



Designation: D5175 – 91 (Reapproved 2003)

# Standard Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D5175; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method (1,2,3)<sup>2</sup> is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and the raw source water:

Analyte	Chemical Abstract Service Registry Number <sup>A</sup>
Alachlor	5972-60-8
Aldrin	309-00-2
Chlordane	57-74-9
Dieldrin	60-57-1
Endrin	72-20-8
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Lindane	58-89-9
Methoxychlor	72-43-5
Toxaphene	8001-35-2
Aroclor <sup>B</sup> 1016	12674-11-2
Aroclor <sup>B</sup> 1221	11104-28-2
Aroclor <sup>B</sup> 1232	11141-16-5
Aroclor <sup>B</sup> 1242	53469-21-9
Aroclor <sup>B</sup> 1248	12672-29-6
Aroclor <sup>B</sup> 1254	11097-69-1
Aroclor <sup>B</sup> 1260	11096-82-5

<sup>A</sup> Numbering system of CAS Registry Services, P.O. Box 3343, Columbus, OH 43210-0334.

<sup>B</sup> Aroclor is a registered trademark of Monsanto Co.

1.2 Detection limits for most test method analytes are less than 1  $\mu\text{g/L}$ . Actual detection limits are highly dependent on the characteristics of the sample matrix and the gas chromatography system. Table 1 contains the applicable concentration range for the precision and bias statements. Only Aroclor 1016 and 1254 were included in the interlaboratory test used to derive the precision and bias statements. Data for other PCB products are likely to be similar.

1.3 Chlordane, toxaphene, and Aroclor products (polychlorinated biphenyls) are multicomponent materials. Precision and bias statements reflect recovery of these materials dosed into water samples. The precision and bias statements may not

apply to environmentally altered materials or to samples containing complex mixtures of polychlorinated biphenyls (PCBs) and organochlorine pesticides.

1.4 For compounds other than those listed in 1.1 or for other sample sources, the analyst must demonstrate the applicability of this test method by collecting precision and bias data on spiked samples (groundwater, tap water) (4) and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS) (5) or by GC analysis using dissimilar columns.

1.5 This test method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results using the procedure described in Section 13.

1.6 Analytes that are not separated chromatographically, (analytes that have very similar retention times) cannot be individually identified and measured in the same calibration mixture or water sample unless an alternative technique for identification and quantitation exists (see section 13.4).

1.7 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.

1.8 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

1.9 *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 specific hazard statements, see Section 9.

## 2. Referenced Documents

2.1 ASTM Standards:<sup>3</sup>

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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<sup>2</sup> The boldface numbers in parentheses refer to a list of references at the end of this test method.

<sup>3</sup> 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.

