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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography[1]

This standard is issued under the fixed designation D 5175; 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—Footnotes were deleted editorially in December 1996.

1. Scope

1.1 This test method **(1,2,3)**[2] 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 [A]
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 [B] 1016	12674-11-2
Aroclor [B] 1221	11104-28-2
Aroclor [B] 1232	11141-16-5
Aroclor [B] 1242	53469-21-9
Aroclor [B] 1248	12672-29-6
Aroclor [B] 1254	11097-69-1
Aroclor [B] 1260	11096-82-5

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

[B] Aroclor is a registered trademark of Monsanto Co.

1.2 Detection limits for most test method analytes are less than 1 µg/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:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 3534 Test Method for Polychlorinated Biphenyls (PCBs) in Water[4]

[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 Sept. 15, 1991. Published February 1992.

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

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

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

TABLE 1 Test Method Precision and Bias [A] as Functions of Concentration

Compound	Applicable Concentration Range, µg/L	Water Type[B C D E]	
		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	$S_o = 0.122X + 0.12$ $S_t = 0.282X + 0.05$ $X = 0.872C - 0.01$	$S_o = 0.126X + 0.17$ $S_t = 0.396X + 0.02$ $X = 0.938C - 0.02$

[A] Bias = $C - X$.
[B] X = Mean recovery.
[C] C = True concentration value.
[D] S_t = Overall standard deviation.
[E] S_o = Single analyst standard deviation.

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]

D 4128 Practice for Identification of Organic Compounds in Water by Combined Gas Chromatography and Electron Impact Mass Spectrometry[4]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]

E 355 Practice for Gas Chromatography Terms and Relationships[5]

2.2 *EPA Standards:*

Method 505, Analysis of Organohalide Pesticides and Aroclors in Water by Microextraction and Gas Chromatography[6]

[5] *Annual Book of ASTM Standards*, Vol 14.02.

[6] Available from US EPA, Environmental Monitoring Systems Laboratory, Cincinnati, OH 45268.

Method 680, Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry[6]

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), 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 µL 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 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 over 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 µL.

7.5 *Micro syringe*, 25 µL 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.

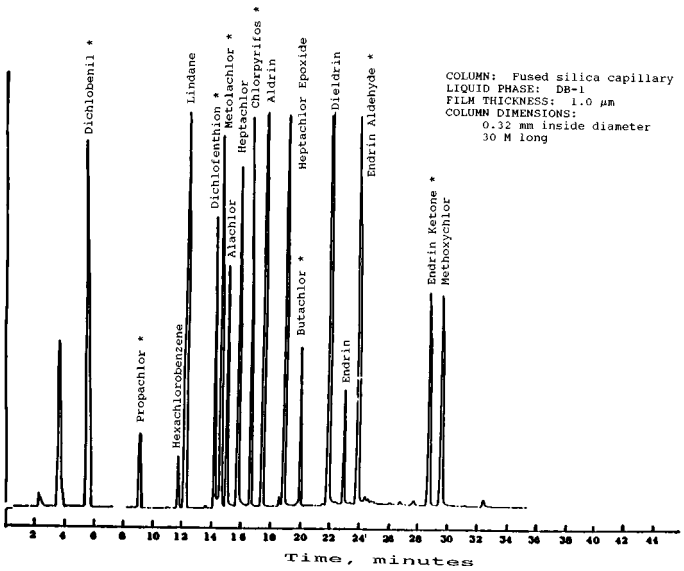
7.7.3 *Column 2 (Alternative Column)*—A 0.32 mm inside diameter by 30 m long fused silica capillary with a 1:1 mixed phase of dimethyl silicone and polyethylene glycol. Helium carrier gas flow is about 25 cm/s linear velocity and oven temperature is programmed from 100 to 210°C at 8°C/min and held at 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

