CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8121 describes the determination of chlorinated hydrocarbons in extracts prepared from environmental samples and RCRA wastes. It describes wide-bore open-tubular, capillary column gas chromatography procedures using both single column/single detector and dual-column/dual-detector approaches. The following compounds can be determined by this method:

Compound Name	CAS Registry No.[a]
Benzal chloride	98-87-3
Benzotrichloride	98-07-7
Benzyl chloride	100-44-7
2-Chloronaphthalene	91-58-7
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-1
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
α-Hexachlorocyclohexane (α-BHC)	319-84-6
β-Hexachlorocyclohexane (β-BHC)	319-85-7
γ-Hexachlorocyclohexane (γ-BHC)	58-89-9
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Pentachlorobenzene	608-93-5
1,2,3,4-Tetrachlorobenzene	634-66-2
1,2,4,5-Tetrachlorobenzene	95-94-2
1,2,3,5-Tetrachlorobenzene	634-90-2
1,2,4-Trichlorobenzene	120-82-1
1,2,3-Trichlorobenzene	87-61-6
1,3,5-Trichlorobenzene	108-70-3

[a] Chemical Abstract Services Registry Number.

1.2 The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and two identical detectors. When compared to the packed columns, the megabore fused-silica open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis.

1.3 Table 1 lists method detection limits (MDL) for each compound in an organic-free reagent water matrix. The MDLs for the compounds of a specific sample may differ from those listed in Table 1 because they are dependent upon

the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQL) for other matrices.

1.4 Table 3 lists the compounds that have been determined by this method and their retention times using the single column technique. Table 4 lists dual column/dual detector retention time data. Figures 1 and 2 are chromatograms showing the single column technique. Figure 3 shows a chromatogram of the target analytes eluted from a pair of DB-5/DB-1701 columns and detected with electron capture detectors (ECD) under the prescribed GC conditions listed in Table 2.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms.

2.0 SUMMARY OF METHOD

2.1 Method 8121 provides gas chromatographic conditions for the detection of ppb concentrations of chlorinated hydrocarbons in water and soil or ppm concentrations in waste samples. Prior to use of this method, appropriate sample extraction techniques must be used for environmental samples (refer to Chapt. 2). Both neat and diluted organic liquids (Method 3580) may be analyzed by direct injection. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Analysis is accomplished by gas chromatography utilizing an instrument equipped with wide bore capillary columns and single or dual electron capture detectors.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 The electron capture detector responds to all electronegative compounds. Therefore, interferences are possible by other halogenated compounds, as well as phthalates and other oxygenated compounds, and, organonitrogen, organosulfur and organophosphorus compounds. Second column confirmation or GC/MS confirmation are necessary to ensure proper analyte identification unless previous characterization of the sample source will ensure proper identification.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the syringe used for injection must be rinsed out between samples with solvent. Whenever an extract concentration exceeds that of the highest calibration standard, it should be followed by the analysis of a solvent blank to check for cross-contamination. Additional solvent blanks interspersed with the sample extracts should be considered whenever the analysis of a solvent blank indicates cross-contamination problems.

3.4 Phthalate esters, if present in a sample, will interfere only with the BHC isomers because they elute in Fraction 2 of the Florisil procedure described in Method 3620. The presence of phthalate esters can usually be

minimized by avoiding contact with any plastic materials and by following standard decontamination procedures of reagents and glassware.

3.5 The presence of elemental sulfur will result in large peaks, and can often mask the region of compounds eluting after 1,2,4,5-tetrachlorobenzene. The tetrabutylammonium (TBA)-sulfite procedure (Method 3660) works well for the removal of elemental sulfur.

3.6 In certain cases some compounds coelute on either one or both columns. In these cases the compounds must be reported as coeluting. The mixture can be reanalyzed by GC/MS techniques, see Sec. 8.7 and Method 8270.

3.6.1 Using the dual column system of analysis the following compounds coeluted:

DB-5	1,4-dichlorobenzene/benzyl chloride
	1,2,3,5-tetrachlorobenzene/1,2,4,5-tetrachlorobenzene
	1,2,3,4-tetrachlorobenzene/2-chloronaphthalene
DB-1701	benzyl chloride/1,2-dichlorobenzene/hexachloroethane
	benzal chloride/1,2,4-trichlorobenzene/ hexachlorobutadiene

Some of the injections showed a separation of 1,2,4-trichlorobenzene from the other two compounds, however, this is not always the case, so the compounds are listed as coeluting.

3.7 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: An analytical system complete with a gas chromatograph suitable for on-column and split-splitless injection, and all required accessories, including syringes, analytical columns, gases, and two electron capture detectors. A data system for measuring peak areas, and dual display of chromatograms is recommended. A GC equipped with a single GC column and detector are acceptable, however, second column confirmation is obviously more time consuming. Following are the single and dual column configurations used for developing the retention time data presented in the method. The columns listed in the dual column configuration may also be used for single column analysis.

4.1.1 Single Column Analysis:

4.1.1.1 Column 1 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl silicone (DB-210 or equivalent).

4.1.1.2 Column 2 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol (DB-WAX or equivalent).

4.1.2 Dual Column Analysis:

4.1.2.1 Column 1 - 30 m x 0.53 mm ID fused-silica open-tubular column, crosslinked and chemically bonded with 95 percent dimethyl and 5 percent diphenyl-polysiloxane (DB-5, RT_x-5, SPB-5, or equivalent), 0.83 µm or 1.5 µm film thickness.

4.1.2.2 Column 2 - 30 m x 0.53 mm ID fused-silica open-tubular column crosslinked and chemically bonded with 14 percent cyanopropylphenyl and 86 percent dimethyl-polysiloxane (DB-1701, RT_x-1701, or equivalent), 1.0 µm film thickness.

4.1.3 Splitter: If the splitter approach to dual column injection is chosen, following are three suggested splitters. An equivalent splitter is acceptable. See Sec. 7.5.1 for a caution on the use of splitters.

