Designation: D4947 – 05

Standard Test Method for Chlordane and Heptachlor Residues in Indoor Air[1]

This standard is issued under the fixed designation D4947; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the sampling and analysis of indoor atmospheres for residues of chlordane and heptachlor.

1.2 This test method is based upon the collection of chlordane and heptachlor from air onto polyurethane foam (PUF) and analysis by gas chromatography coupled with electron capture detection.

1.3 This test method is applicable to concentrations of chlordane varying from 0.1 to 100 μg/m^3 and heptachlor varying from 0.01 to 80.0 μg/m^3 with sampling periods to collect at least 0.25 m^3 of air. Detection limits will depend upon the conditions of the gas chromatography (GC) and the length of the sampling period.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

D3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method

D4185 Practice for Measurement of Metals in Workplace Atmospheres by Flame Atomic Absorption Spectrophotometry

D4861 Practice for Sampling and Selection of Analytical Techniques for Pesticides and Polychlorinated Biphenyls in Air

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *EPA Methods:*

Compendium of Methods for the Determination to Toxic Organic Compounds in Ambient Air, EPA 600/R-96/010b [3]

2.3 *Other Documents:*

Indoor Sampling Guidelines for Termiticides [4]

3. Terminology

3.1 *Definitions:*

3.1.1 Refer to Terminology D1356, Practice E355, and Practice D4861 for definitions of terms used in this test method.

3.1.2 The term "chlordane" refers to a technical-grade mixture consisting mostly of chlorinated Diels-Alder addition products of cyclopentadiene and hexachlorocyclopentadiene. The mixture consists of 50 or more compounds, 10 of which are major components (**1**).[5] The isomers α-(or *cis*-) and γ-(or *trans*-) chlordane, heptachlor, and *trans*-nonachlor are among these.

3.1.2.1 The terms "chlordane" and "technical" chlordane are used interchangeably.

3.1.3 Heptachlor is a single chemical compound, which may be used alone or in formulations with technical chlordane. It is also a component of technical chlordane.

4. Summary of Practice

4.1 A low-volume (1 to 5 L/min) sampler is used to collect airborne chlordane and heptachlor on a sorbent cartridge containing PUF. The method is taken from Refs. (**2**) through (**4**) and Practice D4861.

4.2 Chlordane and heptachlor are extracted from the sorbent cartridge with 5 % diethyl ether in hexane and analyzed on a gas chromatograph (GC) equipped with an electron capture detector (ECD).

4.3 Because of the possibility of interfering materials having similar retention times to chlordane and heptachlor peaks,

[1] This practice is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from the U.S. Department of Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161.

[4] Available from Wood Protection Council, National Institute for Building Sciences, Washington, DC, 1987.

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

column chromatography or the use of a second chromatographic column of a different type is necessary to obtain accurate identification and quantification. Mass spectrometry may be required for unambiguous determination.

5. Significance and Use

5.1 This test method is intended to be used primarily for non-occupational exposure monitoring in domiciles, public access buildings and offices.

5.2 Chlordane has been used widely as a general insecticide for crops (for example, cotton) and as a termiticide. Heptachlor is a major component of technical chlordane and an insecticide in its own right. Although their use in the United States was discontinued in 1988, residues of the chemicals may remain in indoor air for many years after application.

6. Interferences

6.1 The electron capture detector responds to a wide variety of organic compounds. It is likely that such compounds will be encountered as interferences during GC-ECD analysis. Although mass spectrometry can provide positive identification of chlordane and heptachlor, some laboratories do not possess such instrumentation.

6.2 Chlordane was used primarily as the technical grade, a complex mixture of chemically-related chlorinated compounds, including 8 to 10 % by weight of heptachlor. Similar chlorinated compounds can cause difficulty in identifying and quantifying this multiple-component mixture.

6.3 In addition, contaminated glassware and sampling tubes can be a major source of error when attempting to quantitate multiple-component mixtures with an ECD. To minimize this source of error, careful attention to glassware cleaning and sample handling procedures must be followed.