**TABLE 1 Test Method Precision and Bias<sup>A</sup> as Functions of Concentration**

Compound	Applicable Concentration Range, $\mu$ g/L	Water Type <sup>B C D E</sup>	
		Reagent water	Ground water
Alachlor	0.50 to 37.50	$S_o = 0.077X + 0.09$ $S_t = 0.107X + 0.15$ $X = 1.004C - 0.08$	$S_o = 0.075X + 0.05$ $S_t = 0.086X + 0.29$ $X = 1.059C + 0.03$
Aldrin	0.04 to 1.42	$S_o = 0.030X + 0.02$ $S_t = 0.251X + 0.00$ $X = 1.066C + 0.00$	$S_o = 0.115X + 0.00$ $S_t = 0.189X + 0.01$ $X = 0.945C - 0.00$
Chlordane	0.51 to 50.90	$S_o = 0.083X + 0.06$ $S_t = 0.125X + 0.19$ $X = 1.037C + 0.06$	$S_o = 0.062X + 0.09$ $S_t = 0.147X + 0.24$ $X = 0.941C + 0.09$
Dieldrin	0.10 to 7.53	$S_o = 0.091X + 0.01$ $S_t = 0.199X + 0.02$ $X = 1.027C + 0.00$	$S_o = 0.089X + 0.04$ $S_t = 0.221X + 0.04$ $X = 0.961C + 0.01$
Endrin	0.10 to 7.50	$S_o = 0.116X + 0.01$ $S_t = 0.134X + 0.02$ $X = 0.958C + 0.01$	$S_o = 0.045X + 0.15$ $S_t = 0.196X + 0.07$ $X = 0.958C + 0.05$
Heptachlor	0.04 to 1.41	$S_o = 0.104X + 0.01$ $S_t = 0.206X + 0.02$ $X = 1.002C + 0.02$	$S_o = 0.058X + 0.02$ $S_t = 0.153X + 0.02$ $X = 0.964C + 0.02$
Heptachlor Epoxide	0.04 to 1.42	$S_o = 0.031X + 0.02$ $S_t = 0.127X + 0.02$ $X = 0.952C + 0.00$	$S_o = 0.032X + 0.00$ $S_t = 0.103X + 0.02$ $X = 0.932C + 0.01$
Hexachlorobenzene	0.01 to 0.37	$S_o = 0.104X + 0.00$ $S_t = 0.231X + 0.00$ $X = 1.028C - 0.00$	$S_o = 0.148X + 0.00$ $S_t = 0.301X + 0.00$ $X = 0.901C - 0.00$
Lindane	0.04 to 1.39	$S_o = 0.056X + 0.01$ $S_t = 0.141X + 0.00$ $X = 1.009C - 0.00$	$S_o = 0.095X + 0.00$ $S_t = 0.134X - 0.00$ $X = 0.909C + 0.00$
Methoxychlor	0.20 to 15.00	$S_o = 0.115X + 0.12$ $S_t = 0.122X + 0.21$ $X = 0.950C + 0.15$	$S_o = 0.179X + 0.02$ $S_t = 0.210X + 0.08$ $X = 1.014C + 0.07$
Toxaphene	5.63 to 70.40	$S_o = 0.132X - 0.32$ $S_t = 0.273X - 0.72$ $X = 1.087C + 0.24$	$S_o = 0.067X + 0.28$ $S_t = 0.181X + 1.52$ $X = 0.903C + 0.50$
PCB-1016	0.50 to 49.80	$S_o = 0.106X + 0.31$ $S_t = 0.144X + 0.46$ $X = 0.856C + 0.31$	$S_o = 0.141X + 0.13$ $S_t = 0.218X + 0.06$ $X = 0.958C + 0.07$
PCB-1254	0.50 to 50.40	$S_o = 0.122X + 0.12$ $S_t = 0.282X + 0.05$ $X = 0.872C - 0.01$	$S_o = 0.126X + 0.17$ $S_t = 0.396X + 0.02$ $X = 0.938C - 0.02$

<sup>A</sup> Bias =  $C - X$ .

<sup>B</sup>  $X$  = Mean recovery.

<sup>C</sup>  $C$  = True concentration value.

<sup>D</sup>  $S_t$  = Overall standard deviation.

<sup>E</sup>  $S_o$  = Single analyst standard deviation.

[D3534 Test Method for Polychlorinated Biphenyls \(PCBs\) in Water<sup>4</sup>](#)

[D3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water](#)

[D4128 Guide for Identification and Quantitation of Organic Compounds in Water by Combined Gas Chromatography and Electron Impact Mass Spectrometry](#)

[D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data<sup>4</sup>](#)

[E355 Practice for Gas Chromatography Terms and Relationships](#)

2.2 *EPA Standards:*

<sup>4</sup> Withdrawn. The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

**Method 505.** Analysis of Organohalide Pesticides and Aroclors in Water by Microextraction and Gas Chromatography<sup>5</sup>

**Method 680.** Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry<sup>5</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology **D1129** and Practice **E355**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *field duplicates (FD 1 and FD 2)*, *n*—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 give 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)*, *n*—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 if analytes or other interferences are present in the field environment.

3.2.3 *instrument performance check solution (IPC)*, *n*—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)*, *n*—two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD 1 and LD 2 give a measure of the precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

3.2.5 *laboratory fortified blank (LFB)*, *n*—an aliquot of reagent water to which known quantities of the 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)*, *n*—an aliquot of an environmental sample to which known quantities of the analytes are added in the laboratory. The LFM is analyzed as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

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

3.2.8 *standard solution, secondary dilution*, *n*—a solution of several analytes prepared in the laboratory from stock

standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.2.9 *standard solution, stock*, *n*—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.

