METHOD 8120A

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8120 is used to determine the concentration of certain chlorinated hydrocarbons. The following compounds can be determined by this method:

		Appropriate Preparation Techniques				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
2-Chloronaphthalene	91-58-7	X	X	X	X	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclohexane	608-73-1	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Pentachlorohexane	--	X	X	X	X	X
Tetrachlorobenzenes	--	X	ND	ND	ND	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X

a Chemical Abstract Services Registry Number.
x Greater than 70 percent recovery by this technique
ND Not determined.

1.2 Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8120 provides gas chromatographic conditions for the detection of ppb concentrations of certain chlorinated hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 µL aliquot of the extract is injected into a gas chromatograph (GC), and compounds in the GC effluent are detected by an electron capture detector (ECD).

2.2 If interferences are encountered in the analysis, Method 8120 may also be performed on extracts that have undergone cleanup using Method 3620.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 1.8 m x 2 mm ID glass column packed with 1% SP-1000 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2 - 1.8 m x 2 mm ID glass column packed with 1.5% OV-1/2.4% OV-225 on Supelcoport (80/100 mesh) or equivalent.

4.1.3 Detector - Electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm$ 5°C). The bath should be used in a hood.

4.5 Volumetric flasks - 10, 50, and 100 mL, with ground glass stoppers.

4.6 Microsyringe - 10 µL.

4.7 Syringe - 5 mL.

4.8 Vials - Glass, 2, 10, and 20 mL capacity with Teflon lined screw-caps or crimp tops.

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 reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.3.2 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

5.3.3 Isooctane, C_8H_{18}. Pesticide quality or equivalent.

5.4 Stock standard solutions

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in isooctane or hexane and diluting 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.

5.4.2 Transfer the stock standard solutions into vials with Teflon lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards.

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared through dilution of the stock standards with isooctane or hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Sec. 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane or hexane.

5.6.3 Analyze each calibration standard according to Sec. 7.0.

5.7 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with one or two surrogates (e.g. chlorinated hydrocarbons that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500 details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

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 under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two 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.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Sec. 7.1.2.3. If cleanup is needed, proceed to Sec. 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw cap or crimp top. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5 mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 minutes. At the proper rate of

distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min
Column temperature = 65°C isothermal, unless otherwise specified (see Table 1).

7.2.2 Column 2

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min
Column temperature = 75°C isothermal, unless otherwise specified (see Table 1).

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injecting.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for certain chlorinated hydrocarbons are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and 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 peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup: If required, the samples may be cleaned up using the Methods presented in Chapter 4.

7.5.1 Proceed with Method 3620 using the 2 mL hexane extracts obtained from Sec. 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One 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 Procedures to check the GC system operation are found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest at the following concentrations in acetone: hexachloro-substituted hydrocarbon, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 356 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons, and Category 8 - Phenols," Report for EPA Contract 68-03-2625.

2. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

3. "EPA Method Validation Study 22, Method 612 (Chlorinated Hydrocarbons)," Report for EPA Contract 68-03-2625.

4. "Method Performance for Hexachlorocyclopentadiene by Method 612," Memorandum from R. Slater, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, December 7, 1983.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. "Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625.

TABLE 1.
GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention time (min) Col. 1	Col. 2	Method Detection limit (µg/L)
2-Chloronaphthalene	2.7[a]	3.6[b]	0.94
1,2-Dichlorobenzene	6.6	9.3	1.14
1,3-Dichlorobenzene	4.5	6.8	1.19
1,4-Dichlorobenzene	5.2	7.6	1.34
Hexachlorobenzene	5.6[a]	10.1[b]	0.05
Hexachlorobutadiene	7.7	20.0	0.34
Hexachlorocyclohexane			
Hexachlorocyclopentadiene	ND	16.5[c]	0.40
Hexachloroethane	4.9	8.3	0.03
Pentachlorohexane	--	--	--
Tetrachlorobenzenes	--	--	--
1,2,4-Trichlorobenzene	15.5	22.3	0.05

ND = Not determined.

[a]150°C column temperature.

[b]165°C column temperature.

[c]100°C column temperature.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION
LIMITS (EQL) 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
Non-water miscible waste	100,000

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

TABLE 3.
QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range P, P_s (%)
2-Chloronaphthalene	100	37.3	29.5-126.9	9-148
1,2-Dichlorobenzene	100	28.3	23.5-145.1	9-160
1,3-Dichlorobenzene	100	26.4	7.2-138.6	D-150
1,4-Dichlorobenzene	100	20.8	22.7-126.9	13-137
Hexachlorobenzene	10	2.4	2.6-14.8	15-159
Hexachlorobutadiene	10	2.2	D-12.7	D-139
Hexachlorocyclopentadiene	10	2.5	D-10.4	D-111
Hexachloroethane	10	3.3	2.4-12.3	8-139
1,2,4-Trichlorobenzene	100	31.6	20.2-133.7	5-149

s = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.

