METHOD 8110

HALOETHERS BY GAS CHROMATOGRAPHY

## 1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of certain haloethers. The following compounds can be determined by this method:

| | | Appropriate Technique | | | | |
|---|---|---|---|---|---|---|
| Compound Name | CAS No.[a] | 3510 | 3520 | 3540 | 3550 | 3580 |
| Bis(2-chloroethoxy)methane | 111-91-1 | X | X | X | X | X |
| Bis(2-chloroethyl) ether | 111-44-4 | X | X | X | X | X |
| Bis(2-chloroisopropyl) ether | 108-60-1 | X | X | X | X | X |
| 4-Bromophenyl phenyl ether | 101-55-3 | X | X | X | X | X |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | X | X | X | X | X |

[a] Chemical Abstract Services Registry Number.
X Greater than 70 percent recovery by this technique.

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions of a second GC column that can be used to confirm measurements made with the primary column. Method 8270 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract from this method.

1.3 The method detection limit (MDL, defined in Section 9.1) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from that listed, depending upon the nature of interferences in the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

1.5 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified

in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified.

## 2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. GC conditions are described which permit the separation and measurement of the compounds in the extract using a halide specific detector.

2.2 Method 8110 provides gas chromatographic conditions for the detection of ppb concentrations of haloethers. 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) using the solvent flush technique, and compounds in the GC effluent are detected by an electrolytic conductivity detector (HECD).

## 3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 7.3 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

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 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. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

## 4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - An analytical system complete with temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical

columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

4.1.2 Columns

4.1.2.1 Column 1 - 1.8 m x 2 mm ID pyrex glass, packed with Supelcoport, (100/120 mesh) coated with 3% SP-1000 or equivalent. This column was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate column packings are provided in Section 7.3.1.

4.1.2.2 Column 2 - 1.8 m x 2 mm ID pyrex glass, packed with 2,6-diphenylene oxide polymer (Tenax-GC 60/80 mesh) or equivalent.

4.1.3 Detector - Electrolytic conductivity or microcoulometric. These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope of this method. The Hall conductivity detector (HECD) was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate detectors are provided in Section 7.3.1. Although less selective, an electron capture detector (ECD) is an acceptable alternative.

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-570001-0500 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 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Vials - Amber glass, 10 to 15 mL capacity, with Teflon lined screw-cap or crimp top.

4.4 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Balance - Analytical, 0.0001 g.

4.7 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

## 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic 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 Acetone, $CH_3COCH_3$ - Pesticide quality or equivalent.

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

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

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

5.6.1 Prepare stock standard solutions by accurately weighing 0.1000 ± 0.0010 g of pure material. Dissolve the material in pesticide quality acetone and dilute to volume in a 100 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 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.

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

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

5.7 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared through dilution of the stock standards with isooctane. 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.

5.8 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.

5.8.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.7.

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

5.8.3 Analyze each calibration standard according to Section 7.0.

5.9 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 reagent blank with one or two surrogates (e.g. haloethers 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, Section 4.1. Extracts must be stored at 4°C 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 Method 3540 or 3550.

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.

7.1.2 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 Section 7.1.2.3. If cleanup is needed, proceed to Section 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 Teflon lined screw-cap vial. 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 either Method 3610 or 3620.

7.2 Cleanup

7.2.1 Proceed with Method 3620, using the 2 mL hexane extracts obtained from Section 7.1.2.5.

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

7.3 Gas Chromatography Conditions

7.3.1 Table 1 summarizes the recommended operating conditions for

the gas chromatograph. This table includes retention times and MDLs that were obtained under these conditions. Examples of the parameter separations achieved by these columns are shown in Figures 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

7.4 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.

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

7.4.2 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 confirm elution patterns and the absence of interferents from the reagents.

7.5 Gas chromatographic analysis

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

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

7.5.3 Examples of GC/HECD chromatograms for haloethers are shown in Figures 1 and 2.

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

7.5.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Method 8000 for calculation equations.