6.4 General approaches that can be followed to minimize interferences are given as follows:

6.4.1 Chlordane and heptachlor can be cleaned up by column chromatography on Florisil[6]. See Ref **(5).**

6.4.2 Chlordane- and heptachlor-containing samples can be cleaned up with sulfuric acid treatment. See Ref **(6).**

7. Apparatus

7.1 *Air Sampler*—Refer to the appropriate section of Practice D4861 for specifications on air sampling equipment.

7.2 *Equipment and Reagents for Sample Extraction and Concentration*—Refer to the applicable section of Practice D4861 for required equipment and reagents.

7.3 *Equipment for Analysis*:

7.3.1 Gas chromatograph equipped with a Nickel-63 electron capture detector.

7.3.2 Gas chromatographic columns: A 15-m by 0.53 mm inside diameter bonded, crosslinked (50%-phenyl)-methylpolysiloxane[7] fused-silica capillary column, film thickness 3 µm, for quantitation; and a 30-m by 0.53-mm inside diameter poly(5% -diphenyl-95% dimethylsiloxane) fused-silica capillary column,[8] film thickness 1.5 µm, for confirmation.

7.3.3 Microsyringes, 5-µL volume.

8. Sampling Procedures

8.1 Follow the applicable section of Practice D4861 for clean-up and proper storage of the PUF sampling plugs.

8.2 At least one assembled sampling cartridge from each batch should be analyzed as a laboratory blank prior to using. The blank level should be <0.10 µg/plug for chlordane, <0.01 µg/plug for heptachlor.

8.3 After the sampling system has been assembled and calibrated as described in Section 9, it can be used to collect air samples as described in 9.5.1 to 9.5.9 of Practice D4861.

9. Calibration of Pump

9.1 Refer to the applicable Annex in Practice D3686 or the applicable Annex Practice D4185 for procedures to calibrate small volume air pumps. See also Practice D4861.

10. Sample Extraction Procedure

10.1 All samples should be extracted within one week after collection in accordance with the procedures outlined in Section 10 of the Practice D4861.

10.2 Adjust final volume of sample extract to 1 mL for analysis.

11. Analysis Procedures

11.1 Prepare analytical standard solutions of technical chlordane in pesticide-quality[9] 2,2,4-Trimethylpentane ("iso-octane"). Analytically pure standards of technical chlordane and heptachlor are available from several commercial sources.

11.2 When not in use, store standard solutions at 4°C or below and protect from light. Replace after six months, or sooner if comparison with check standards indicates a problem.

11.3 Chlordane and heptachlor are responsive to detection by GC/ECD at low concentrations, which will be dependent upon the condition of the chromatograph, columns (see 7.3.2) and detector.

11.4 A gas chromatograph (GC) with dual injector ports and dual electron capture detectors is recommended.

11.5 Set up both the quantitation and confirmatory GC columns in the same GC oven.

11.6 Provide helium carrier gas at a nominal flow rate of 10 mL/min at approximately 170 kPa (25 psig) to each column.

11.7 Set the temperature for both injectors at 235°C and the ECD at 350°C.

11.8 Allow samples and standard solutions to warm to room temperature before analysis.

11.9 Set column temperature program for 60°C (2 min), then programmed to 140°C at 25°C/min, then to 270°C at 4°C/min.

[6] "Florisil" is a trademark of the Floridin Corp., Tallahassee, FL 32303. It is a natural magnesium silicate; it is available from several commercial sources.

[7] This column is available from several commercial sources under such trade names as OV-17, DB-17, SPB-17, and others.

[8] This column is available from several commercial sources under such trade names as DB-5, SPB-5, RTX-5, HP-5, OV-5, BP-5, and others.

[9] Glass distilled and certified for pesticides analysis by GC/ECD.

11.10 Calibrate gas chromatograph by injecting 2 µL aliquots of standard solutions (See Practice D3687 for technique) in order to establish response factors, linearity of the ECD, dynamic range, and retention time windows.