4.1.3.1 Splitter 1 - J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733).

4.1.3.2 Splitter 2 - Supelco 8 in. glass injection tee, deactivated (Supelco, Catalog no. 2-3665M).

4.1.3.3 Splitter 3 - Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405).

4.1.4 Column rinsing kit (optional): Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

4.1.5 Microsyringes - 100 µL, 50 µL, 10 µL (Hamilton 701 N or equivalent), and 50 µL (Blunted, Hamilton 705SNR or equivalent).

4.1.6 Balances - Analytical, 0.0001 g.

4.1.7 Volumetric flasks, Class A - 10 mL to 1000 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the chemicals are of sufficiently high purity to permit their use without affecting the accuracy of the determinations.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. All standard solutions must be replaced after six months or sooner if routine QC (Sec. 8) indicates a problem.

5.2 Solvents

5.2.1 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.2.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.2.3 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.3 Stock standard solutions (1000 mg/L): Can be prepared from pure standard materials or can be purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10 mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 For those compounds which are not adequately soluble in hexane or isooctane, mixtures of acetone and hexane are recommended.

5.4 Composite stock standard: Can be prepared from individual stock solutions. For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, and mix the solutions in a 25 mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 40 mg/L. This composite solution can be further diluted to obtain the desired concentrations.

5.5 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. A suggested list of calibration solution standards is found in Table 7.

5.6 Recommended internal standard: Make a solution of 1000 mg/L of 1,3,5-tribromobenzene. (Two other internal standards, 2,5-dibromotoluene and alpha,alpha'-dibromo-m-xylene, are suggested if matrix interferences are a problem.) For spiking, dilute this solution to 50 ng/µL. Use a spiking volume of 10 µL/mL of extract. The spiking concentration of the internal standards should be kept constant for all samples and calibration standards. Store the internal standard spiking solutions at 4°C in Teflon-sealed containers in the dark.

5.7 Recommended surrogate standards: Monitor the performance of the method using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. Make a solution of 1000 mg/L of 1,4-dichloronaphthalene and dilute it to 100 ng/µL. Use a spiking volume of 100 µL for a 1 L aqueous sample. If matrix interferences are a problem, two alternative surrogates are: alpha, 2,6-trichlorotoluene or 2,3,4,5,6-pentachlorotoluene.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

6.2 Extracts must be stored at 4 °C and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction and Cleanup:

7.1.1 Refer to Chapter Two and Method 3500 for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Methods 3540, 3541, or 3550 with methylene chloride/acetone (1:1) as the extraction solvent.

7.1.2 If required, the samples may be cleaned up using Method 3620 (Florisil) and/or Method 3640 (Gel Permeation Chromatography). See Chapter Two, Sec. 2.3.2 and Method 3600 for general guidance on cleanup and method selection. Method 3660 is used for sulfur removal.

7.1.3 Prior to gas chromatographic analysis, the extraction solvent must exchanged into hexane using the Kuderna-Danish concentration step found in any of the extraction methods. Any methylene chloride remaining in the extract will cause a very broad solvent peak.

7.2 Gas Chromatographic Conditions:

7.2.1 Retention time information for each of the analytes is presented in Tables 3 and 4. The recommended GC operating conditions are provided in Tables 5 and 6. Figures 1, 2 and 3 illustrate typical chromatography of the method analytes for both the single column approach and the dual column approach when operated at the conditions specified in Tables 5 and 6.

7.3 Calibration:

7.3.1 Prepare calibration standards using the procedures in Sec. 5.0. Refer to Method 8000 for proper calibration procedures. The procedure for internal or external calibration may be used.

7.3.2 Refer to Method 8000 for the establishment of retention time windows.

7.4 Gas chromatographic analysis:

7.4.1 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.4.2 Automatic injections of 1 µL are recommended. Hand injections of no more than 2 µL may be used if the analyst demonstrates quantitation precision of $\leq$ 10 percent relative standard deviation. The solvent flush technique may be used if the amount of solvent is kept at a minimum. If the internal standard calibration technique is used, add 10 µL of the internal standard to each mL of sample extract prior to injection.

7.4.3 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.

7.4.4 Validation of gas chromatographic system qualitative performance: Use the midconcentration standards interspersed throughout the analysis sequence (Sec. 7.3) to evaluate this criterion. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it (see Sec. 7.5).

7.4.5 Record the volume injected to the nearest 0.05 µL and the resulting peak size in peak height or area units. Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.4.6 If the responses exceed the linear range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.4.7 If partially overlapping or coeluting peaks are found, change columns or try a GC/MS technique (see Sec. 8.7 and Method 8270). Interferences that prevent analyte identification and/or quantitation may be removed by the cleanup techniques mentioned above.

7.4.8 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.5 Instrument Maintenance:

7.5.1 Injection of sample extracts from waste sites often leaves a high boiling residue in: the injection port area, splitters when used, and the injection port end of the chromatographic column. This residue effects chromatography in many ways (i.e., peak tailing, retention time shifts, analyte degradation, etc.) and, therefore, instrument maintenance is very important. Residue buildup in a splitter may limit flow through one leg and therefore change the split ratios. If this occurs during an analytical run, the quantitative data may be incorrect. Proper cleanup techniques will minimize the problem and instrument QC will indicate when instrument maintenance is required.

7.5.2 Suggested chromatograph maintenance: Corrective measures may require any one or more of the following remedial actions. Also see Sec. 7 in Method 8000 for additional guidance on corrective action for capillary columns and the injection port.

7.5.2.1 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Quality control required to evaluate the GC system operation is found in Method 8000, Sec. 8.3.

8.3 Calculate surrogate standard recoveries for all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Sec. 8). If the recovery is not within limits, the following are required:

8.3.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.3 Reextract and reanalyze the sample if none of the above are a problem, or flag the data as "estimated concentrations".

8.4 Data from systems that automatically identify target analytes on the basis of retention time or retention time indices should be reviewed by an experienced analyst before they are reported.

8.5 When using the internal standard calibration technique, an internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 50 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.6 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-concentration calibration must be within $\pm$ 15 percent of the average values for the multiconcentration calibration. When the response factors fall outside that limit, all samples analyzed after that mid-concentration calibration standard must be reanalyzed after performing instrument maintenance to correct the usual source of the problem. If this fails to correct the problem, a new calibration curve must be established.