TABLE 2 Retention Times for Method Analytes

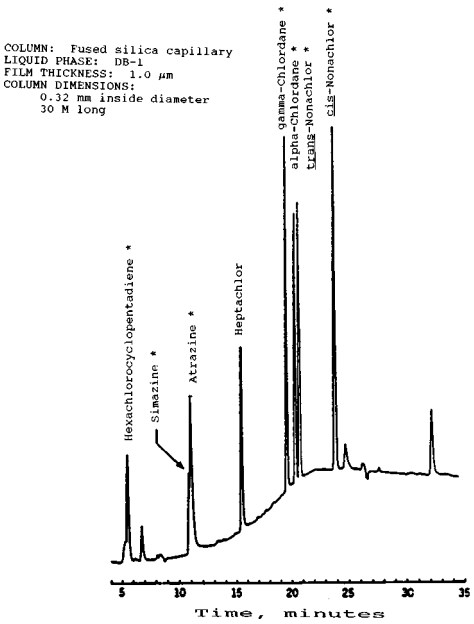
Analyte	Primary	Retention Time, [A] min	
		Confirm 1	Confirm 2
Hexachlorobenzene	11.9	13.4	15.6
Lindane	12.3	18.4	18.7
Alachlor	15.1	19.7	21.1
Heptachlor	15.9	17.5	20.0
Aldrin	17.6	18.4	21.4
Heptachlor Epoxide	19.0	24.6	24.6
Dieldrin	22.1	45.1	27.8
Endrin	24.2	33.3	29.2
Methoxychlor	30.0	58.5	36.4
		Primary[B]	
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		

[A] Columns and analytical conditions are described in 7.7.2, 7.7.3, and 7.7.4.
[B] 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 µg/L with Heptachlor and Lindane; 9.14 µg/L with Heptachlor Epoxide; 11.4 µg/L with Aldrin and Hexachlorobenzene; 23 µg/L with Butachlor, Chlorpyrifos, Chlorpyrifosmethyl, Diclobenil, Dieldrin, Endrin, Metolochlor, and Propachlor; and 44.9 µg/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 µg/L withAtrazine, 60 µg/L with Simazine, 0.45 µg/L with Cis-nonachlor, and 0.35 µg/L with Hexachlorocyclopentadiene, Heptachlor, Alpha Chlordane, Gamma Chlordane, and Trans-nonachlor.

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 Analytical Reagents of the American Chemical Society.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without decreasing the accuracy of the test method.