P,P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 612. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Chloronaphthalene	0.75C+3.21	0.28$\bar{x}$-1.17	0.38$\bar{x}$-1.39
1,2-Dichlorobenzene	0.85C-0.70	0.22$\bar{x}$-2.95	0.41$\bar{x}$-3.92
1,3-Dichlorobenzene	0.72C+0.87	0.21$\bar{x}$-1.03	0.49$\bar{x}$-3.98
1,4-Dichlorobenzene	0.72C+2.80	0.16$\bar{x}$-0.48	0.35$\bar{x}$-0.57
Hexachlorobenzene	0.87C-0.02	0.14$\bar{x}$+0.07	0.36$\bar{x}$-0.19
Hexachlorobutadiene	0.61C+0.03	0.18$\bar{x}$+0.08	0.53$\bar{x}$-0.12
Hexachlorocyclopentadiene[a]	0.47C	0.24$\bar{x}$	0.50$\bar{x}$
Hexachloroethane	0.74C-0.02	0.23$\bar{x}$+0.07	0.36$\bar{x}$-0.00
1,2,4-Trichlorobenzene	0.76C+0.98	0.23x-0.44	0.40x-1.37

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of x, in µg/L.

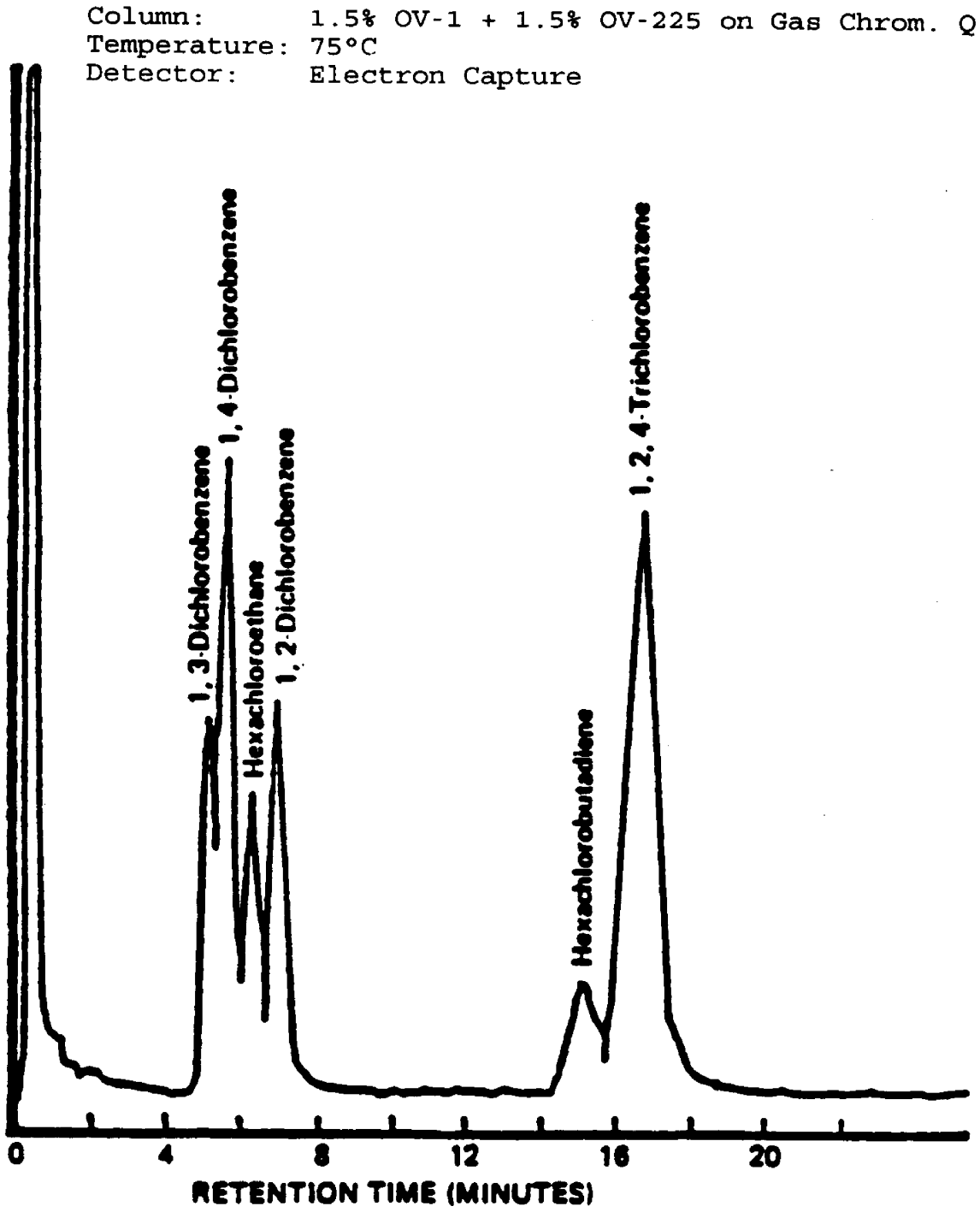
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