8.7 GC/MS confirmation:

8.7.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements specified in Method 8270. Ensure that there is sufficient concentration of the analyte(s) to be confirmed, in the extract for GC/MS analysis.

8.7.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.7.3 To confirm an identification of a compound, the background corrected mass spectrum of the compound must be obtained from the sample extract and must be compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The identification criteria specified in Method 8270 must be met for qualitative confirmation.

8.7.3.1 Should the MS procedure fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional sample cleanup.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDLs listed in Table 1 were obtained by using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDLs actually achieved in a given analysis will vary since they depend on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using organic-free reagent water, sandy loam samples and extracts which were spiked with the test compounds at one concentration. Single-operator precision and method accuracy were found to be related to the concentration of compound and the type of matrix.

9.3 Single laboratory accuracy data were obtained for chlorinated hydrocarbons in a clay soil. The spiking concentrations ranged from 500 to 5000 µg/kg, depending on the sensitivity of the analyte to the electron capture detector. The spiking solution was mixed into the soil during addition and then immediatly transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated Soxhlet). The data represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Method 8121 for the chlorinated hydrocarbons. These data are listed in Table 9 and were taken from Reference 4.

10.0 REFERENCES

1. Lopez-Avila, V., N.S. Dodhiwala, and J. Milanes, "Single Laboratory Evaluation of Method 8120, Chlorinated Hydrocarbons", 1988, EPA Contract Numbers 68-03-3226 and 68-03-3511.

2. Glazer, J.A., G.D. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15:1426-1431, 1981.

3. Lopez-Avila, V.; Baldin, E.; Benedicto, J; Milanes, J.; Beckert, W. F. "Application of Open-Tubular Columns to SW 846 GC Methods"; final report to the U.S. Environmental Protection Agency on Contract 68-03-3511; Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

4. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, US EPA, Environmental Monitoring Systems Laboratory-Las Vegas, October 1991.

TABLE 1
METHOD DETECTION LIMITS FOR CHLORINATED HYDROCARBONS
SINGLE COLUMN METHOD OF ANALYSIS

Compound name	CAS Reg. No.	MDL[a] (ng/L)
Benzal chloride	98-87-3	2-5[b]
Benzotrichloride	98-07-7	6.0
Benzyl chloride	100-44-7	180
2-Chloronaphthalene	91-58-7	1,300
1,2-Dichlorobenzene	95-50-1	270
1,3-Dichlorobenzene	541-73-1	250
1,4-Dichlorobenzene	106-46-1	890
Hexachlorobenzene	118-74-1	5.6
Hexachlorobutadiene	87-68-3	1.4
α-Hexachlorocyclohexane (α-BHC)	319-84-6	11
β-Hexachlorocyclohexane (β-BHC)	319-85-7	31
γ-Hexachlorocyclohexane (γ-BHC)	58-89-9	23
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8	20
Hexachlorocyclopentadiene	77-47-4	240
Hexachloroethane	67-72-1	1.6
Pentachlorobenzene	608-93-5	38
1,2,3,4-Tetrachlorobenzene	634-66-2	11
1,2,4,5-Tetrachlorobenzene	95-94-2	9.5
1,2,3,5-Tetrachlorobenzene	634-90-2	8.1
1,2,4-Trichlorobenzene	120-82-1	130
1,2,3-Trichlorobenzene	87-61-6	39
1,3,5-Trichlorobenzene	108-70-3	12

[a] MDL is the method detection limit for organic-free reagent water. MDL was determined from the analysis of eight replicate aliquots processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis).

$$MDL = T/DC_{(n-1,\alpha = .99)}(s)$$

where $t_{(n-1,0.99)}$ is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the eight replicate measurements.

[b] Estimated from the instrument detection limit.

TABLE 2

ESTIMATED QUANTITATION LIMIT (EQL) FACTORS FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Waste not miscible with water	100,000

[a] EQL = [Method detection limit (see Table 1)] x [Factor found in this table]. For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

TABLE 3
GAS CHROMATOGRAPHIC RETENTION TIMES FOR CHLORINATED HYDROCARBONS: SINGLE COLUMN METHOD OF ANALYSIS

Compound name	Retention time (min) DB-210[a]	DB-WAX[b]
Benzal chloride	6.86	15.91
Benzotrichloride	7.85	15.44
Benzyl chloride	4.59	10.37
2-Chloronaphthalene	13.45	23.75
1,2-Dichlorobenzene	4.44	9.58
1,3-Dichlorobenzene	3.66	7.73
1,4-Dichlorobenzene	3.80	8.49
Hexachlorobenzene	19.23	29.16
Hexachlorobutadiene	5.77	9.98
α-BHC	25.54	33.84
γ-BHC	24.07	54.30
δ-BHC	26.16	33.79
Hexachlorocyclopentadiene	8.86	c
Hexachloroethane	3.35	8.13
Pentachlorobenzene	14.86	23.75
1,2,3,4-Tetrachlorobenzene	11.90	21.17
1,2,4,5-Tetrachlorobenzene	10.18	17.81
1,2,3,5-Tetrachlorobenzene	10.18	17.50
1,2,4-Trichlorobenzene	6.86	13.74
1,2,3-Trichlorobenzene	8.14	16.00
1,3,5-Trichlorobenzene	5.45	10.37
Internal Standards		
2,5-Dibromotoluene	9.55	18.55
1,3,5-Tribromobenzene	11.68	22.60
α,α'-Dibromo-meta-xylene	18.43	35.94
Surrogates		
α,2,6-Trichlorotoluene	12.96	22.53
1,4-Dichloronaphthalene	17.43	26.83
2,3,4,5,6-Pentachlorotoluene	18.96	27.91

[a] GC operating conditions: 30 m x 0.53 mm ID DB-210 fused-silica capillary column; 1 µm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 65°C to 175°C (hold 20 minutes) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

[b] GC operating conditions: 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1 µm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 60°C to 170°C (hold 30 minutes) at 4°C/min; injector temperature 200°C; detector temperature 230°C.