11.11 Set retention time windows at ±0.10 min for the quantitation primary column and ±0.05 min for the confirmatory column.

11.12 Typical chromatograms of technical chlordane are shown in Fig. 1 and Fig. 2 for the quantitation and confirmatory columns, respectively. The ten numbered peaks are to be used for identification and quantitation of chlordane in the sample.

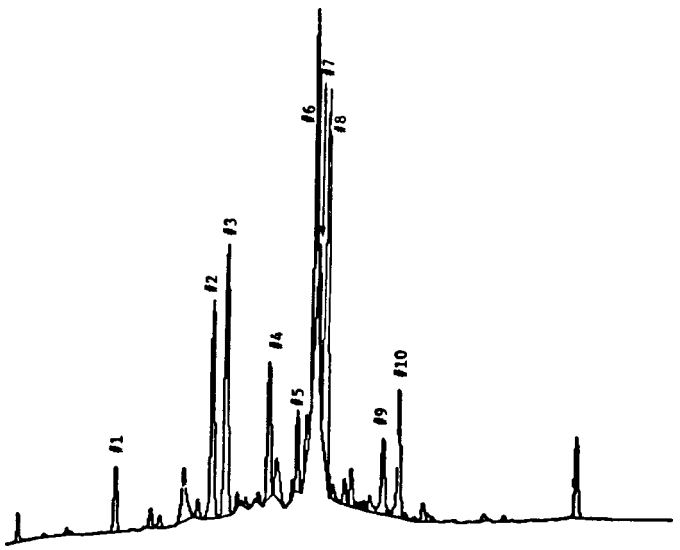
11.13 Typical retention times for the two columns are given in Table 1.

11.14 Inject 2 µl of sample extract on quantitation column and obtain a tentative identification of technical chlordane by comparison of chromatographic peaks in the sample with those in the standard in accordance with the flow chart in Fig. 3 and the following steps:

11.14.1 On a worksheet, list the measured retention times (in minutes) and corresponding areas of each chromatographic peak that appears to match any of the ten reference peaks from the standard.

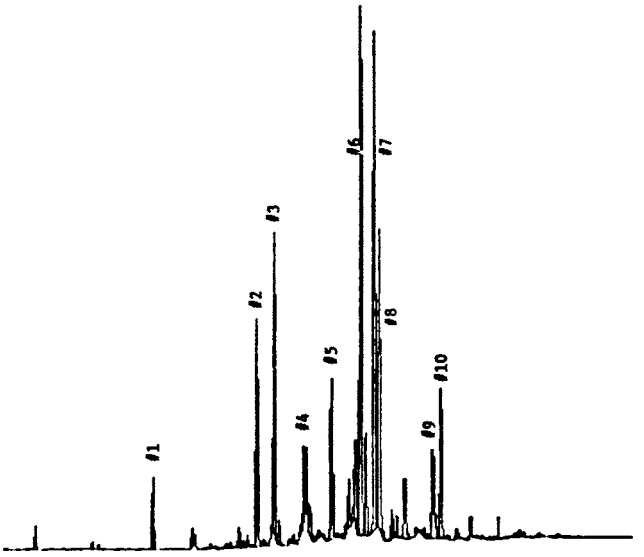
11.14.2 Compare the retention time of each of the ten peaks in the sample chromatogram to the absolute retention time of the respective standard peak using a retention window of ±0.10 min around each standard peak. Draw a line through the retention time and area of all sample peaks that are outside the retention window. However, when a consistent shift is evident in the retention times of many of the sample peaks, the experienced analyst may expand the acceptable retention window in the direction of the shift.

11.14.3 If all ten peaks qualify, tentative confirmation is obtained and the sample may be subjected to final confirmation by analysis on the DB-5 column in accordance with 11.15.



NOTE 1—Refer to Table 1 for typical retention times of peaks.

