describing the single operator precision, overall precision, and test method bias are presented in Table 1 and Table 2. Recoveries and statistical parameters calculated from regression equations are given in Table 5 and Table 6.

15.1.1 The R^2 is the "coefficient of determination" or the "square of the correlation coefficient." For a regression such as $Y = aX + b$, a R^2 value of 0.75 means that 75 % of the variation in Y is explained by the change in X. Only one of the mean recovery regressions given in Table 1 has an $R^2 < 0.987$; $R^2 = 0.960$ for heptachlor in reagent water. Only three of the overall standard deviation regressions in Table 1 and Table 2 have an $R^2 < 0.624$; $R^2 = 0.420$ for δ-BHC in tap water, $R^2 = 0.227$ for heptachlor in tap water, and $R^2 = 0.116$ for heptachlor in reagent water. The R^2 is greater than 0.735 for every single-operator standard deviation regression in Table 1 and Table 2. Additional summary statistics are available from ASTM in the research report for this test method.[12]

[12] Additional information is available from ASTM Headquarters. Request RR: D19-1154.

TABLE 5 Estimated Recoveries Calculated from Regression Equations by Compound and by Water Type, as Percent of True Concentration[A]

Compound	Concentration, µg/L [B]	Recovery,%		Compound	Concentration, µg/L [B]	Recovery, %	
		Reagent Water	Finished Drinking Water			Reagent Water	Finished Drinking Water
Aldrin	0.7	92.0	83.8	endosulfan II	0.7	97.9	90.4
α-BHC	0.5	102.3	94.6	endosulfan sulfate	0.7	99.3	96.1
β-BHC	0.5	98.7	93.4	endrin	0.7	99.4	89.5
γ-BHC	0.7	100.6	94.2	endrin aldehyde	1.0	94.8	87.7
δ-BHC	0.5	96.9	92.0	etridiazole	1.0	96.7	92.5
α-Chlordane	0.7	101.3	87.6	heptachlor	0.5	97.9	99.0
γ-Chlordane	0.7	94.3	87.2	heptachlor epoxide	1.0	95.7	95.0
Chlorobenzilate	25.0	100.4	88.3	hexachlorobenzene	0.25	85.4	84.9
Chloroneb	25.0	95.3	89.2	methoxychlor	2.0	105.2	94.4
Chlorothalonil	1.0	95.7	92.1	*cis*-permethrin	25.0	95.1	84.1
DCPA	1.0	101.0	93.5	*trans*-permethrin	25.0	94.5	82.5
4,4′-DDD	1.0	97.5	91.6	propachlor	25.0	99.1	93.9
4,4′-DDE	0.5	98.2	84.6	trifluralin	1.0	89.2	85.4
4,4′-DDT	3.0	97.9	86.1				
Dieldrin	1.0	97.1	88.8	average		97.1	90.1
Endosulfan I	0.7	96.6	90.3	standard deviation		3.9	4.2

[A] Weighted linear regression equations.
[B] Midpoint value in concentration range studied.

TABLE 6 Statistical Parameters Calculated from Regression Equations by Compound and by Water Type [A]

Compound	Concentration, µg/L [B]	Reagent Water		Finished Drinking Water		Reagent Water		Finished Drinking Water	
		s_r	s_R	s_r	s_R	RSD_r,%	RSD_R, %	RSD_r,%	RSD_R, %
Aldrin	0.7	6.2	13.2	4.9	15.3	6.7	14.3	5.8	18.2
α-BHC	0.5	6.3	14.1	8.9	18.8	6.2	13.8	9.4	19.9
β-BHC	0.5	4.1	15.7	13.2	21.8	4.2	15.9	14.1	23.3
γ-BHC	0.7	5.4	15.8	6.5	13.8	5.4	15.7	6.9	14.7
δ-BHC	0.5	5.0	12.0	7.0	12.9	5.2	12.4	7.6	14.0
α-Chlordane	0.7	6.3	14.0	6.1	14.4	6.2	13.8	7.0	16.4
γ-Chlordane	0.7	4.7	12.4	6.3	12.1	5.0	13.1	7.2	13.9
Chlorobenzilate	25.0	6.8	18.4	12.7	22.5	6.8	18.3	14.4	25.5
Chloroneb	25.0	9.5	16.2	8.8	16.9	10.0	17.0	9.9	19.0
Chlorothalonil	1.0	9.4	23.4	9.3	16.9	9.8	24.4	10.1	18.3
DCPA	1.0	5.1	16.5	12.4	20.8	5.0	16.3	13.3	22.2
4,4′-DDD	1.0	8.4	14.7	9.4	13.6	8.6	15.1	10.3	14.8
4,4′-DDE	0.5	9.2	16.3	6.8	16.8	9.4	16.6	8.0	19.9
4,4′-DDT	3.0	4.9	13.7	9.3	14.4	5.0	14.0	10.8	16.7
Dieldrin	1.0	8.7	15.3	5.8	12.4	9.0	15.8	6.5	14.0
Endosulfan I	0.7	6.8	13.4	6.6	10.9	7.0	13.9	7.3	12.1
Endosulfan II	0.7	5.9	12.0	5.8	11.0	6.0	12.3	6.4	12.2
Endosulfan sulfate	0.7	11.8	16.8	12.7	23.4	11.9	16.9	13.2	24.3
Endrin	0.7	10.6	13.5	5.6	11.0	10.5	13.6	6.3	12.3
Endrin aldehyde	1.0	9.7	11.8	6.7	8.9	10.2	12.4	7.6	10.2
Etridiazole	1.0	4.9	15.4	6.9	22.2	5.1	15.9	7.5	24.0
Heptachlor	0.5	6.9	12.0	7.3	9.3	7.0	12.3	7.4	9.4
Heptachlor epoxide	1.0	4.9	12.2	6.5	8.3	5.1	12.7	6.8	8.7
Hexachlorobenzene	0.25	4.4	11.7	1.8	10.0	5.1	13.7	2.1	11.8
Methoxychlor	2.0	11.2	19.8	13.2	26.5	10.6	18.8	14.0	28.1
cis-Permethrin	25.0	7.5	13.9	9.5	14.5	7.9	14.6	11.3	17.3
trans-Permethrin	25.0	14.6	26.1	14.9	33.6	15.4	27.6	18.1	40.7
Propachlor	25.0	5.5	13.3	8.5	15.5	5.6	13.4	9.0	16.5
Trifluralin	1.0	6.0	13.2	5.8	12.9	6.7	14.8	6.8	15.1
Average						7.5	15.5	9.1	17.7
Standard deviation						2.6	3.4	3.4	6.7

[A] s_r and s_R = standard deviations for repeatability and reproducibility, respectively; RSD_r and RSD_R = corresponding relative standard deviations.
[B] Midpoint value in concentration range studied.

15.1.2 In the test method study, 12.8 % (490 of 3828 data points) were rejected as outliers. The drinking water matrix had 285 rejected data points, while reagent water had 205 rejected data points. Aldrin had the fewest rejected data points (0) for single compounds, while trifluralin had the highest number of rejected data points (24 %). Two zero values (for hexachlorobenzene in drinking water) were reported.

15.1.3 Mean recoveries of the 29 pesticides tended to be lower in the drinking water than in the reagent water (Table 5). Although precision estimates for drinking water tended to be

higher than related estimates for reagent water data, the overall and single-analyst precisions were similar (Table 6). The DCPA, α-chlordane, 4,4′-DDE, and methoxychlor had lower recoveries and poorer overall precision in drinking water at all concentration levels compared with reagent water.

16. Keywords

16.1 gas chromatography; organochlorine pesticides

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