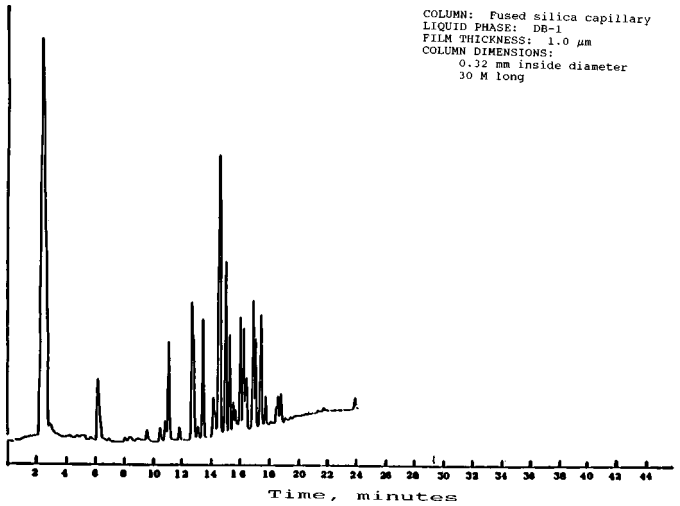


FIG. 3 Hexane Spiked at 11.4 µg/L with Aroclor 1016

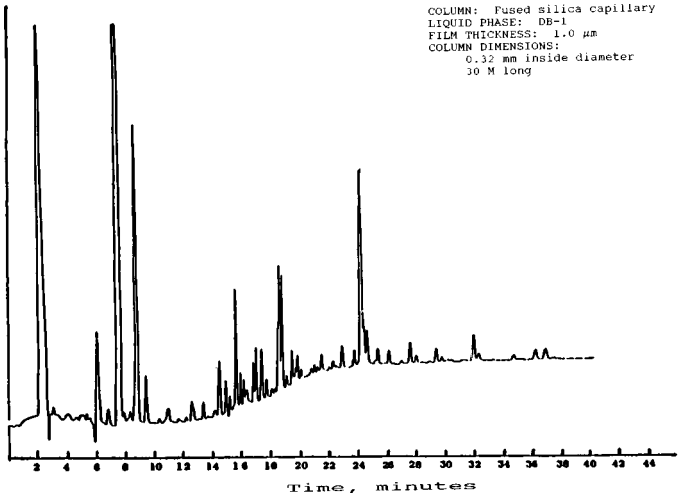


FIG. 4 Hexane Spiked at 171.4 µg/L with Aroclor 1221

8.2 *Purity of Water*—Reagent water conforming to Specification D 1193, Type II and shown to contain no interfering compounds at concentrations sufficient to interfere with the analytes listed in 1.1.

8.3 *n-Hexane*, pesticide grade or equivalent.

8.4 *Methyl Alcohol*, pesticide grade or equivalent.

8.5 *Acetone*, pesticide grade or equivalent.

8.6 *Sodium Chloride*, for treatment before use, pulverize a batch of sodium chloride and place in a muffle furnace at room

[7] *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.