7.5.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

## 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, Section 8.6.

8.2.1 The quality control (QC) reference sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at 20 mg/L.

8.2.2 Table 1 indicates the recommended operating conditions, retention times, and MDLs that were obtained under these conditions. Table 2 gives method accuracy and precision 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, Section 8.10).

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

- Check to be sure that 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 This method has been tested for linearity of recovery from spiked organic-free reagent water and has been demonstrated to be applicable for the concentration range from 4 x MDL to 1000 x MDL.

9.2 In a single laboratory (Monsanto Research Center), using spiked wastewater samples, the average recoveries presented in Table 2 were obtained. Each spiked sample was analyzed in triplicate on three separate occasions. The standard deviation of the percent recovery is also included in Table 2.

## 10.0 REFERENCES


1. Fed. Regist. 1984, 49, 43234; October 26.
2. Mills, P.A. "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns"; Journal of the Association of Official Analytical Chemists 1968, 51, 29.
3. Handbook of Analytical Quality Control in Water and Wastewater Laboratories; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1979; EPA-600/4-79-019.

4. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

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

6. "EPA Method Validation Study 21 Methods 611 (Haloethers)," Report for EPA Contract 68-03-2633.

7. "Determination of Haloethers in Industrial and Municipal Wastewaters"; Report for EPA Contract 68-03-2633 (In preparation).

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

| Analyte | Retention Time (minutes) Column 1 | Column 2 | Method Detection Limit (µg/L) |
|---|---|---|---|
| Bis(2-chloroisopropyl) ether | 8.4 | 9.7 | 0.8 |
| Bis(2-chloroethyl) ether | 9.4 | 9.1 | 0.3 |
| Bis(2-chloroethoxy)methane | 13.1 | 10.0 | 0.5 |
| 4-Chlorophenyl phenyl ether | 19.4 | 15.0 | 3.9 |
| 4-Bromophenyl phenyl ether | 21.2 | 16.2 | 2.3 |

Column 1 conditions:
- Carrier gas (He) flow rate: 40 mL/min
- Initial temperature: 60°C, hold for 2 minutes
- Temperature program: 60°C to 230°C at 8°C/min
- Final temperature: 230°C, hold for 4 minutes

Under these conditions the retention time for aldrin is 22.6 minutes.

Column 2 conditions:
- Carrier gas (He) flow rate: 40 mL/min
- Initial temperature: 150°C, hold for 4 minutes
- Temperature program: 150°C to 310°C at 16°C/min
- Final temperature: 310°C

Under these conditions the retention time for aldrin is 18.4 minutes.

TABLE 2.
SINGLE OPERATOR ACCURACY AND PRECISION

| Analyte | Average Percent Recovery | Standard Deviation % | Spike Range (µg/L) | Number of Analyses | Matrix Types |
|---|---|---|---|---|---|
| Bis(2-chloroethoxy)methane | 62 | 5.3 | 138 | 27 | 3 |
| Bis(2-chloroethyl) ether | 59 | 4.5 | 97 | 27 | 3 |
| Bis(2-chloroisopropyl) ether | 67 | 4.0 | 54 | 27 | 3 |
| 4-Bromophenyl phenyl ether | 78 | 3.5 | 14 | 27 | 3 |
| 4-Chlorophenyl phenyl ether | 73 | 4.5 | 30 | 27 | 3 |

