METHOD 8111

HALOETHERS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8111 is a gas chromatographic (GC) method used to determine the concentration of haloethers. It describes wide-bore open-tubular, capillary column gas chromatography procedures using the a dual-column/dual-detector approach, however, a single column/single detector approach is acceptable. The following RCRA analytes can be determined by this method:

Compound	CAS No.[a]
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
4-Chlorophenyl phenyl ether	7005-72-3

[a]Chemical Abstract Service Registry Number

1.2 The following non-RCRA analytes may also be analyzed by this method:

Compound	CAS No.
4-Bromophenyl phenyl ether	101-55-3
2-Chlorophenyl 4-nitrophenyl ether	209-61-4
3-Chlorophenyl 4-nitrophenyl ether	2303-23-3
4-Chlorophenyl 4-nitrophenyl ether	1836-74-4
2,4-Dibromophenyl 4-nitrophenyl ether	2671-93-4
2,4-Dichlorophenyl 3-methyl-4-nitrophenyl ether	42488-57-3
2,6-Dichlorophenyl 4-nitrophenyl ether	2093-28-9
3,5-Dichlorophenyl 4-nitrophenyl ether	NA
2,5-Dichlorophenyl 4-nitrophenyl ether	391-48-7
2,4-Dichlorophenyl 4-nitrophenyl ether	1836-75-5
2,3-Dichlorophenyl 4-nitrophenyl ether	82239-20-1
3,4-Dichlorophenyl 4-nitrophenyl ether	22532-80-5
4-Nitrophenyl phenyl ether	620-88-2
2,4,6-Trichlorophenyl 4-nitrophenyl ether	1836-77-7
2,3,6-Trichlorophenyl 4-nitrophenyl ether	NA
2,3,5-Trichlorophenyl 4-nitrophenyl ether	NA
2,4,5-Trichlorophenyl 4-nitrophenyl ether	22532-68-9
3,4,5-Trichlorophenyl 4-nitrophenyl ether	NA
2,3,4-Trichlorophenyl 4-nitrophenyl ether	NA

NA = CAS numbers not assigned at this time.

1.3 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 8111 provides gas chromatographic conditions for the detection of ppb concentrations of haloethers in water and soil or ppm concentrations in waste samples.

2.2 Prior to use of this method, appropriate sample extraction techniques must be used for environmental samples (refer to Chap. Two and Method 3500).

2.3 Both neat and diluted organic liquids (Method 3580) may be analyzed by direct injection.

2.4 Analysis is accomplished by gas chromatography utilizing an instrument equipped with a wide-bore capillary column and an electron capture detector.

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 such as 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 Dichlorobenzenes are known to coelute with haloethers under some gas chromatographic conditions. If these materials are present in a sample, it may be necessary to analyze the extract with two different column packings to completely resolve all of the compounds.

3.4 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 thoroughly rinsed between samples with solvent. Whenever a highly concentrated sample is encountered, 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.

3.5 Some compounds coelute using this procedure. In these cases, the compounds must be reported as coeluting. The mixture may be reanalyzed for peak confirmation by GC/MS techniques if concentration permits (see Method 8270).

3.6 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 necessary accessories, including syringes,

analytical columns, gases and two electron capture detectors. A data system for measuring peak areas and/or peak heights is recommended.

4.2 Suggested GC columns - Alternative columns may be used to provide the separation required to resolve all target analytes listed in Sec. 1.1 of this method. Refer to Chapter 1 and Method 8000 for additional information regarding column performance and QC requirements.

4.2.1 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.

4.2.2 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.

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

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

4.5 Balances - Analytical, capable of accurately weighing 0.0001 g, and top-loading, capable of accurately weighing 0.01 g.

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

5.0 REAGENTS

5.1 Reagent grade 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.

5.2 Solvents - All solvents must be pesticide quality or equivalent.

5.2.1 Hexane, C_6H_{14}

5.2.2 Acetone, CH_3COCH_3

5.2.3 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$

5.3 Stock standard solutions (1000 mg/L) - May 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 may 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, dissolve the compound initially with a small volume of toluene, ethyl acetate or acetone and dilute to volume with isooctane or hexane.

5.4 Composite stock standard - Can be prepared from individual stock solutions. For composite stock standards containing less than 25 components, transfer exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, mix the solutions, and bring to volume 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 - These should be prepared at a minimum of five concentrations with dilution of the composite stock standard with isooctane or hexane. The standard concentrations should correspond to the expected range of concentrations present in the field samples and should bracket the linear range of the detector.