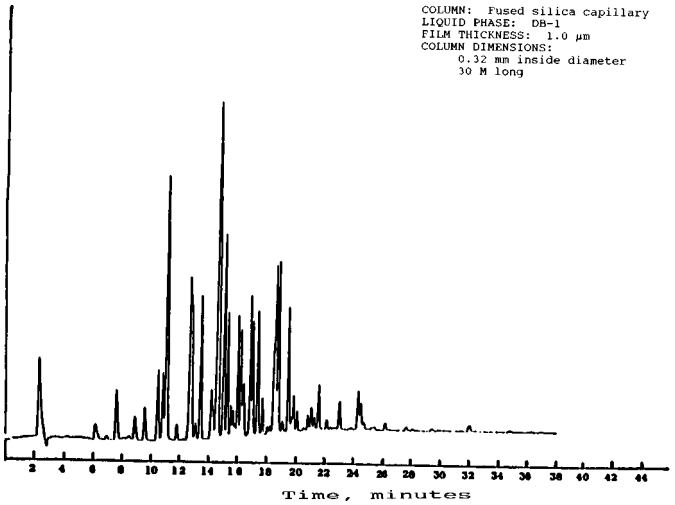


FIG. 5 Hexane Spiked at 57.1 µg/L with Aroclor 1232

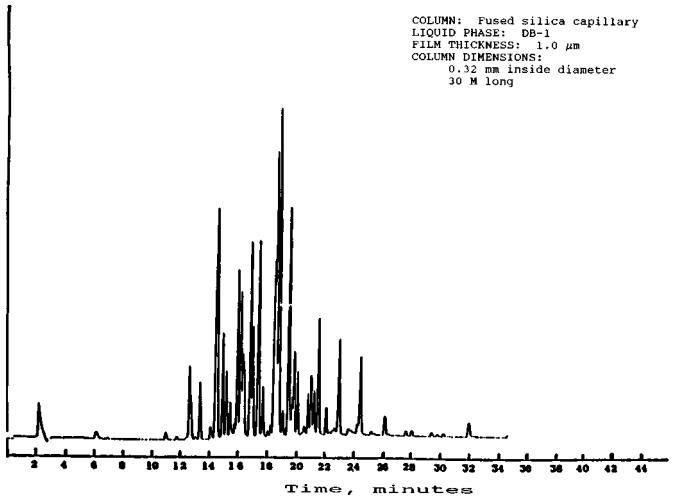


FIG. 7 Hexane Spiked at 57.1 µg/L with Aroclor 1248

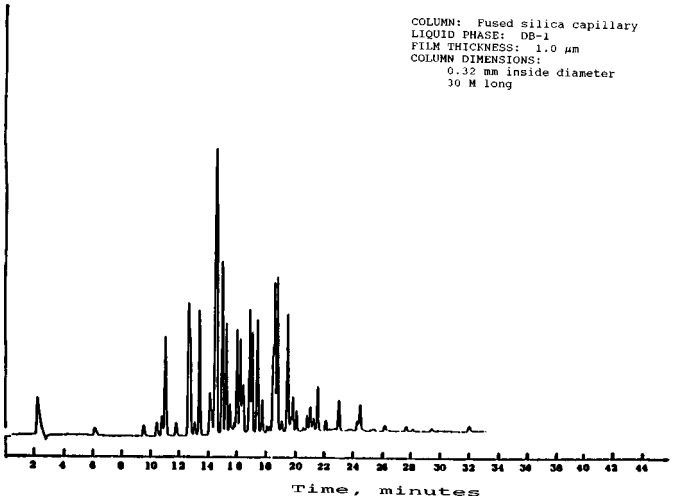


FIG. 6 Hexane Spiked at 57.1 µg/L with Aroclor 1242

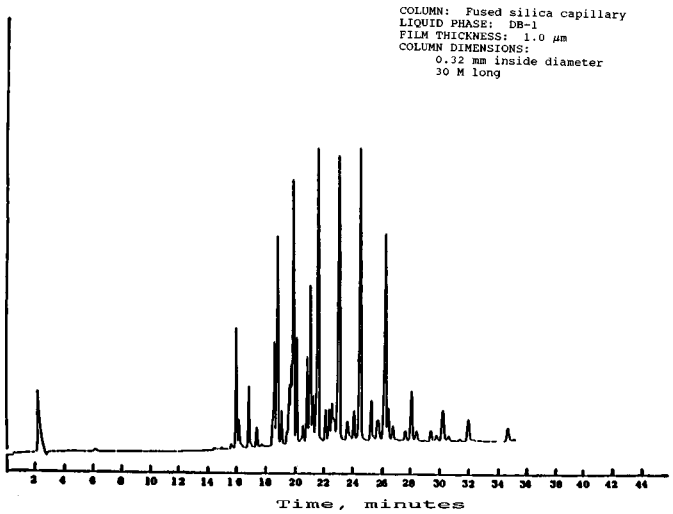


FIG. 8 Hexane Spiked at 42.9 µg/L with Aroclor 1254

temperature. Increase the temperature to 400°C and hold for 30 min. Place in a bottle and cap.

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

8.8 *Standard Solutions, Stock*—These solutions may be obtained as certified solutions or prepared from pure standard materials using the following procedures:

8.8.1 Prepare stock standard solutions (5000 µg/mL) by accurately weighing about 0.0500 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When 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 by an independent source.

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

8.8.3 Stock standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

8.9 *Standard Solutions, Secondary Dilution*—Use stock standard solutions to prepare secondary dilution standard solutions that contain the analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards in 11.2.1 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 calibration standards. The storage time described for stock standard solutions in 8.8.3 also applies to secondary dilution standard solutions.

8.10 *Instrument Performance Check (IPC) Solution*—Prepared by combining microlitre aliquots of appropriate secondary dilution standard solutions in a hexane solvent. Concentrations of the analytes should be approximately equal to those shown in Figs. 1-11. Not all analytes can be combined into a single IPC. (See 1.6 and 13.4)