3.2.10 *quality control sample (QCS)*, *n*—a sample containing analytes or a solution of analytes in a water-miscible solvent 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.

### 4. Summary of Test Method

4.1 This is a microextraction method in which 35 mL of sample are extracted with 2 mL of hexane. Two  $\mu$ L of the extract are injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous calibration standards are extracted and analyzed in an identical manner to compensate for possible extraction losses.

4.2 The extraction and analysis time is 30 to 50 min per sample depending upon the analytes and the analytical conditions chosen.

4.3 This test method is based largely on EPA Method 505.

### 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 laboratory reagent blanks as described in **12.2**.

6.1.1 Glassware must be scrupulously cleaned (**2**). Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot tap water and detergent and thoroughly rinsing with tap and reagent water. Drain dry and heat in an oven or muffle furnace at 400°C for 1 h. Do not heat volumetric ware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

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

6.2 Phthalate esters, frequently found in plastics, paints, and other common laboratory items, produce a positive response on

<sup>5</sup> Available from US EPA, Environmental Monitoring Systems Laboratory, Cincinnati, OH 45268.

an electron capture detector. Therefore, samples and solvents should come in contact only with 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-sample rinsing of the sample syringe and associated equipment with hexane can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of hexane should be made to ensure that accurate values are obtained for the next sample.

6.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all the analytes listed in the scope are not resolved from each other on any one column; one analyte of interest may be an interferent for another analyte of interest. The extent of matrix interferences will vary considerably from source to source depending upon the water sampled. Cleanup of sample extracts may be necessary. Positive identifications should be confirmed (see section 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. If this is not the case, chromatographic comparability of standards to sample may be affected.

6.6 Caution must be taken in the determination of endrin since it has been reported that the splitless injector may cause endrin degradation (6). 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 adhere to glass surfaces. It is recommended that sample transfers and glass surface contacts be minimized.

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

6.9 An interfering, erratic peak has been observed within 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 randomly vary in numerical value from successive injections made from the same vial. This type of outlying observation normally is recognized. If encountered, additional analyses will be necessary.

## 7. Apparatus

7.1 *Sample Containers*, 40-mL screw cap vials each equipped with a size 24 cap with a flat, disc-like PTFE facing backed with a polyethylene film/foam extrusion. Prior to use, wash vials and septa with detergent and rinse with tap and reagent waters. Allow the vials and septa to air dry at room temperature. Place the vials in a 400°C oven for 1 h. Remove and allow to cool in an area known to be free of organics.

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

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

7.4 *Micro syringe*, 10 and 100  $\mu\text{L}$ .

7.5 *Micro syringe*, 25  $\mu\text{L}$  with a 50 by 0.15 mm (2 by 0.006-in.) needle.

7.6 *Standard Solution Storage Containers*, 15-mL bottles with PTFE-lined screw caps.

7.7 *Gas Chromatograph*, analytical system equipped with temperature programming capability, splitless injector (0.5 min splitless mode), capillary column, and linearized electron capture detector. A computer data system is recommended for measuring peak areas. Table 2 lists retention times observed using the columns and conditions described below.

7.7.1 Three gas chromatographic columns are recommended. Column 1 (see 7.7.2) should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Validation data presented in this test method were obtained using this column. Columns 2 and 3 are recommended for use as confirmatory columns when GC/MS confirmation is not available. Alternative columns may be used in accordance with the provisions described in 12.3.

7.7.2 *Column 1 (Primary Column)*—A 0.32 mm inside diameter by 30 m long fused silica capillary with chemically bonded methyl polysiloxane phase. Helium carrier gas flow is about 25 cm/s linear velocity, measured at 180° with 9 psi column head pressure. The oven temperature is programmed from 180 to 260°C at 4°C/min and held at 260°C until all expected compounds have eluted. Injector temperature is 200°C. Detector temperature is 290°C. Sample chromatograms for selected pesticides are presented in Fig. 1 and Fig. 2. Chromatograms of the PCBs, toxaphene, and technical chlordane are presented in Figs. 3-11.