[c] Compound decomposes on-column.

TABLE 4
RETENTION TIMES OF THE CHLORINATED HYDROCARBONS[a]
DUAL COLUMN METHOD OF ANALYSIS

	DB-5	DB-1701
Compound	RT(min)	RT(min)
1,3-Dichlorobenzene	5.82	7.22
1,4-Dichlorobenzene	6.00	7.53
Benzyl chloride	6.00	8.47
1,2-Dichlorobenzene	6.64	8.58
Hexachloroethane	7.91	8.58
1,3,5-Trichlorobenzene	10.07	11.55
Benzal chloride	10.27	14.41
1,2,4-Trichlorobenzene	11.97	14.54
1,2,3-Trichlorobenzene	13.58	16.93
Hexachlorobutadiene	13.88	14.41
Benzotrichloride	14.09	17.12
1,2,3,5-Tetrachlorobenzene	19.35	21.85
1,2,4,5-Tetrachlorobenzene	19.35	22.07
Hexachlorocyclopentadiene	19.85	21.17
1,2,3,4-Tetrachlorobenzene	21.97	25.71
2-Chloronaphthalene	21.77	26.60
Pentachlorobenzene	29.02	31.05
α-BHC	34.64	38.79
Hexachlorobenzene	34.98	36.52
β-BHC	35.99	43.77
γ-BHC	36.25	40.59
δ-BHC	37.39	44.62
Internal Standard		
1,3,5-Tribromobenzene	11.83	13.34
Surrogate		
1,4-Dichloronaphthalene	15.42	17.71

[a] The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0 µm film thickness) connected to an 8-in injection tee (Supelco Inc.). Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min then to 240°C (2 min hold) at 5°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

TABLE 5
GC OPERATING CONDITIONS FOR CHLOROHYDROCARBONS
SINGLE COLUMN METHOD OF ANALYSIS

Column 1: DB-210 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl silicone

Carrier gas (He)	10 mL/min	
Column temperature:		
	Initial temperature	65°C
	Temperature program	65°C to 175°C at 4°C/min
	Final temperature	175°C, hold 20 minutes.
Injector temperature	220°C	
Detector temperature	250°C	
Injection volume	1-2 µL	

Column 2: DB-WAX 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol

Carrier gas (He)	10 mL/min	
Column temperature:		
	Initial temperature	60°C
	Temperature program	60°C to 170°C at 4°C/min
	Final temperature	170°C, hold 30 minutes.
Injector temperature	200°C	
Detector temperature	230°C	
Injection volume	1-2 µL	

TABLE 6
GC OPERATING CONDITIONS FOR CHLORINATED HYDROCARBONS
DUAL COLUMN METHOD OF ANALYSIS

Column 1:

Type: DB-1701 (J&W Scientific) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 1.0 (µm)

Column 2:

Type: DB-5 (J&W Scientific) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 0.83 (µm)

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Nitrogen)

Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min then to 240°C (2 min hold) at 5°C/min.

Injector temperature: 250°C

Detector temperature: 320°C

Injection volume: 2 µL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual ECD

Range: 10

Attenuation: 32 (DB-1701)/32 (DB-5)

Type of splitter: Supelco 8-in injection tee

TABLE 7

SUGGESTED CONCENTRATIONS FOR THE CALIBRATION SOLUTIONS[a]

	Concentration (ng/µL)				
Benzal chloride	0.1	0.2	0.5	0.8	1.0
Benzotrichloride	0.1	0.2	0.5	0.8	1.0
Benzyl chloride	0.1	0.2	0.5	0.8	1.0
2-Chloronaphthalene	2.0	4.0	10	16	20
1,2-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,3-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,4-Dichlorobenzene	1.0	2.0	5.0	8.0	10
Hexachlorobenzene	0.01	0.02	0.05	0.08	0.1
Hexachlorobutadiene	0.01	0.02	0.05	0.08	0.1
α-BHC	0.1	0.2	0.5	0.8	1.0
β-BHC	0.1	0.2	0.5	0.8	1.0
γ-BHC	0.1	0.2	0.5	0.8	1.0
δ-BHC	0.1	0.2	0.5	0.8	1.0
Hexachlorocyclopentadiene	0.01	0.02	0.05	0.08	0.1
Hexachloroethane	0.01	0.02	0.05	0.08	0.1
Pentachlorobenzene	0.01	0.02	0.05	0.08	0.1
1,2,3,4-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,3,5-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
Surrogates					
α,2,6-Trichlorotoluene	0.02	0.05	0.1	0.15	0.2
1,4-Dichloronaphthalene	0.2	0.5	1.0	1.5	2.0
2,3,4,5,6-Pentachlorotoluene	0.02	0.05	0.1	0.15	0.2

[a] One or more internal standards should be spiked prior to GC/ECD analysis into all calibration solutions. The spike concentration of the internal standards should be kept constant for all calibration solutions.

TABLE 8

ELUTION PATTERNS OF CHLORINATED HYDROCARBONS
FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER (FRACTION 1)
AND 1:1 PETROLEUM ETHER/DIETHYL ETHER (FRACTION 2)

Compound	Amount (µg)	Recovery (percent)[a]	
		Fraction 1[b]	Fraction 2[c]
Benzal chloride[d]	10	0	0
Benzotrichloride	10	0	0
Benzyl chloride	100	82	16
2-Chloronaphthalene	200	115	
1,2-Dichlorobenzene	100	102	
1,3-Dichlorobenzene	100	103	
1,4-Dichlorobenzene	100	104	
Hexachlorobenzene	1.0	116	
Hexachlorobutadiene	1.0	101	
α-BHC	10		95
β-BHC	10		108
γ-BHC	10		105
δ-BHC	10		71
Hexachlorocyclopentadiene	1.0	93	
Hexachloroethane	1.0	100	
Pentachlorobenzene	1.0	129	
1,2,3,4-Tetrachlorobenzene	10	104	
1,2,4,5-Tetrachlorobenzene[e]	10	102	
1,2,3,5-Tetrachlorobenzene[e]	10	102	
1,2,4-Trichlorobenzene	10	59	
1,2,3-Trichlorobenzene	10	96	
1,3,5-Trichlorobenzene	10	102	

[a] Values given represent average values of duplicate experiments.