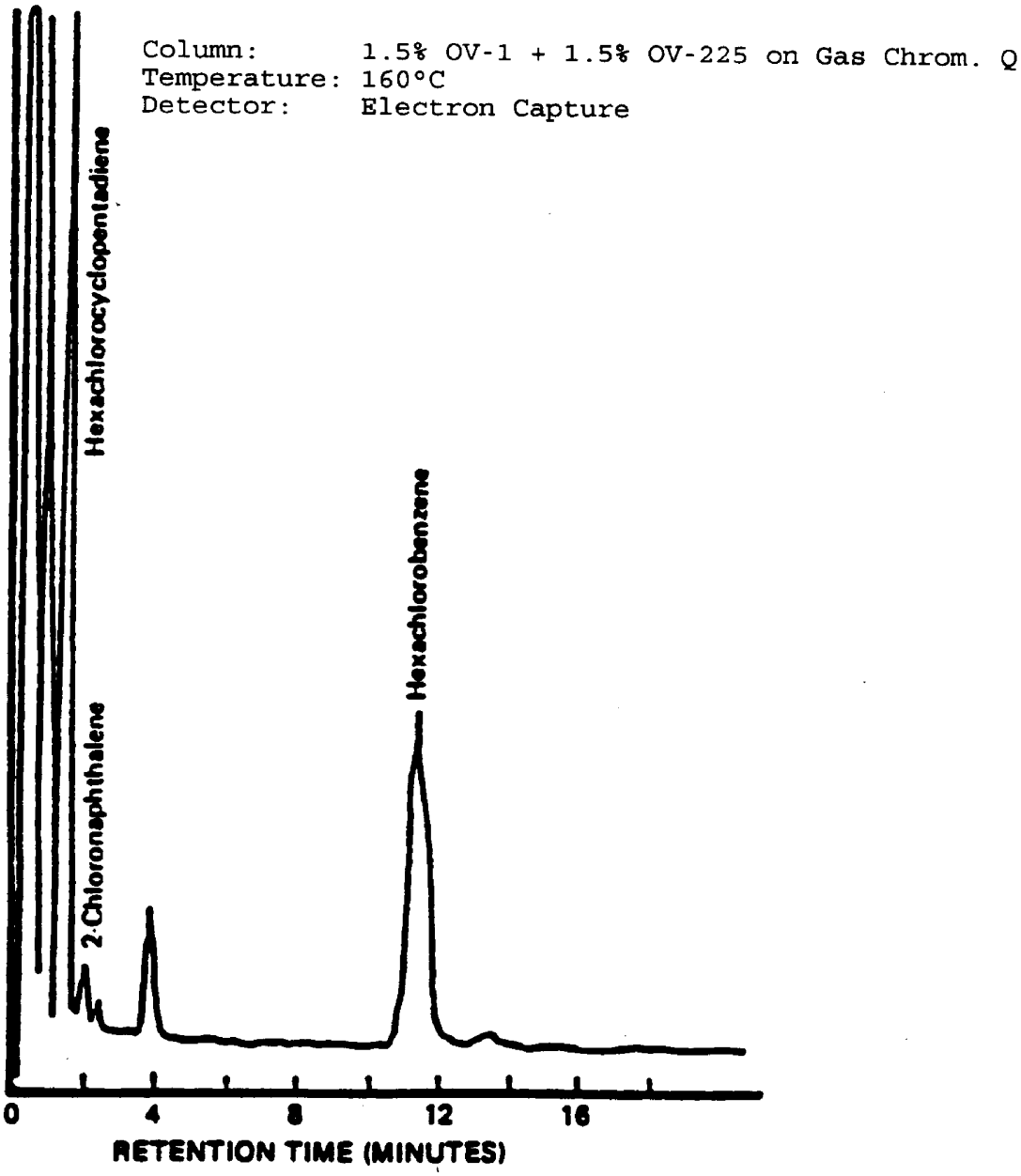
a Estimates based upon the performance in a single laboratory.