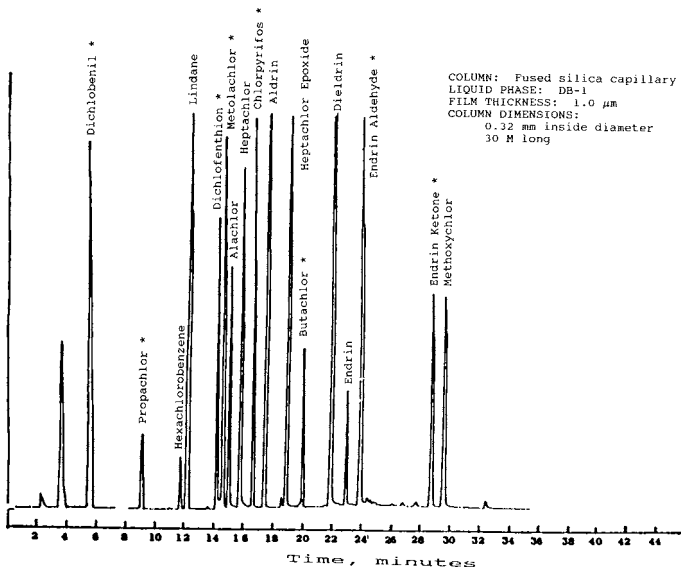
7.7.3 *Column 2 (Alternative Column)*—A 0.32 mm inside diameter by 30 m long fused silica capillary with a 1:1 mixed phase of dimethyl silicone and polyethylene glycol. Helium

**TABLE 2 Retention Times for Method Analytes**

Analyte	Primary	Retention Time, <sup>A</sup> min	
		Confirm 1	Confirm 2
Hexachlorobenzene	11.9	13.4	15.6
Lindane	12.3	18.4	18.7
Alachlor	15.1	19.7	21.1
Heptachlor	15.9	17.5	20.0
Aldrin	17.6	18.4	21.4
Heptachlor Epoxide	19.0	24.6	24.6
Dieldrin	22.1	45.1	27.8
Endrin	24.2	33.3	29.2
Methoxychlor	30.0	58.5	36.4
		Primary <sup>B</sup>	
Aroclor 1016	13.6, 14.8, 15.2, 16.2, 17.7		
Aroclor 1221	7.7, 9.0, 15.9, 19.1, 24.7		
Aroclor 1232	11.2, 14.7, 13.6, 15.2, 17.7		
Aroclor 1242	11.2, 13.6, 14.7, 15.2, 17.7, 19.8		
Aroclor 1248	14.8, 16.2, 17.1, 17.7, 19.8, 22.0		
Aroclor 1254	19.1, 21.9, 23.4, 24.9, 26.7		
Aroclor 1260	23.4, 24.9, 26.7, 28.2, 29.9, 32.6		
Chlordane	15.1, 15.9, 20.1, 20.9, 21.3		
Toxaphene	21.7, 22.5, 26.7, 27.2		

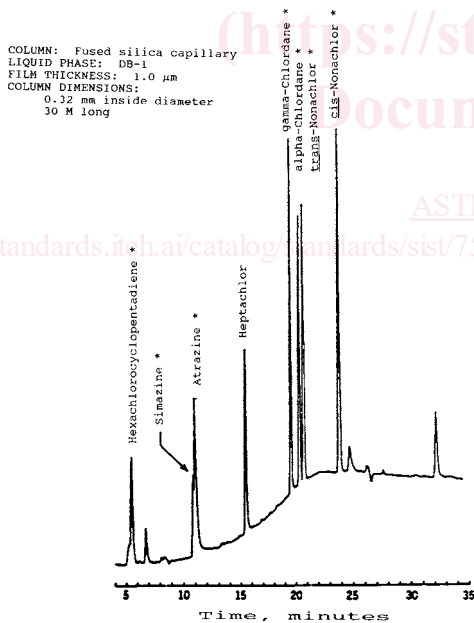
<sup>A</sup> Columns and analytical conditions are described in 7.7.2, 7.7.3, and 7.7.4.