[b] Fraction 1 was eluted with 200 mL petroleum ether.

[c] Fraction 2 was eluted with 200 mL petroleum ether/diethyl ether (1:1).

[d] This compound coelutes with 1,2,4-trichlorobenzene; separate experiments were performed with benzal chloride to verify that this compound is not recovered from the Florisil cleanup in either fraction.

[e] This pair cannot be resolved on the DB-210 fused-silica capillary columns.

TABLE 9
SINGLE LABORATORY ACCURACY DATA FOR THE EXTRACTION OF
CHLORINATED HYDROCARBONS FROM SPIKED CLAY SOIL BY METHOD 3541
(AUTOMATED SOXHLET)[a]

Compound Name	Spike Level	% Recovery	
	µg/kg	DB-5	DB-1701
1,3-Dichlorobenzene	5000	b	39
1,2-Dichlorobenzene	5000	94	77
Benzal chloride	500	61	66
Benzotrichloride	500	48	53
Hexachlorocyclopentadiene	500	30	32
Pentachlorobenzene	500	76	73
alpha-BHC	500	89	94
delta-BHC	500	86	b
Hexachlorobenzene	500	84	88

a The operating conditions for the automated Soxhlet were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil, extraction solvent, 1:1 acetone/hexane. No equilibration time following spiking.

b Not able to determine because of interference.

Data taken from Reference 4.

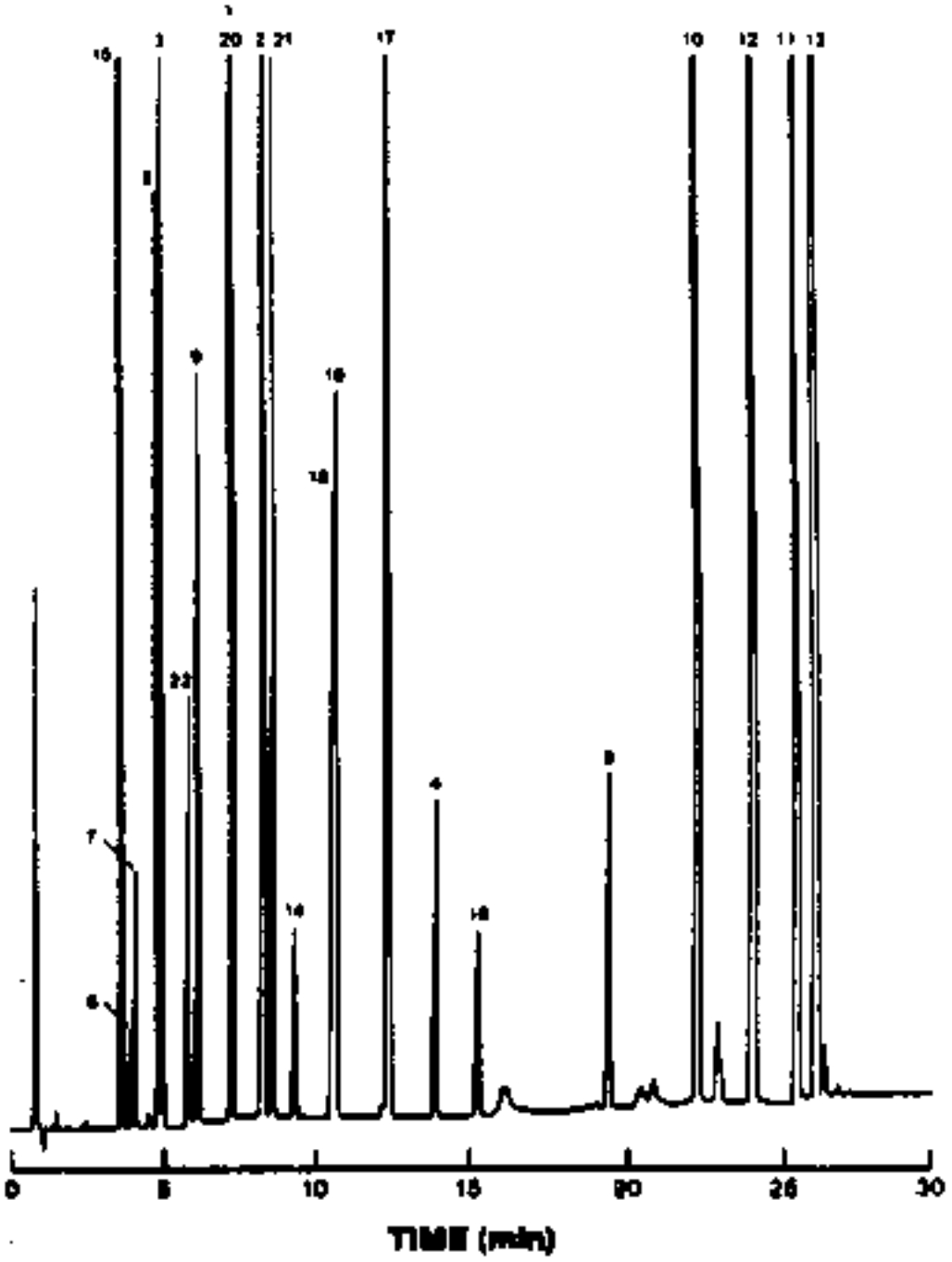


Figure 1. GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-210 fused-silica capillary column. GC operating conditions are given in Sec. 7.4. See Table 3 for compound identification.