FIG. 1 Typical Chromatogram of Technical Chlordane on Quantitation Megabore Column



NOTE 1—Refer to Table 1 for typical retention times of peaks.

FIG. 2 Typical Chromatogram of Technical Chlordane on Confirmatory Megabore Column

TABLE 1 Typical Gas Chromatographic Retention Times of Technical Chlordane Components[A]

Quantitation Megabore Column			Confirmatory Megabore Column		
Peak[B]	RT, min	Compound	Peak[C]	RT, min	Compound
1	12.74		1	16.56	
2	18.07		2	22.23	
3	18.80	Heptachlor	3	23.19	Heptachlor
4	21.17		4	24.98	
5	22.75		5	26.37	
6	23.64	γ-Chlordane	6	27.97	γ-Chlordane
7	23.87	*t*-Nonachlor	7	28.72	α-Chlordane
8	24.32	α-Chlordane	8	28.99	*t*-Nonachlor
9	27.51		9	31.97	
10	28.36		10	32.40	

[A] Refer to Section 11 for chromatographic conditions.
[B] Refer to Fig. 1.
[C] Refer to Fig. 2.

11.14.4 When only some of the ten peaks are present in the sample chromatogram, the priority order of peak presence for identification as chlordane is as follows:

11.14.4.1 α- and γ-Chlordane (peaks 8 and 6) (highest priority),

11.14.4.2 Heptachlor component (peak 3),

11.14.4.3 *Trans* -nonachlor (peak 7),

11.14.4.4 Last two components (peaks 9 and 10), and

11.14.4.5 Component immediately preceding heptachlor (peak 2).

11.14.5 If all seven of these peaks listed in 11.14.4 are present in the sample (for example, found to be within its retention window as in 11.14.2), then tentative assignment of technical chlordane is made.

11.14.6 If peaks 2, 3, 6, 8, 9, and 10 are present in the sample, then the tentative assignment of chlordane is made.

11.14.7 As illustrated in the flow chart in Fig. 3, when the number of peaks within the windows falls to four or five, the area ratios are compared as described.

NOTE 1—Components of similar volatility must be compared (for

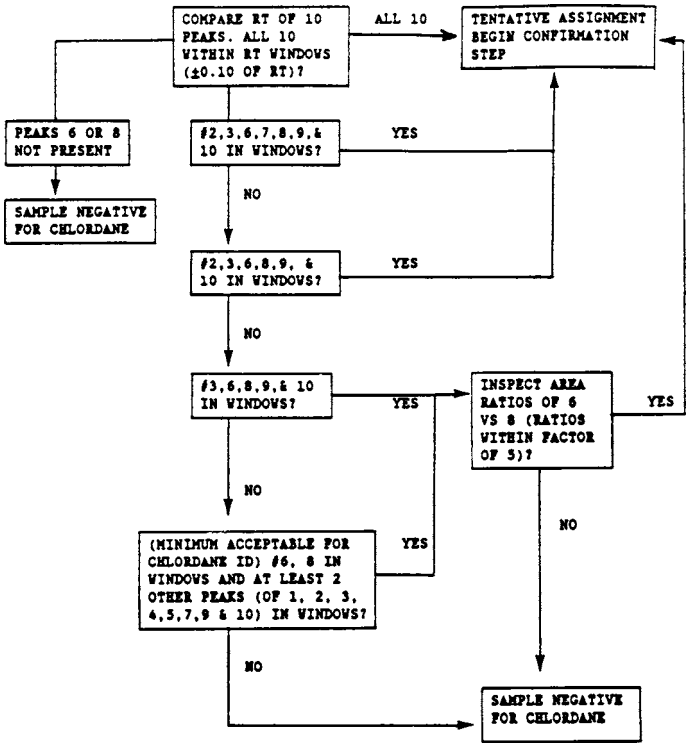


FIG. 3 Flow Chart for Tentative Identification of Chlordane Using the Primary Column

example, α-chlordane versus γ-chlordane).