FIGURE 1

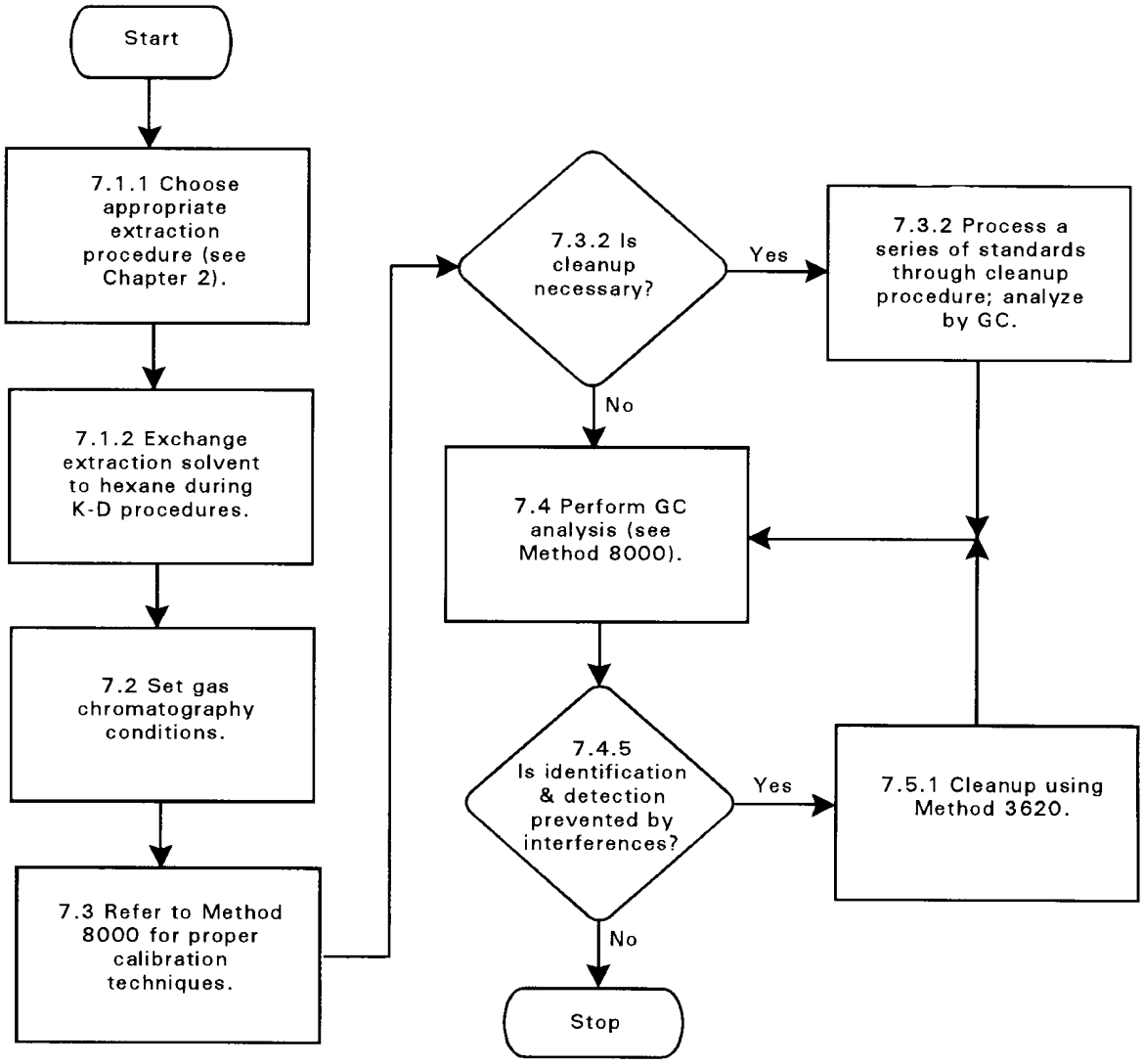


Gas chromatogram of chlorinated hydrocarbons (high molecular weight compounds).

FIGURE 2



Gas chromatogram of chlorinated hydrocarbons (low molecular weight compounds).


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2).
7.1.2 Exchange extraction solvent to hexane during K-D procedures.
7.2 Set gas chromatography conditions.
7.3 Refer to Method 8000 for proper calibration techniques.
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC.
No
7.4 Perform GC analysis (see Method 8000).
7.4.5 Is identification & detection prevented by interferences?
Yes
7.5.1 Cleanup using Method 3620.
No
Stop