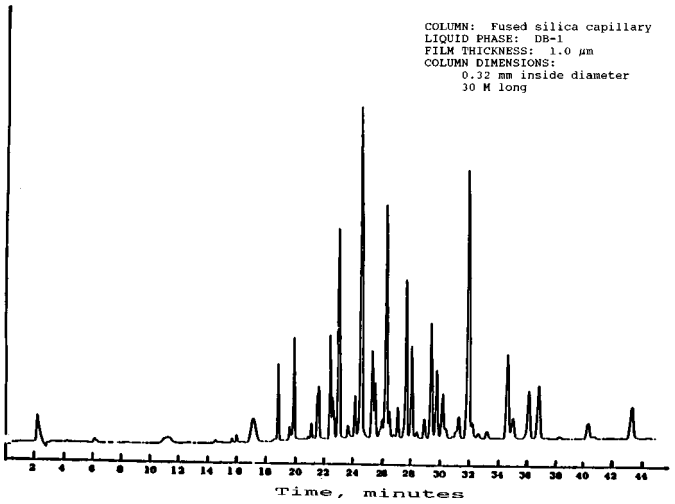


FIG. 9 Hexane Spiked at 34.3 µg/L with Aroclor 1260

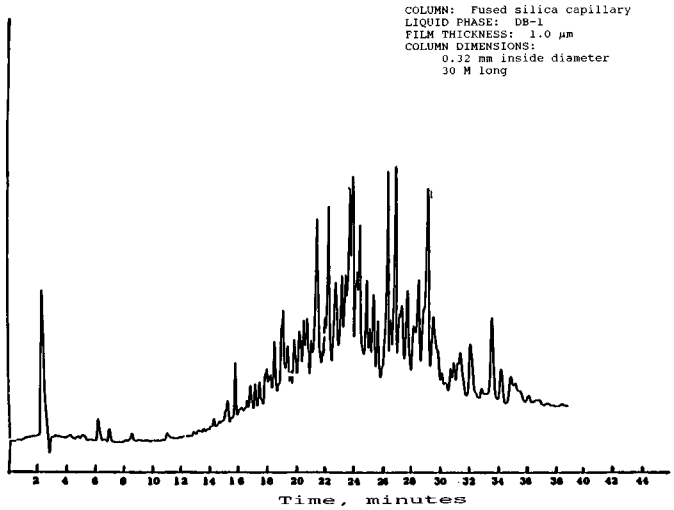


FIG. 11 Hexane Spiked at 57.1 µg/L with Toxaphene

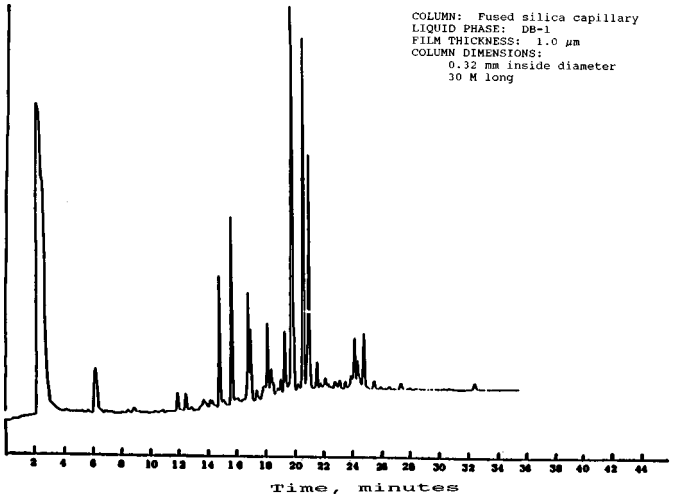


FIG. 10 Hexane Spiked at 28.6 µg/L with Chlordane

9. Hazards

9.1 **Precaution**—The toxicity and carcinogenicity of chemicals used in this test method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this test method. Additional references to laboratory safety are available **(7, 8, 9)** for the information of the analyst.

9.2 **Warning**—The following organohalides have been tentatively classified 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 all samples in 40-mL vials into which 3 mg of sodium thiosulfate crystals have been added to the empty bottles just prior to shipping to the sampling site. Alternately, 75 µL of freshly prepared sodium thiosulfate solution (0.04 g/mL) may be added to empty 40-mL vials just prior to sample collection. In collecting field samples, add sodium thiosulfate solution at the sampling site.

10.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream.

10.1.3 When sampling from a well, fill a wide-mouth bottle or beaker with sample and carefully fill 40-mL sample vials.

10.2 *Sample Preservation*—The samples must be chilled to 4°C at the time of collection and maintained at that temperature until the analyst is prepared for the extraction process. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be maintained at 4°C until arrival at the laboratory.

10.3 *Sample Storage*:

10.3.1 Store samples and extracts at 4°C until analysis has been completed.

10.3.2 Extract all samples as soon as possible after collection. Results of holding time studies suggest that all analytes with the possible exception of heptachlor were stable for 14 days when stored under these conditions. In general, heptachlor showed inconsistent results. If heptachlor is to be determined, samples should be extracted within seven days of collection. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

11. Calibration and Standardization

11.1 Establish GC operating parameters equivalent to those indicated in 7.7.

11.2 At least three calibration standards are needed; five are recommended. One should contain analytes at a concentration near but greater than the estimated detection limit for each compound. The other two should be at concentrations that bracket the range expected in samples. For example, if the estimated detection limit is 0.01 µg/L and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous

standards should be prepared at concentrations of 0.02, 0.10, and 0.20 µg/L.