5.6 Recommended internal standard - Prepare a solution of 1000 mg/L of 4,4'-dibromobiphenyl. For spiking, dilute this solution to 50 ng/µL. (This concentration may need to be more dilute depending on the detector sensitivity. The internal standard response should be approximately 50 to 90% of full scale.) 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 polytetrafluoroethylene (PTFE)-sealed containers in the dark.

5.7 Recommended surrogate standards - The performance of the method should be monitored using surrogate compounds. Surrogates are added to all samples, method blanks, matrix spikes, and calibration standards. Prepare a solution of 1000 mg/L each of 2,4-dichlorodiphenyl ether and 2,3,4-trichlorodiphenyl ether and dilute them to 20 ng/µL. Use a spiking volume of 100 µL for a 1-L aqueous sample. (This concentration may need to be adjusted depending on the detector sensitivity. The surrogate standard response should be approximately 100% of full scale.)

5.8 Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C or cooler in PTFE-sealed containers in the dark. All standard solutions must be replaced after six months or sooner if routine QC (Sec. 8.0) indicates a problem.

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 stored in the dark at or below 4°C and be 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 any of the extraction methods for solids listed in Method 3500, as appropriate.

7.1.2 If necessary, the samples may be cleaned up using Method 3620 (Florisil) and/or Method 3640 (Gel Permeation Chromatography). See Chapter Two, Sec. 2, and Method 3600 for general guidance on cleanup and method selection. Method 3660 may be used for sulfur removal.

7.1.3 Prior to gas chromatographic analysis, the extraction solvent should be exchanged to hexane. The exchange is performed during the K-D procedures listed in each of the extraction methods. Any methylene chloride remaining in the extract will cause a very broad solvent peak.

NOTE: Some of the haloethers are very volatile and significant losses will occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D apparatus from the hot water bath.

7.2 Gas Chromatography (GC) Conditions - Retention time information for each of the target analytes is presented in Table 1. Retention times of non-RCRA analytes are presented in Table 2. GC operating conditions under which these retention times were obtained are provided in the appropriate table. Figures 1 and 2 illustrate typical chromatography of the haloethers.

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 procedures for establishing retention time windows.

7.4 Gas chromatographic analysis

7.4.1 Method 8000, provides instructions on calibration, establishing retention time windows, the analysis sequence, appropriate dilutions, 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 1 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 absolute retention time window. Normally confirmation is required. Confirmation techniques include analysis on a second column with dissimilar stationary phase, by GC/MS (full scan or SIM) or by using a different detector and getting comparable data. See Method 8000 for further information.

7.4.3.1 If partially overlapping or coeluting peaks are present, install columns with a dissimilar liquid phase or use a GC/MS technique.

7.4.3.1 Interferences that prevent analyte identification and/or quantitation may possibly be removed by the cleanup techniques mentioned above.

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

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

7.4.4.2 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.

7.4.5 Determine the concentration of each identified analyte using the calculation formulas in Sec. 7.0 of Method 8000.

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.). 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 remedial actions.

7.5.2.1 Column rinsing - The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone; methylene chloride is a satisfactory final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to remain flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

7.5.2.2 See Method 8000 for additional guidance on corrective action for capillary columns and the injection port.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and includes evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Table 1 lists the retention times and recoveries of the target analytes. The recoveries presented were obtained from the analysis of spiked sandy loam soils. No recovery data is currently available on Bis(2-chloro-ethoxy)methane and Bis(2-chloroethyl) ether.

9.2 Table 2 lists the compounds that may be determined by this method and their retention times. Figure 1 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 GC conditions listed in Table 2.

10.0 REFERENCES

1. 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 US EPA on Contract 68-03-3511; Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

2. Tsang, S.; Marsden, P.; Chau, N. "Performance Data for Methods 8041, 8091, 8111, and 8121A"; draft report to US EPA on Contract 68-W9-0011; Science Applications International Corp., San Diego, CA, 1992.

TABLE 1

RETENTION TIMES AND RECOVERY OF TARGET HALOETHERS

Analyte	RT (min)	Spiking Conc. (µg/g)	Recovery (%)	RSD (%)
Bis(2-chloroisopropyl) ether	3.06	2.5	112	4.3
4-Chlorophenyl phenyl ether	15.75	5.0	91.5	3.5
4-Bromophenyl phenyl ether	18.21	0.5	97.0	2.1

Column:	DB-5, 30 m x 0.53 mm id
Temperature program:	125°C (1.0 min hold) to 135°C at 2°C/min., 135°C to 200°C at 5°C/min., 200°C to 275°C at 10°C/min., (3.5 min hold)
Injector:	Packed, wide-bore liner
Injector temperature:	200°C
Detector:	ECD
Detector temperature:	320°C
Nitrogen carrier gas:	5 mL/min
Nitrogen makeup gas:	55 mL/min