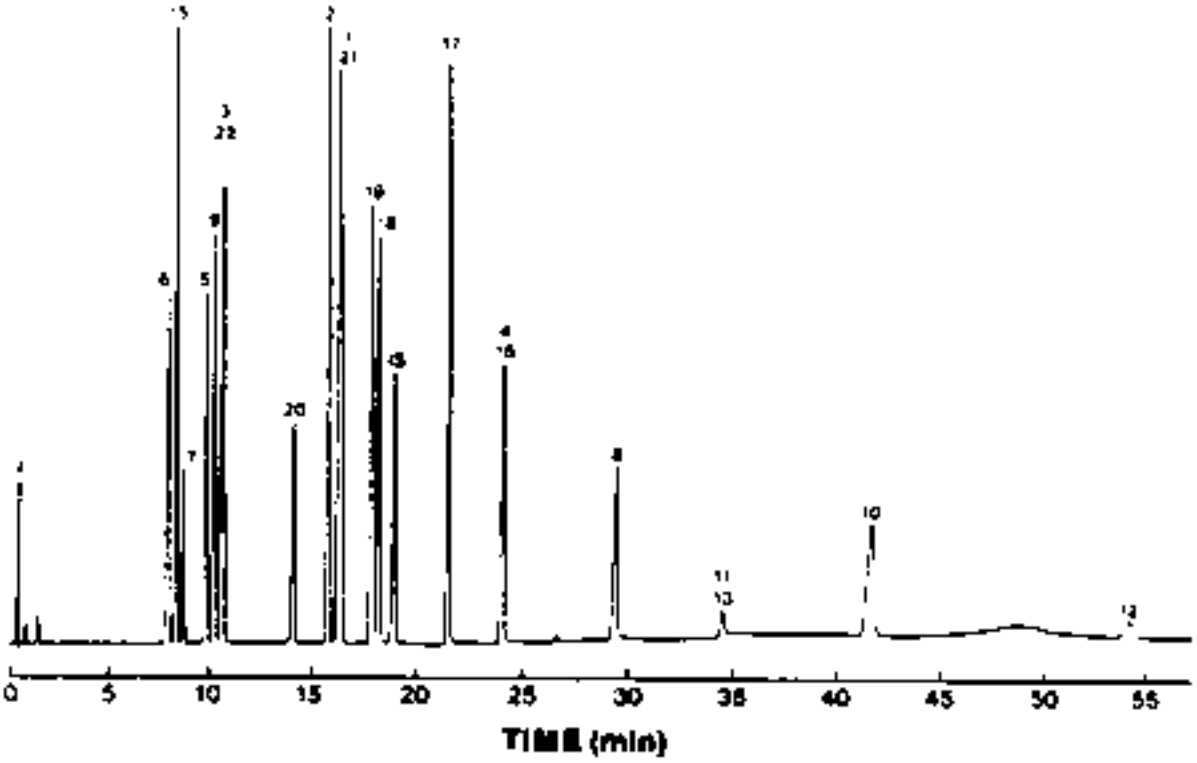


Figure 2. GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-WAX fused-silica capillary column. GC operating conditions are given in Sec. 7.4. See Table 3 for compound identification.