<sup>B</sup> Column and conditions described in 7.7.2. More than one peak listed does not implicate the total number of peaks characteristic of the multicomponent analyte. Listed peaks indicate only the ones chosen for quantification.



NOTE 1—Interlaboratory precision and bias data are not available for those compounds listed with an asterisk. They are shown for informational purposes only.

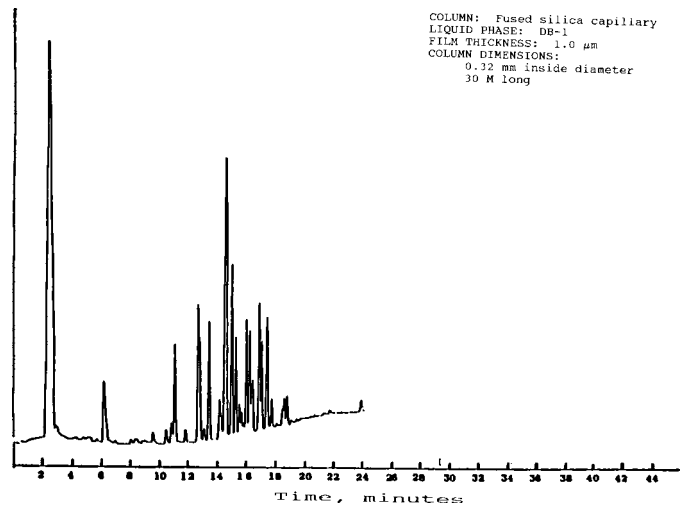
**FIG. 1 Hexane Spiked at 7.71  $\mu\text{g/L}$  with Heptachlor and Lindane; 9.14  $\mu\text{g/L}$  with Heptachlor Epoxide; 11.4  $\mu\text{g/L}$  with Aldrin and Hexachlorobenzene; 23  $\mu\text{g/L}$  with Butachlor, Chlorpyrifos, Chlorpyrifosmethyl, Diclobenil, Dieldrin, Endrin, Metolochlor, and Propachlor; and 44.9  $\mu\text{g/L}$  with Methoxychlor.**



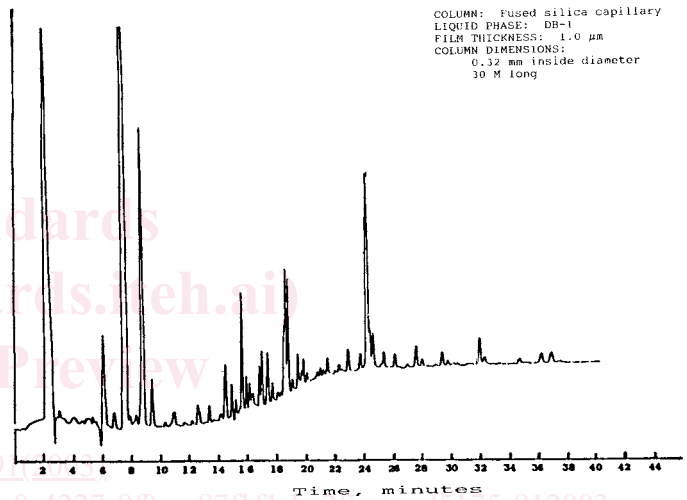
NOTE 1—Interlaboratory precision and bias data are not available for those compounds listed with an asterisk. They are shown for informational purposes only.

**FIG. 2 Extract of Reagent Water Spiked at 20  $\mu\text{g/L}$  with Atrazine, 60  $\mu\text{g/L}$  with Simazine, 0.45  $\mu\text{g/L}$  with Cis-nonachlor, and 0.35  $\mu\text{g/L}$  with Hexachlorocyclopentadiene, Heptachlor, Alpha Chlordane, Gamma Chlordane, and Trans-nonachlor.**

carrier gas flow is about 25 cm/s linear velocity and oven temperature is programmed from 100 to 210°C at 8°C/min and



**FIG. 3 Hexane Spiked at 11.4  $\mu\text{g/L}$  with Aroclor 1016**



**FIG. 4 Hexane Spiked at 171.4  $\mu\text{g/L}$  with Aroclor 1221**

held at 210°C until all expected compounds have eluted. Then the post temperature is programmed to 240°C at 8°C/min for 5 min.