TABLE 2

RETENTION TIMES OF NON-TARGET HALOETHERS

Peak[a]	Compound	Retention Time (min) DB-5	DB-1701
1	4-Bromophenyl-phenyl ether	4.28	5.57
2	Phenyl 4-nitrophenyl ether	6.85	10.86
3	2-Chlorophenyl 4-nitrophenyl ether	10.44	16.31
4	3-Chlorophenyl 4-nitrophenyl ether	10.78	16.70
5	4-Chlorophenyl 4-nitrophenyl ether	11.37	17.68
6	2,6-Dichlorophenyl 4-nitrophenyl ether	14.02	20.84
7	3,5-Dichlorophenyl 4-nitrophenyl ether	14.55	21.33
8	2,5-Dichlorophenyl 4-nitrophenyl ether	14.55	21.54
9	2,4-Dichlorophenyl 4-nitrophenyl ether	15.08	22.30
10	2,3-Dichlorophenyl 4-nitrophenyl ether	16.11	23.87
11	3,4-Dichlorophenyl 4-nitrophenyl ether	16.65	24.54
12	2,4,6-Trichlorophenyl 4-nitrophenyl ether	17.89	24.93
13	2,3,6-Trichlorophenyl 4-nitrophenyl ether	19.40	27.27
14	2,3,5-Trichlorophenyl 4-nitrophenyl ether	19.70	27.56
15	2,4,5-Trichlorophenyl 4-nitrophenyl ether	20.03	28.05
16	2,4-Dibromophenyl 4-nitrophenyl ether	21.63	30.03
17	3,4,5-Trichlorophenyl 4-nitrophenyl ether	21.83	30.42
18	2,3,4-Trichlorophenyl 4-nitrophenyl ether	22.28	31.18
19	2,4-Dichlorophenyl 3-methyl-4-nitrophenyl ether	21.83	31.60
IS	4,4'-Dibromobiphenyl	9.44	12.66
SU-1	2,4-Dichlorodiphenyl ether	4.82	6.17
SU-2	2,3,4-Trichlorodiphenyl ether	8.31	10.95

[a]Peak numbers refer to the chromatogram in Figure 2.

IS = Internal Standard
SU = Surrogate

The GC operating conditions for the above analysis were as follows:

Columns:	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:	180°C (0.5 min hold) to 260°C (1.0 min hold) at 2°C/min.
Injector temperature:	250°C
Detector temperature:	320°C
Helium carrier gas:	6 mL/min
Nitrogen makeup gas:	20 mL/min

FIGURE 1

GC/ECD CHROMATOGRAM OF TARGET ANALYTE HALOETHERS
ANALYZED ON A DB-5 CAPILLARY COLUMN FOR RECOVERY STUDIES

The GC operating conditions are listed in Table 1.