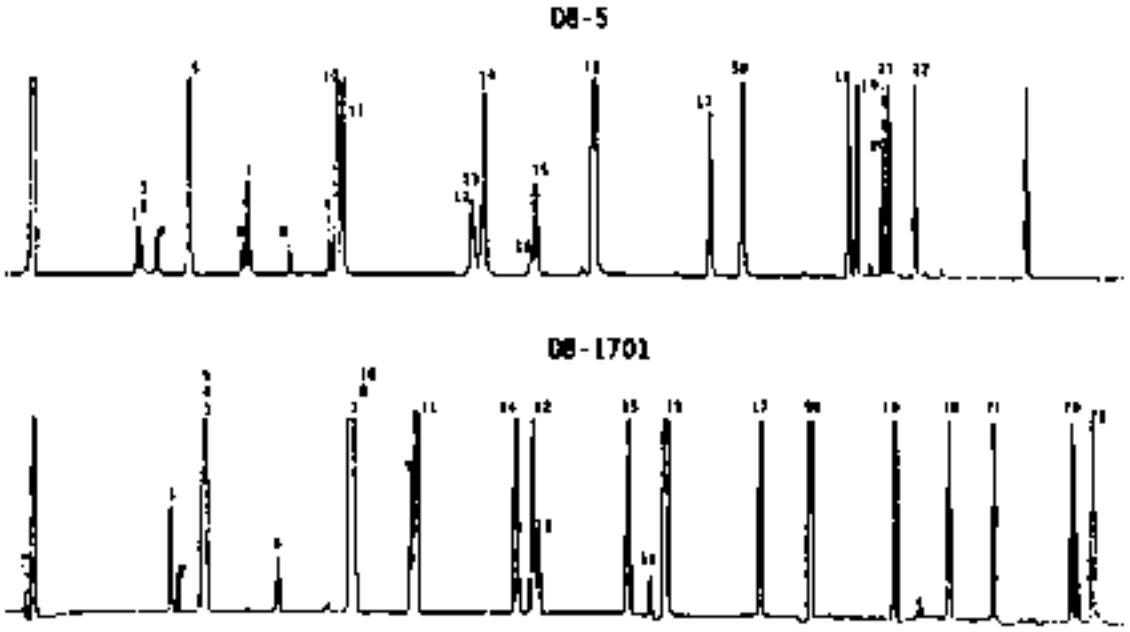
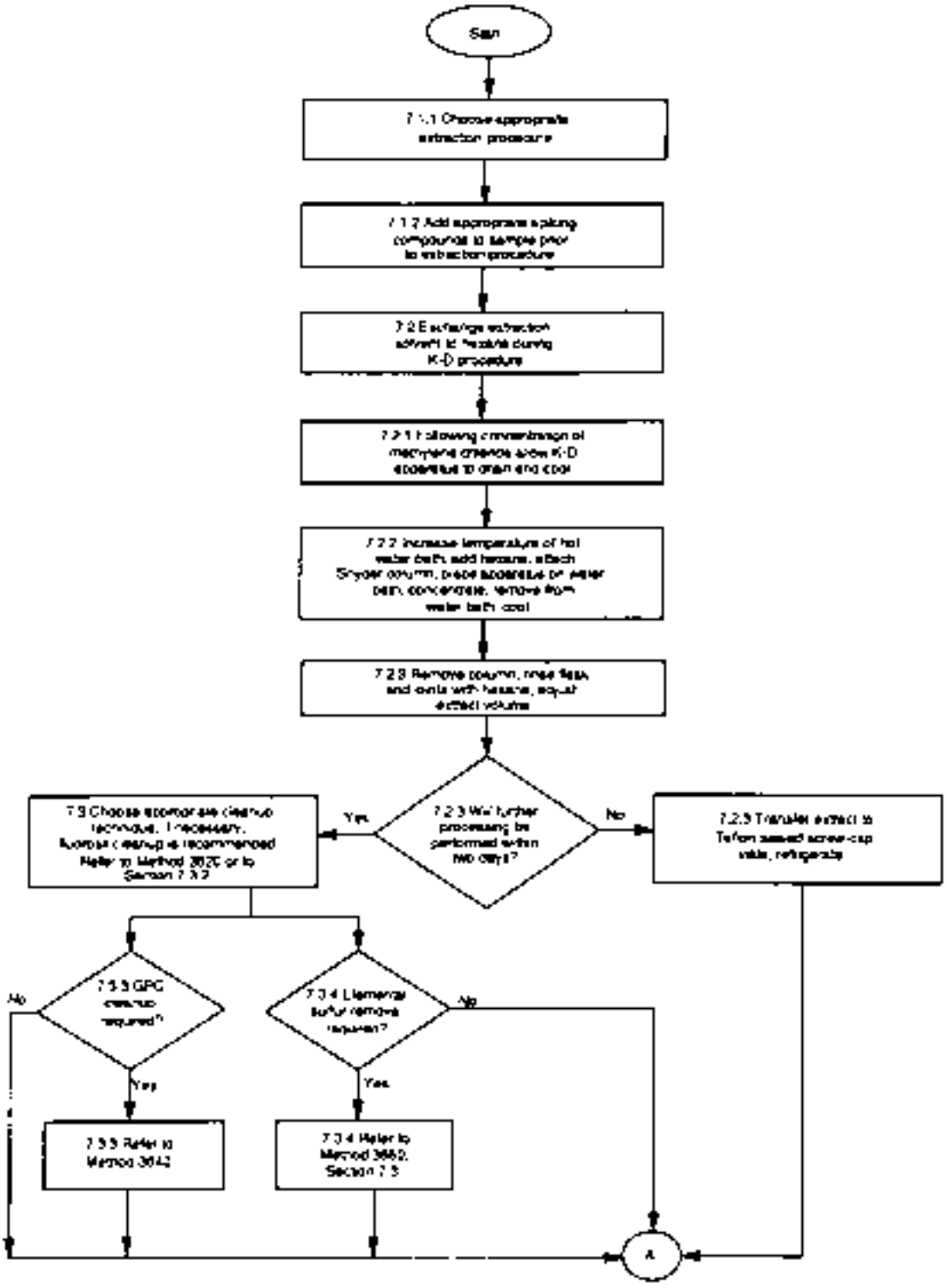
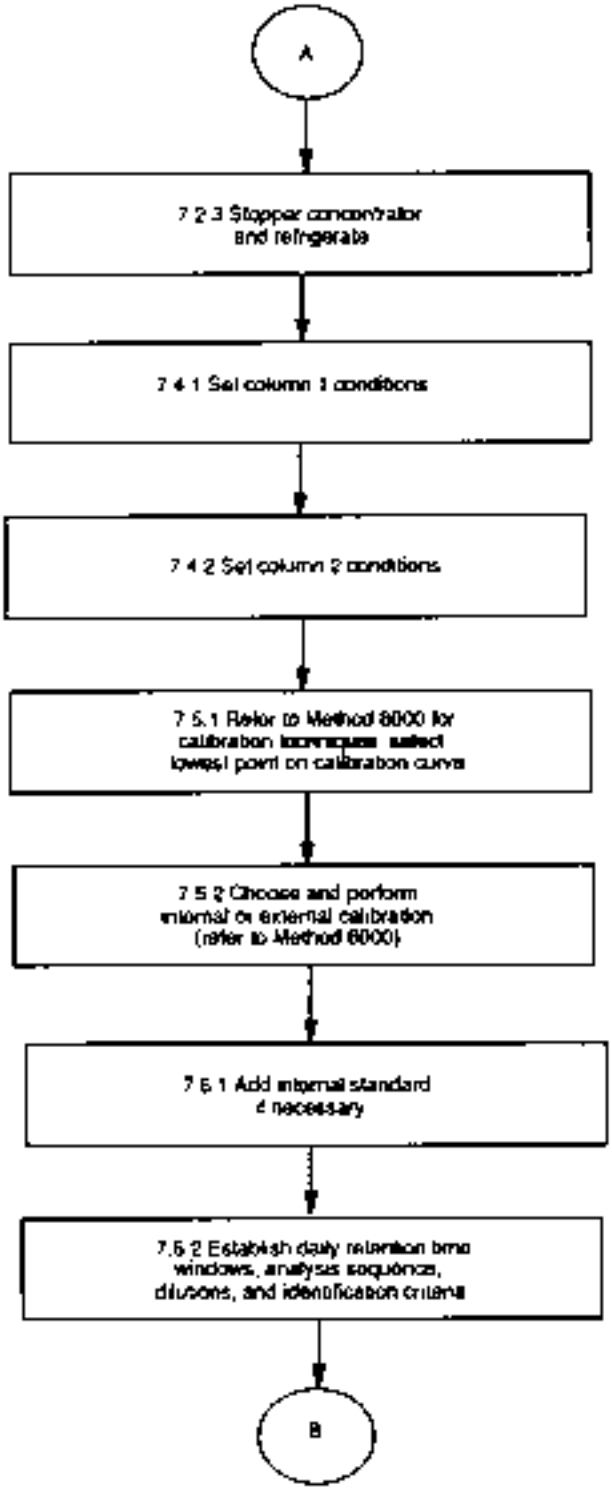
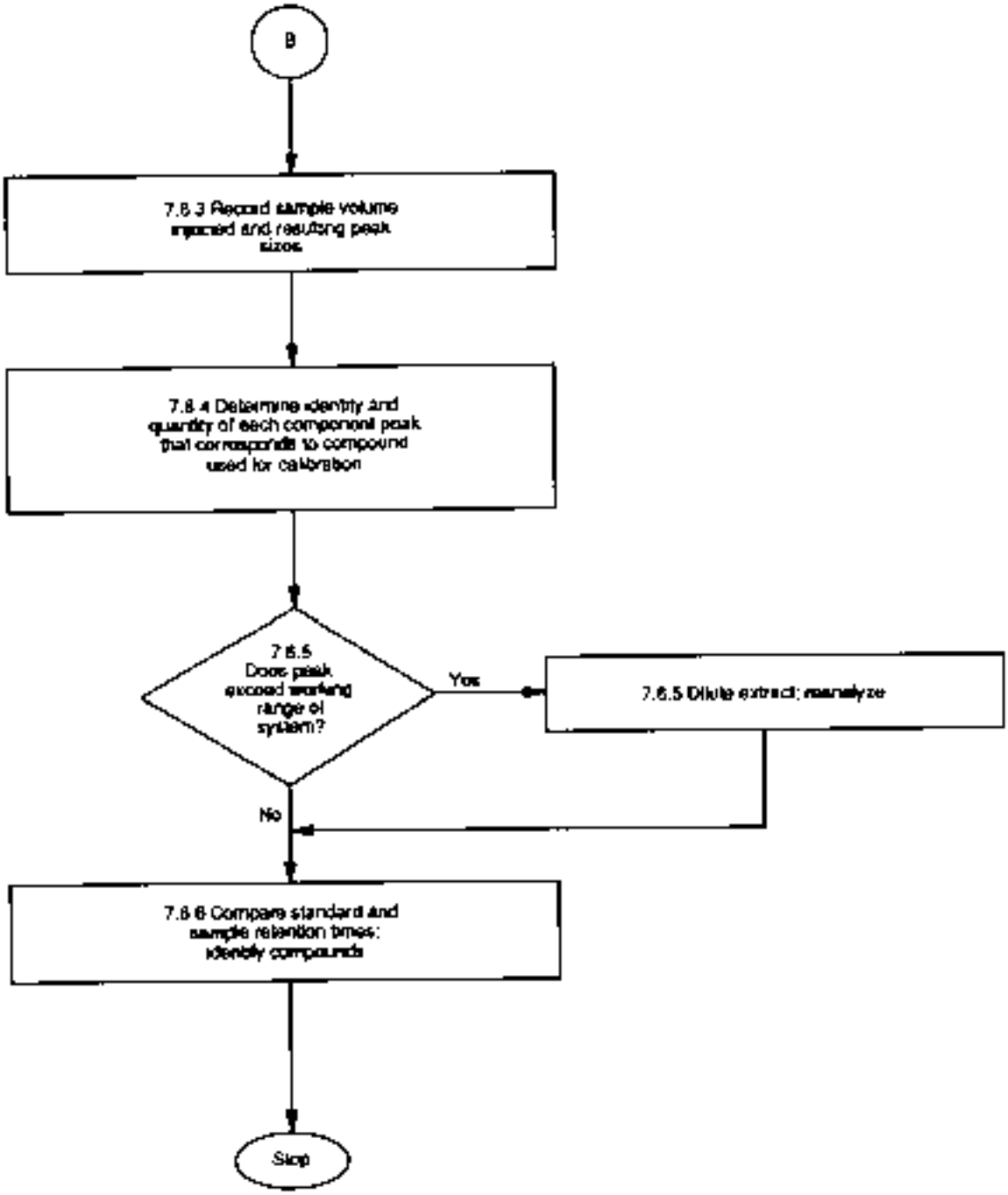