FIGURE 1.
GAS CHROMATOGRAM OF HALOETHERS

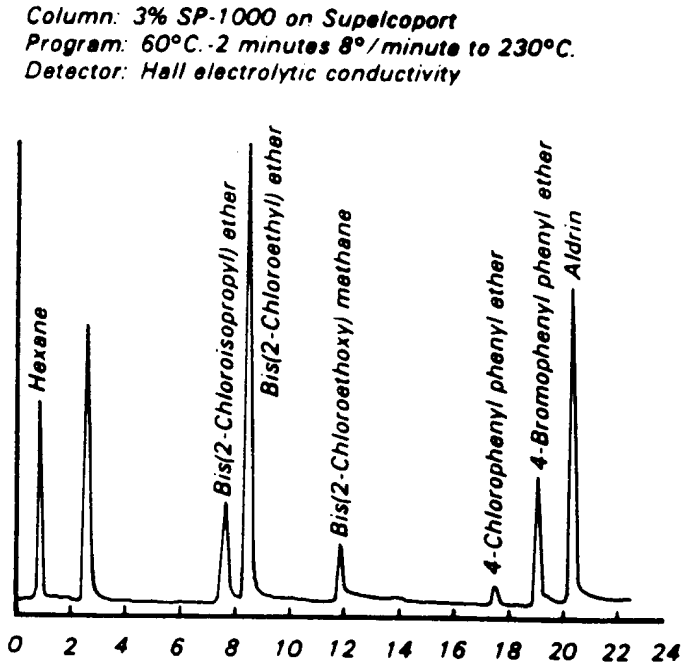
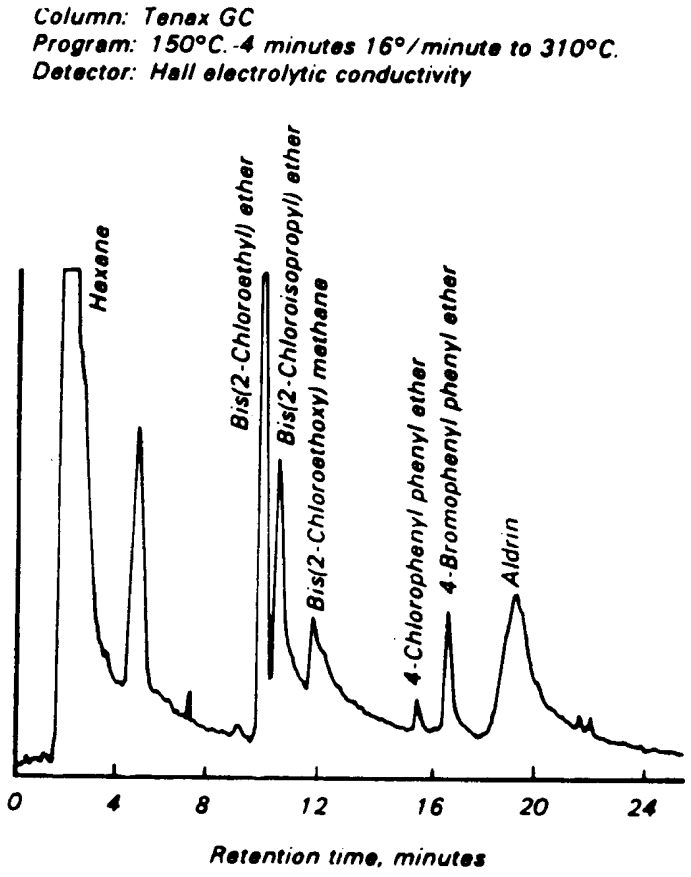
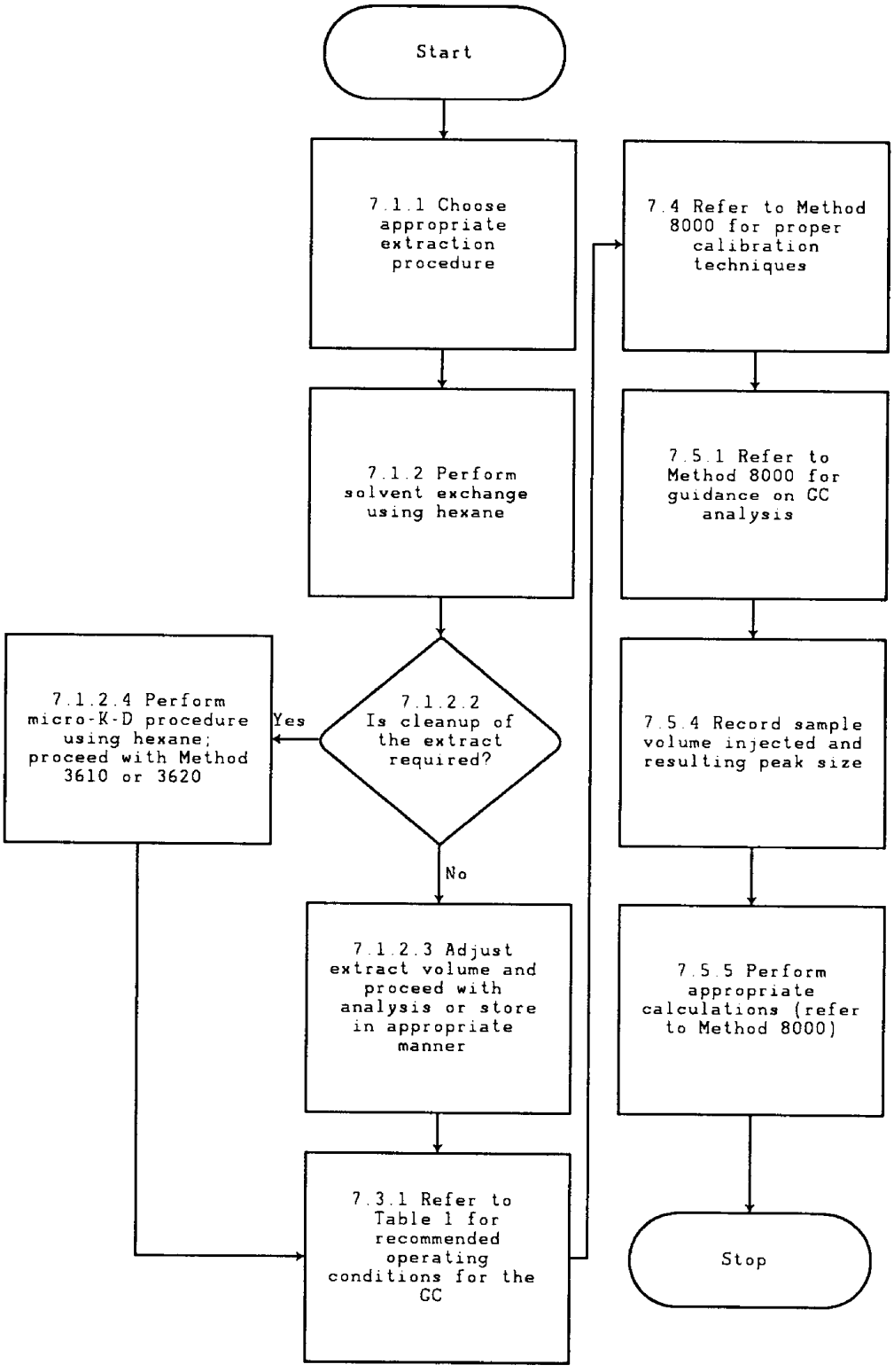


FIGURE 2.
GAS CHROMATOGRAM OF HALOETHERS




Start
7.1.1 Choose appropriate extraction procedure
7.1.2 Perform solvent exchange using hexane
7.1.2.2 Is cleanup of the extract required?
Yes
7.1.2.4 Perform micro-K-D procedure using hexane; proceed with Method 3610 or 3620
No
7.1.2.3 Adjust extract volume and proceed with analysis or store in appropriate manner
7.3.1 Refer to Table 1 for recommended operating conditions for the GC
7.4 Refer to Method 8000 for proper calibration techniques
7.5.1 Refer to Method 8000 for guidance on GC analysis
7.5.4 Record sample volume injected and resulting peak size
7.5.5 Perform appropriate calculations (refer to Method 8000)
Stop