11.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard to a 35-mL aliquot of reagent water in a 40-mL bottle. Do not add less than 20 µL of an alcoholic standard to the reagent water. Use a 25-µL micro syringe and rapidly inject the alcoholic standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. Mix by inverting and shaking the capped bottle several times. Aqueous standards must be prepared fresh daily.

11.2.2 Starting with the standard of lowest concentration, prepare, extract, and analyze each calibration standard beginning with 13.2 and tabulate peak height or area response versus the concentration in the standard. The results are to be used 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 % RSD or less), linearity to the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

11.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for an analyte varies from the predicted response by more than ±20 %, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve.

11.3 *Instrument Performance*—Check the performance of the equipment daily using laboratory reagent blanks (LRB) and the instrument performance check solution (IPC).

11.3.1 Significant peak tailing in excess of that shown for the target compounds in the chromatograms (see Figs. 1-11) must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or operation of the detector.

11.3.2 Check the precision between replicate injections. Poor precision is generally traceable to pneumatic leaks, especially at 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.

11.3.3 Observed relative area responses of endrin (see 6.5) must meet the following general criteria if endrin is a compound of interest:

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

11.3.3.2 The total percent breakdown for endrin must not exceed 20 %. If the breakdown exceeds 20 % in the IPC, LFB, and LFM, then the problem is likely in the instrument or a bad stock solution. The problem must be corrected before proceeding. If breakdown exceeds 20 % only in the LFM, then this should be noted when reporting sample results:

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

where:

EA = endrin aldehyde (found), µg/L,
EK = endrin ketone (found), µg/L, and
E = endrin (injected) µg/L.

12. Quality Control

12.1 Minimum quality control requirements are initial demonstration of laboratory capability, analysis of laboratory reagent blanks (LRB), laboratory fortified blanks (LFB), laboratory fortified sample matrix (LFM), and, if available, quality control samples (QCS). For a general discussion of good laboratory practices, see Guide D 3856 and Practice D 4210.

12.2 *Laboratory Reagent Blanks*—Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, an LRB must be analyzed. 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 (about ten times the estimated detection limit or at the regulatory maximum contaminant level, whichever is lower) for each analyte. Prepare a secondary dilution standard solution (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 35 µL of the concentrate to each of at least four 35-mL aliquots of reagent water and analyze each aliquot according to procedures beginning in Section 13.

12.3.2 For all four aliquots analyzed, the recovery value for each analyte should fall in the range of $R \pm 30$ % (or within $R \pm 35$ % if broader) using the values for R and S for reagent water in Table 3. For those compounds that meet the acceptance criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, initial demonstration procedures should be repeated.

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 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. Each time such method modifications are made, the analyst must repeat the procedures in 12.3.

12.5 *Assessing Laboratory Performance—Laboratory Fortified Blank*:

12.5.1 The laboratory must analyze at least one laboratory fortified blank (LFB) per sample set (all samples extracted within a 24 h period). The spiking concentration of each analyte in the LFB sample should be accurately known and

TABLE 3 Single Laboratory Accuracy and Precision for Analytes from Reagent Water, Ground Water, and Tap Water [A]