11.14.8 When fewer than four of the ten peaks are present, the sample is considered negative for chlordane.

11.14.9 At a minimum, γ- and α-chlordane (peaks 6 and 8) must be present, along with at least two of the other eight peaks (peaks 1, 2, 3, 4, 5, 7, 9, or 10), and the areas of peaks 6 and 8 must be within a factor of 5 in order to consider the sample eligible to confirm for the presence of chlordane (for example, to proceed to 11.15).

11.15 Once tentative confirmation on the quantitation column is obtained, final confirmation is obtained by injecting 2 µL of the sample extract on the confirmatory column (For convenience, the sample may be analyzed simultaneously on both columns). Confirmation is accomplished by following the steps given:

11.15.1 Only the four known chlordane components listed in Table 1 (heptachlor, γ-chlordane, α-chlordane, and *trans*-nonachlor) can be rejected if not confirmed during the confirmation analysis. (Note that the peak corresponding to *trans*-nonachlor, which appears as a trailing shoulder to γ-chlordane on the primary column, is a separate peak on the confirmation column (see Fig. 2)). Conversely, since the identity of the other six primary column peaks on the confirmatory column cannot be positively established, the confirmation analysis cannot be used to reject these unknown components.

11.15.2 On the chlordane identification and quantitation worksheet, list the retention times (in minutes) and areas of the ten reference chlordane component peaks obtained from the confirmatory column analysis of the technical chlordane standard solution.

11.15.3 On the same worksheet, list the retention times and areas of the peaks corresponding to these ten peaks from the sample analysis using the DB-5 confirmation column.

11.15.4 Compare the retention times of peaks 3 (heptachlor), 6 (γ-chlordane), 7 (α-chlordane), and 8 (*trans*-nonachlor) in the confirmation analysis of the sample to the absolute retention times of the respective standard peaks, using a retention window of ±0.05 minutes around each standard peak. Draw a line through the sample retention times and areas for both the confirmation column and the primary quantitation column for any of these four components that are outside the retention window (for example, not present) on the confirmation column. However, when a consistent shift is evident in the retention times of many of the sample peaks, the analyst may expand the acceptable retention window in the direction of the shift. (Remember that the elution sequence of *trans*-nonachlor and α-chlordane are reversed on the OV-17 megabore and DB-5 columns).

11.15.5 If either α-chlordane or γ-chlordane (peaks 6 or 7 on the confirmatory column) is not present within the standard retention time window on the confirmation column, the sample is considered negative for chlordane.

11.15.6 If heptachlor (peak 3) or *trans*-nonachlor (peak 8) is outside its standard retention time window on the confirmation column, cross out its respective retention times and areas for both the confirmation and primary columns.

11.15.7 If α- and γ-chlordane are present on the confirmation column, and if criterion in 11.14.9 remains satisfied after considering the confirmation column, chlordane is confirmed in the sample. Proceed to the chlordane quantitation procedures in Section 12.

12. Calculations

12.1 *Determination of the Concentration of Technical Chlordane*:

12.1.1 Sum the areas of all matching GC peaks from the quantitation column analysis of the sample *except peak 3* (*heptachlor*). Likewise, determine the total areas of the corresponding peaks in the quantitation column analysis of the standard.

12.1.2 Calculate the amount of technical chlordane on the PUF plug using the following equation:

$$C_p = \frac{A_s}{A_p} \times C_s \times V_p \quad (1)$$

where:

C_p = quantity of technical chlordane on the PUF plug, µg,
A_p = total area of the appropriate GC peaks in the sample,
A_s = total area of the GC peaks in the standard,
C_s = concentration of standard, µg/mL, and
V_p = sample volume, mL.

NOTE 2—Injection volumes are excluded from the equation, since the same volume is injected for both the sample extract and standard solution.

12.1.3 If the area of one of the positive sample peaks differs markedly from the predicted value based on the standard (for example, ten times too large), the peak is excluded from the quantitation. Since many considerations are involved, such exclusions are based on the judgment of the analyst.