**7.7.4 Column 3 (Alternative Column)**—A 0.32 mm inside diameter by 25 m long fused silica capillary with chemically bonded 50:50 methyl-phenyl silicone. Helium carrier gas flow is about 40 cm/s linear velocity, and the oven temperature is programmed from 100 to 260°C at 4°C/min and held at 260°C until all expected compounds have eluted.

## 8. Reagents and Materials

**8.1 Purity of Reagents**—Reagent grade chemicals shall be used. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on

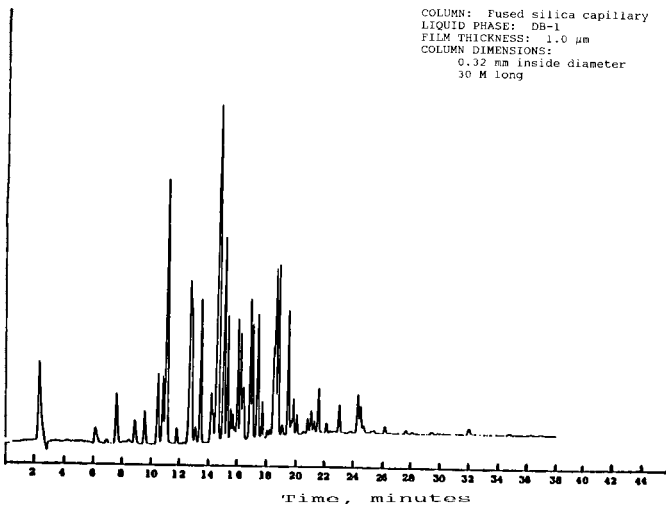


FIG. 5 Hexane Spiked at 57.1  $\mu\text{g/L}$  with Aroclor 1232