Analyte	Spike Level, [B] µg/L	Recovery and Standard Deviation					
		Reagent Water		Ground Water		Tap Water	
		R [C]	S [D]	R	S	R	S
Alachlor	0.50	102	13.4	... [E]	... [E]	... [E]	... [E]
Aldrin	0.05	106	20.0	86	16.3	... [E]	... [E]
Chlordane	0.17	NA [F]	8.0	... [E]	... [E]	105	12.4
	3.4	NA [F]	3.6	... [E]	... [E]	95	9.6
Dieldrin	0.10	87	17.1	67	10.1	92	15.7
	3.6	114	9.1	94	8.6	81	14.0
Endrin	0.10	119	29.8	94	20.2	106	14.0
	3.6	99	6.5	100	11.3	85	12.4
Heptachlor	0.032	77	10.2	37	6.8	200	22.6
	1.2	80	7.4	71	9.8	106	16.8
Heptachlor Epoxide	0.04	100	15.6	90	14.2	112	7.5
	1.4	115	6.6	103	6.9	81	5.9
Hexachlorobenzene	0.003	104	13.5	91	10.9	100	15.6
	0.09	103	6.6	101	4.4	88	13.4
Lindane	0.03	91	6.5	88	7.7	103	8.1
	1.2	111	5.0	109	3.4	93	18.4
Methoxychlor	2.10	100	21.0	... [E]	... [E]	... [E]	... [E]
	7.03	98	10.9	... [E]	... [E]	... [E]	... [E]
Toxaphene	10	NA [F]	12.6	... [E]	... [E]	110	9.5
	80	NA [F]	15.3	... [E]	... [E]	114	13.5
Aroclor 1016	1.0	NA [F]	6.6	... [E]	... [E]	97	7.5
Aroclor 1221	180	NA [F]	8.3	... [E]	... [E]	92	9.6
Aroclor 1232	3.9	NA [F]	13.5	... [E]	... [E]	86	7.3
Aroclor 1242	4.7	NA [F]	6.0	... [E]	... [E]	96	7.4
Aroclor 1248	3.6	NA [F]	11.5	... [E]	... [E]	... [E]	... [E]
	3.4	... [E]	... [E]	... [E]	... [E]	84	9.9
Aroclor 1254	1.8	NA [F]	10.4	... [E]	... [E]	... [E]	... [E]
	1.7	... [E]	... [E]	... [E]	... [E]	85	11.8
Aroclor 1260	2.0	NA [F]	20.7	... [E]	... [E]	... [E]	... [E]
	1.8	NA [F]	... [E]	... [E]	... [E]	88	19.8

[A] Data corrected for amount detected in blank and represent the mean of five to eight samples.
[B] Refers to spike levels used to generate *R* and *S* data for the three types of water matrices.
[C] Average percent recovery.
[D] Standard deviation about percent recovery.
[E] No analyses conducted.
[F] NA = Not applicable. A separate set of aqueous standards was not analyzed, and the values shown for reagent were used to calculate a recovery for the tap water matrix.

approximately equal to the lower limit of the applicable concentration range shown in Table 1. Calculate accuracy as percent recovery (X_j). If the recovery of any analyte falls outside the control limits (see 12.5.2), that analyte is judged out of control, and the source of the problem should be identified and corrected before continuing analyses.

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 in 12.3.2 that are derived from the data in Table 3. 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:

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

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

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

NOTE 1—**Caution:** 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 At least each quarter, the laboratory should analyze quality control samples (QCS) (if available). If criteria provided with the QCS are not met, corrective action should be taken and documented.

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

12.6.1 The laboratory must add a known spike of each analyte of interest to a minimum of 10 % of the routine samples or one sample spike per set, whichever is greater. The spike concentration should not be less than the background concentration of the sample selected for spiking. Ideally the spike should be the same as that used for the LFB in 12.5. Periodically, samples from all routine sample sources should be spiked.

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

$$R_i = \frac{C_{LFM} - C_{NS}}{C_A} \times 100 \quad (2)$$

where:

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

Compare these values to the control limits established in 12.5.2.

12.6.3 If the recovery of any such analyte falls outside the designated range and the laboratory performance for that analyte is shown to be in control (see 12.5), the recovery problem encountered with the dosed sample is judged to be matrix related not system related. The result for that analyte in the unspiked sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

12.7 The laboratory may adopt additional quality control practices. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements, or field reagent blanks may be used to assess contamination of samples under site conditions, transportation, and storage.

13. Procedure

13.1 *Sample Preparation:*

13.1.1 Remove samples from storage and allow them to equilibrate to room temperature.

13.1.2 Remove the container caps. Withdraw and discard a 5-mL volume using a 10-mL graduated cylinder. Replace the container caps and weigh the containers with contents to the nearest 0.1 g and record these weights for subsequent sample volume determinations in 13.3.