Figure 3. GC/ECD chromatogram of chlorinated hydrocarbons analyzed on a DB 5/DB 1701 fused-silica, open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB 5 (0.83 µm film thickness) and 30 m x 0.53 mm ID DB 1701 (1.0 µm film thickness) connected to an 8 in injection tee (Supelco Inc.). Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min, then to 240°C (2 min hold) at 5°C/min.


Start
7.1.1 Choose appropriate extraction procedure
7.1.2 Add appropriate spiking compounds to sample prior to extraction procedure
7.2 Exchange extraction solvent to hexane during K-D procedure
7.2.1 Following concentration of methylene chloride using K-D apparatus to obtain and cool
7.2.2 Increase temperature of hot water bath, add hexane, attach Snyder column, prewet apparatus by water bath, concentrate, remove from water bath, cool
7.2.3 Remove column, rinse flask and vials with hexane, adjust to final volume
7.2.3 Will further processing be performed within two days?
Yes
No
7.3 Choose appropriate cleanup technique. If necessary, Florisil cleanup is recommended. Refer to Method 3620 or to Section 7.3.2
7.2.3 Transfer extract to Teflon-sealed screw-cap vials, refrigerate
7.3.3 GPC cleanup required?
7.3.4 Elemental sulfur removal required?
No
No
Yes
Yes
7.3.3 Refer to Method 3640
7.3.4 Refer to Method 3660, Section 7.3
A


A
7.2.3 Stopper concentrator and refrigerate
7.4.1 Set column 1 conditions
7.4.2 Set column 2 conditions
7.5.1 Refer to Method 8000 for calibration techniques select lowest point on calibration curve
7.5.2 Choose and perform internal or external calibration (refer to Method 8000)
7.6.1 Add internal standard if necessary
7.6.2 Establish daily retention time windows, analysis sequence, dilutions, and identification criteria
B


B
7.8.3 Record sample volume injected and resulting peak sizes
7.8.4 Determine identity and quantity of each component peak that corresponds to compound used for calibration
7.8.5 Does peak exceed working range of system?
Yes
7.8.5 Dilute extract; reanalyze
No
7.8.6 Compare standard and sample retention times; identify compounds
Stop