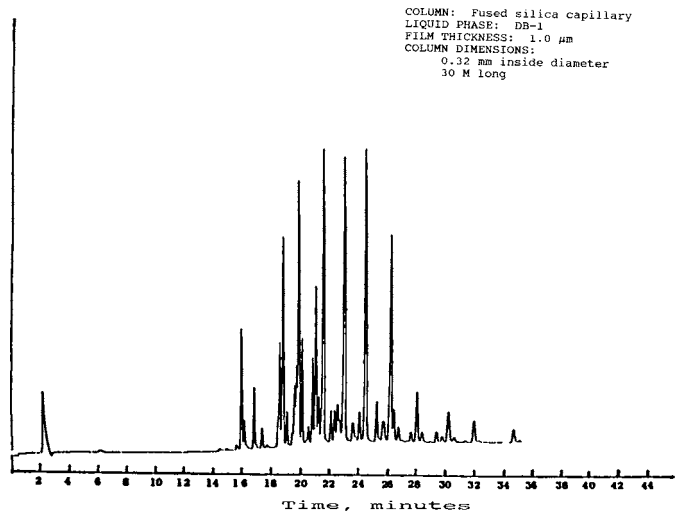


FIG. 8 Hexane Spiked at 42.9  $\mu\text{g/L}$  with Aroclor 1254

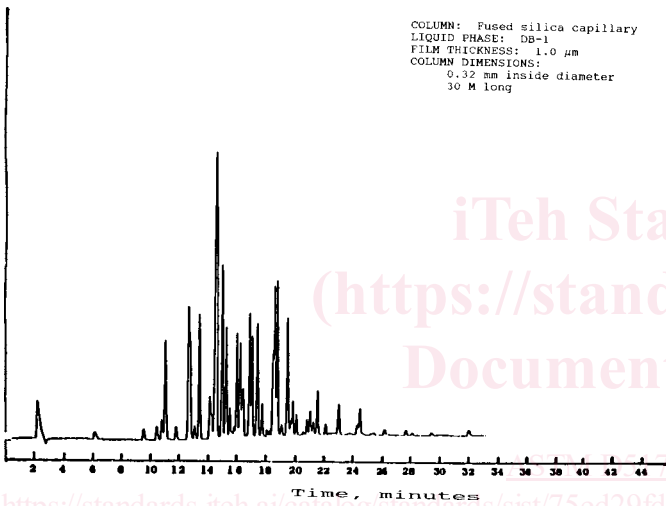


FIG. 6 Hexane Spiked at 57.1  $\mu\text{g/L}$  with Aroclor 1242

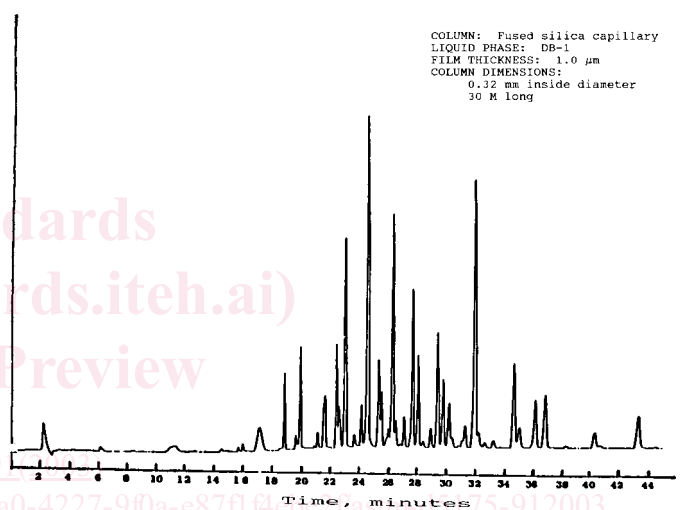


FIG. 9 Hexane Spiked at 34.3  $\mu\text{g/L}$  with Aroclor 1260

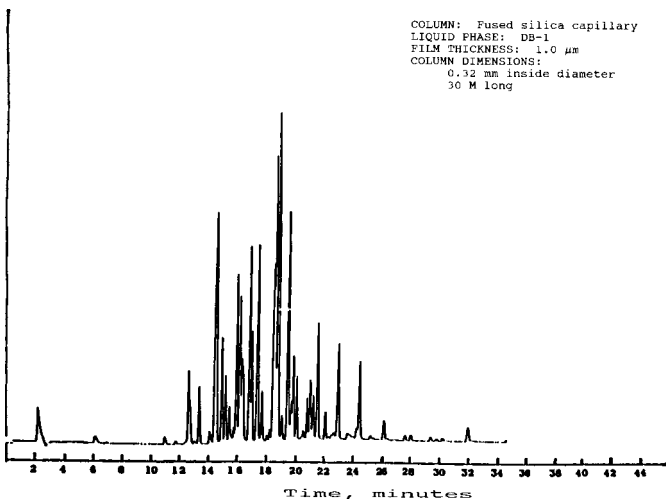


FIG. 7 Hexane Spiked at 57.1  $\mu\text{g/L}$  with Aroclor 1248

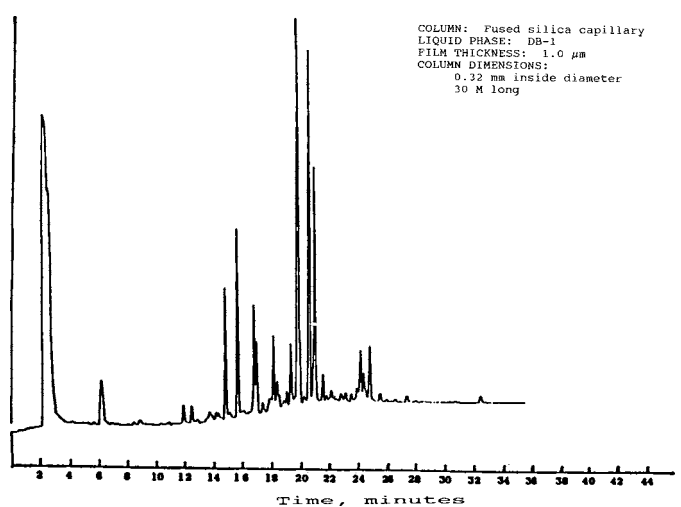


FIG. 10 Hexane Spiked at 28.6  $\mu\text{g/L}$  with Chlordane