13.1.3 Remove the container cap of each sample and add 6 g NaCl to the sample bottle. Recap and dissolve the NaCl by inverting and shaking the bottles several times (approximately 20 s).

13.2 *Extraction and Analysis:*

13.2.1 Remove the cap and using a transfer or automatic dispensing pipet add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min, inverting the vial while shaking. Stand the vial upright and allow the water and hexane phases to separate.

13.2.2 Remove the cap and carefully transfer approximately 0.5 mL of hexane layer into an autosampler vial using a disposable glass pipet.

13.2.3 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second autosampler vial. Reserve this second vial at 4°C for an immediate reanalysis if necessary.

13.2.4 Transfer the first sample vial to an autosampler setup to inject 1 to 2 µL portions into the gas chromatograph for analysis (see 7.7 for GC conditions). Alternatively, 1 to 2 µL portions of samples, blanks, and standards may be manually injected, although an autosampler is strongly recommended.

13.3 *Determination of Sample Volume in Noncalibrated Vials:*

13.3.1 Discard the remaining sample/hexane mixture from the sample bottle. Shake off the remaining few drops using short, brisk wrist movements.

13.3.2 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g (see section 14.3). This net weight (in grams) (see section 14.3) is equivalent to the volume (in millilitres) of water extracted. By using 40 mL vials precalibrated at 35-mL levels, the gravimetric steps can be omitted, thus increasing the speed and ease of this procedure.

13.4 *Identification of Analytes:*

13.4.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds within limits to the retention time of a standard compound, then identification is considered positive. If unfamiliar samples are analyzed, additional steps should be taken to confirm the identity of the analyte(s). See 13.4.3.

13.4.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used 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 judgment when sample components are not resolved chromatographically. When peaks obviously represent more than one sample component (broadened peak with shoulder(s) or valley between two or more maxima) or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternative techniques to help confirm peak identification need to be employed. For example, more positive identification may be made by the use of a different chromatography column or by the use of a mass spectrometer as a GC detector (if analyte concentration is adequate). Procedures for compound identification by gas chromatography/mass spectrometry can be found in Practice D 4128.

13.4.4 If interfering compounds are present or if PCBs are present along with various chlorinated pesticides, a chemical cleanup procedure may allow the compounds of interest to be identified and quantitated. Cleanup procedures are described in Test Method D 3534. If any of these procedures are used, it is the responsibility of the analyst to analyze LFMs and to demonstrate that the procedure does not significantly affect the performance of the test method.

13.4.5 If mixtures of multicomponent materials (PCBs, toxaphene, chlordane) are present or if weathering has altered a material so it no longer resembles the original product, then more advanced data analysis techniques may be required **(10)** (see EPA Method 680).

14. Calculation

14.1 Identify the organohalides in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory fortified blanks.

14.1.1 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 (see Table 2). In the calculations use the sum of the instrument response for peaks indicated in Table 2.

14.2 Use the calibration curve or calibration factor from 11.2.3 to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (calibration factor x response).

14.3 Calculate the sample volume (V_s) in millilitres as equal

to the net sample weight in grams:

$$V_S = \text{gross weight (from 13.1.2)} - \textit{vial tare}\ \text{(from 13.3.2)} \quad (3)$$

14.4 Calculate the corrected sample concentration as:

$$\text{concentration, µg/L} = \frac{35(C_j)}{(V_s)} \quad (4)$$

14.5 Results should be reported with an appropriate number of significant figures.

15. Precision and Bias

15.1 Single laboratory precision and bias at several concentrations in reagent, ground, and tap water matrices are presented in Table 3 **(11)**. These results were obtained from data generated with Column 1 in 7.7.2.

15.2 This test method has been tested by ten laboratories using reagent water and ground water spiked at six concentration levels as three Youden pairs. Single operator precision, overall precision, and test method bias were found to be directly related to the concentration of the analyte and virtually independent of the sample matrix. Linear equations to describe the relationships are presented in Table 1 (see 2.2).

16. Keywords

16.1 gas chromatography; microextraction; organochlorine pesticides; polychlorinated biphenyls (PCBs)

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