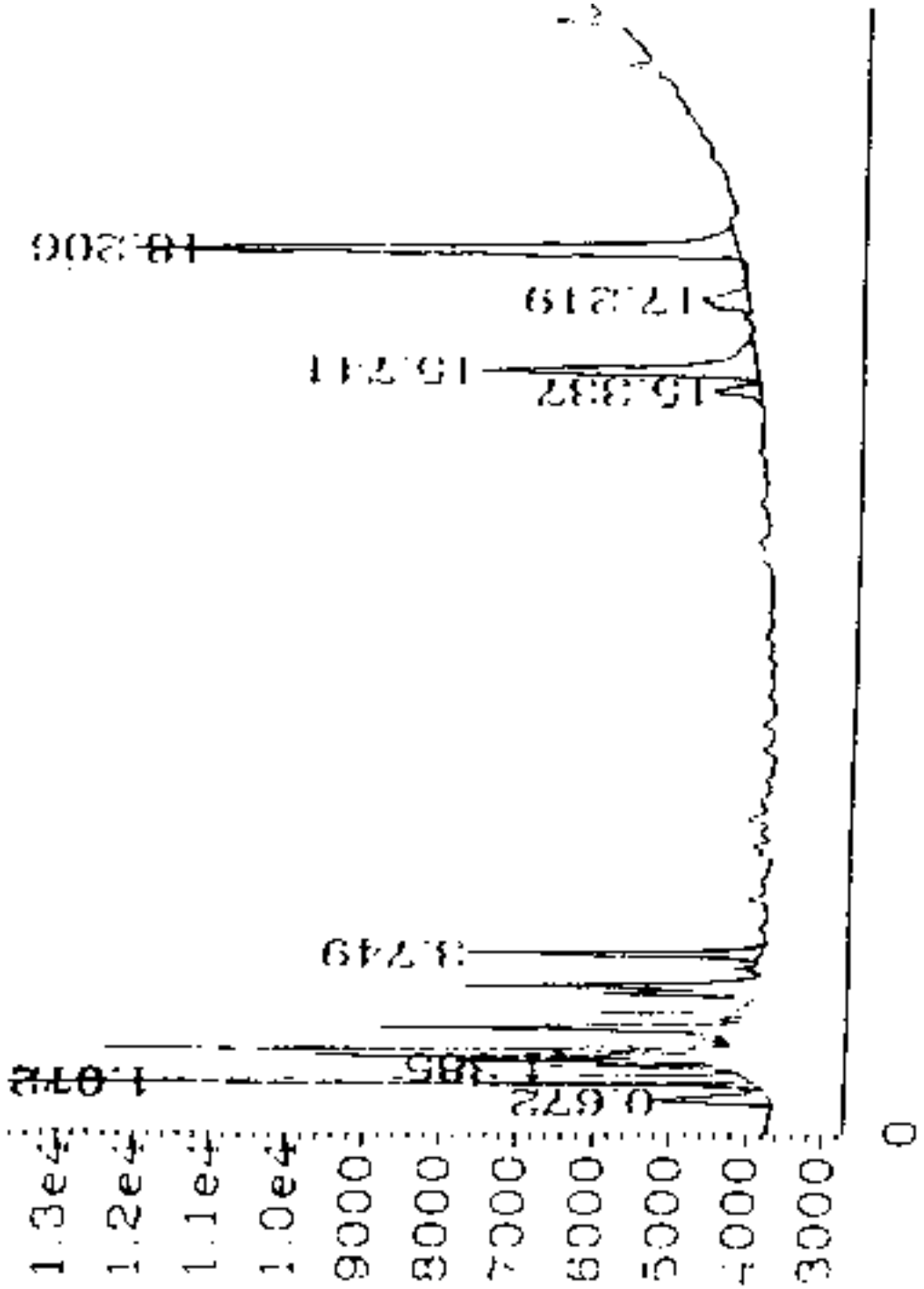
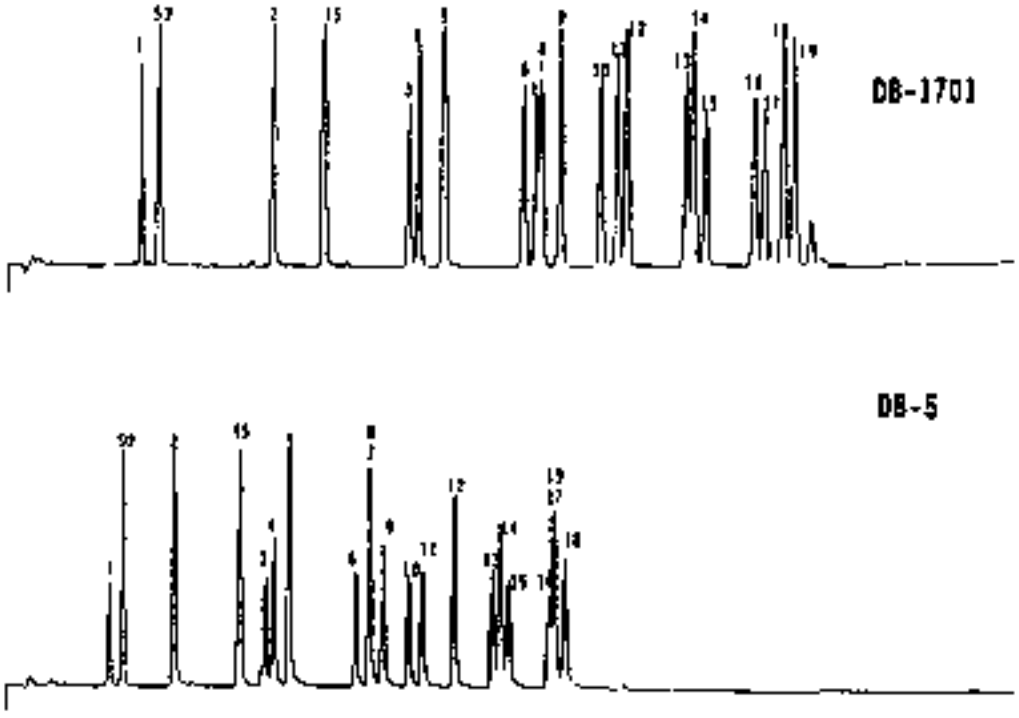
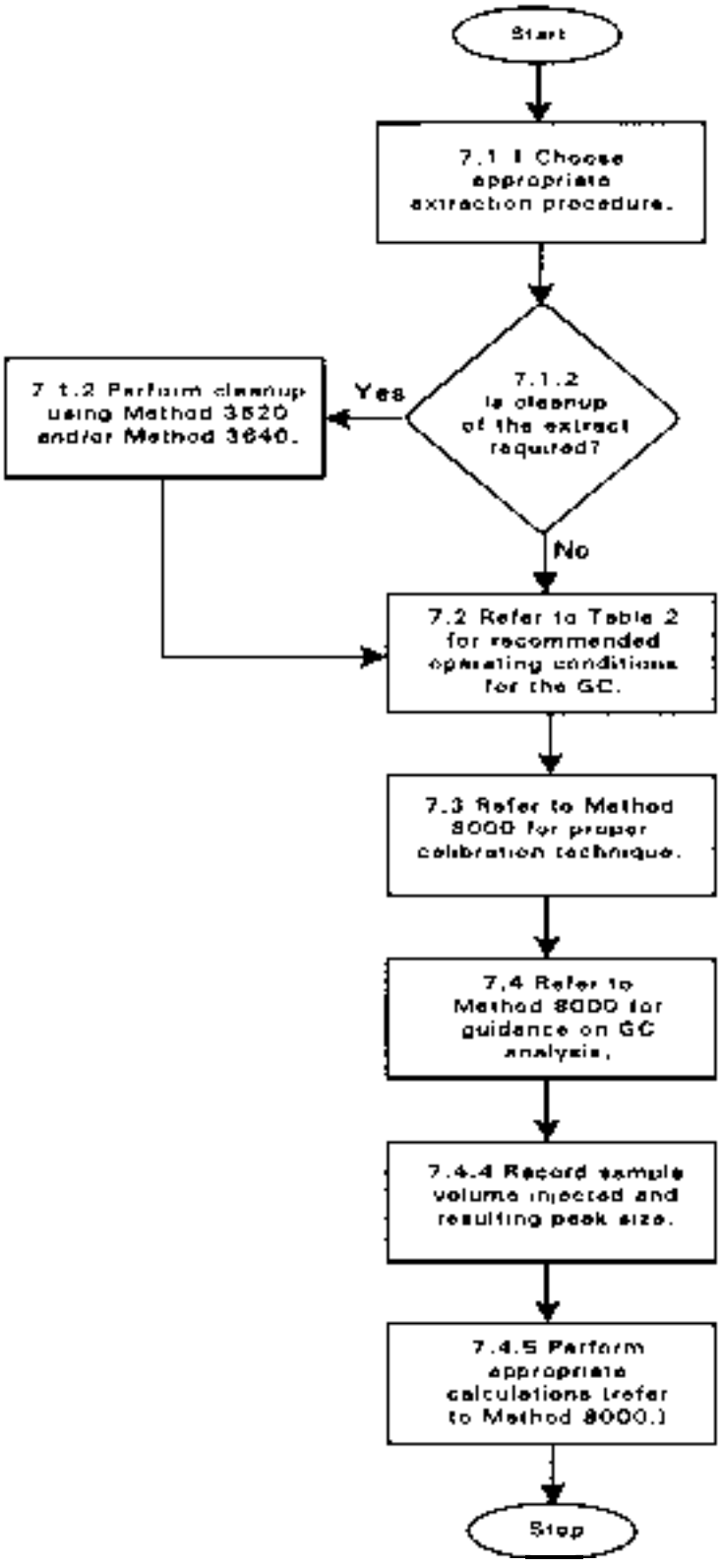


FIGURE 2

GC/ECD CHROMATOGRAM OF HALOETHERS ANALYZED ON A
DB-5/DB-1701 FUSED-SILICA OPEN-TUBULAR COLUMN PAIR

The GC operating conditions are listed in Table 2.




Start
7.1 Choose appropriate extraction procedure.
7.1.2 Is cleanup of the extract required?
Yes
7.1.2 Perform cleanup using Method 3620 and/or Method 3640.
No
7.2 Refer to Table 2 for recommended operating conditions for the GC.
7.3 Refer to Method 8000 for proper calibration technique.
7.4 Refer to Method 8000 for guidance on GC analysis.
7.4.4 Record sample volume injected and resulting peak size.
7.4.5 Perform appropriate calculations (refer to Method 8000.)
Stop