# HALOGENATED VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

## 1.0 SCOPE AND APPLICATION

1.1 Method 8010 is used to determine the concentration of various volatile halogenated organic compounds. The following compounds can be determined by this method:

| Compound Name | CAS No.[a] | Appropriate Technique | |
|---|---|---|---|
| | | Purge-and-Trap | Direct Injection |
| Allyl chloride | 107-05-1 | b | b |
| Benzyl chloride | 100-44-7 | pp | b |
| Bis(2-chloroethoxy)methane | 111-91-1 | pp | pc |
| Bis(2-chloroisopropyl)ether | 39638-32-9 | b | b |
| Bromoacetone | 598-31-2 | pp | b |
| Bromobenzene | 108-86-1 | b | b |
| Bromodichloromethane | 75-27-4 | b | b |
| Bromoform | 75-25-2 | b | b |
| Bromomethane | 74-83-9 | b | b |
| Carbon tetrachloride | 56-23-5 | b | b |
| Chlorobenzene | 108-90-7 | b | b |
| Chloroethane | 75-00-3 | b | b |
| 2-Chloroethanol | 107-07-03 | pp | b |
| 2-Chloroethyl vinyl ether | 110-75-8 | b | b |
| Chloroform | 67-66-3 | b | b |
| 1-Chlorohexane | 544-10-5 | pc | pc |
| Chloromethane | 74-87-3 | b | b |
| Chloromethyl methyl ether | 107-30-2 | pp | pc |
| Chloroprene | 126-99-8 | b | b |
| 4-Chlorotoluene | 106-43-4 | b | b |
| Dibromochloromethane | 124-48-1 | b | b |
| 1,2-Dibromo-3-chloropropane | 96-12-8 | b | b |
| Dibromomethane | 74-95-3 | b | b |
| 1,2-Dichlorobenzene | 95-50-1 | b | b |
| 1,3-Dichlorobenzene | 541-73-1 | b | b |
| 1,4-Dichlorobenzene | 106-46-7 | b | b |
| 1,4-Dichloro-2-butene | 764-41-0 | b | b |
| Dichlorodifluoromethane | 75-71-8 | b | b |
| 1,1-Dichloroethane | 75-34-3 | b | b |
| 1,2-Dichloroethane | 107-06-2 | b | b |
| 1,1-Dichloroethene | 75-35-4 | b | b |
| trans-1,2-Dichloroethene | 156-60-5 | b | b |
| Dichloromethane | 75-09-2 | b | b |
| 1,2-Dichloropropane | 78-87-5 | b | b |
| 1,3-Dichloro-2-propanol | 96-23-1 | pp | b |
| cis-1,3-Dichloropropene | 10061-01-5 | b | b |
| trans-1,3-Dichloropropene | 10061-02-6 | b | b |
| Epichlorhydrin | 106-89-8 | pp | b |

| Compound Name | CAS No.[a] | Appropriate Technique | |
|---|---|---|---|
| | | Purge-and-Trap | Direct Injection |
| Ethylene dibromide | 106-93-4 | b | b |
| Methyl iodide | 74-88-4 | pp | b |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | b | b |
| 1,1,1,2-Tetrachloroethane | 630-20-6 | b | b |
| Tetrachloroethene | 127-18-4 | b | b |
| 1,1,1-Trichloroethane | 71-55-6 | b | b |
| 1,1,2-Trichloroethane | 79-00-5 | b | b |
| Trichloroethene | 79-01-6 | b | b |
| Trichlorofluoromethane | 75-69-4 | b | b |
| 1,2,3-Trichloropropane | 96-18-4 | b | b |
| Vinyl Chloride | 75-01-4 | b | b |

a Chemical Abstract Services Registry Number
b Adequate response using this technique
pp Poor purging efficiency, resulting in high EQLs
pc Poor chromatographic performance.

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

## 2.0 SUMMARY OF METHOD

2.1 Method 8010 provides gas chromatographic conditions for the detection of halogenated volatile organic compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a electrolytic conductivity detector (HECD).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

## 3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

## 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 or purge-and-trap sample introduction and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 8 ft x 0.1 in. ID stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in. ID stainless steel or glass column packed with chemically bonded n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 Detector - Electrolytic conductivity (HECD).

4.2 Sample introduction apparatus, refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes, 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A, Appropriate sizes with ground glass stoppers.

4.5 Microsyringe, 10 and 25 µL with a 0.006 in. ID needle (Hamilton 702N or equivalent) and a 100 µL.

4.6 Analytical balance - 0.0001 g.

## 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 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 Methanol, $CH_3OH$. Pesticide quality or equivalent. Store away from other solvents.

5.4 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.4.2 Add the assayed reference material, as described below.

5.4.2.1 Liquids. Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.2.2 Gases. To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.4.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.4.5 Prepare fresh stock standards for gases weekly or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 20% drift.

5.4.6 Optionally calibration using a certified gaseous mixture can be accomplished daily utilizing commercially available gaseous analyte

mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. These mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.5 Secondary dilution standards. Using stock standard solutions, prepare secondary dilution standards in methanol, as needed, containing the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 5.6 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Calibration standards. Prepare calibration standards in organic-free reagent water from the secondary dilution of the stock standards, at a minimum of five concentrations. 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 the concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.6.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.6.2 Use a 25 µL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.6.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.6.4 Mix aqueous standards by inverting the flask three times only.

5.6.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.6.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.6.7 Aqueous standards are not stable and should be discarded after one hour, unless properly sealed and stored. The aqueous standards can be stored up to 24 hours, if held in sealed vials with zero headspace.

5.7 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. The compounds recommended for use as surrogate spikes (Sec. 5.8) have been used successfully as internal standards, because of their generally unique retention times.

5.7.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Sec. 5.6.

5.7.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Secs. 5.4 and 5.5. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ng/µL of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

5.7.3 Analyze each calibration standard according to Sec. 7.0, adding 10 µL of internal standard spiking solution directly to the syringe.

5.8 Surrogate standards - The analyst should monitor both the performance of the 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 surrogate halocarbons. A combination of bromochloromethane, bromochlorobenzene and bromofluorobenzene is recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Sec. 5.4, add a volume to give 750 µg of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Sec. 5.7.2).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

## 7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph using either direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1:

Helium flow rate = 40 mL/min

Temperature program:

| | |
|---|---|
| Initial temperature = | 45°C, hold for 3 minutes |
| Program = | 45°C to 220°C at 8°C/min |
| Final temperature = | 220°C, hold for 15 minutes. |

7.2.2 Column 2:

Helium flow rate = 40 mL/min
Temperature program:

| | |
|---|---|
| Initial temperature = | 50°C, hold for 3 minutes |
| Program = | 50°C to 170°C at 6°C/min |
| Final temperature = | 170°C, hold for 4 minutes. |

7.3 Calibration. The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 and Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Sec. 7.4.1).

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap) or the direct injection method (see Sec. 7.4.1.1). If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 In very limited applications (e.g. aqueous process wastes) direct injection of the sample onto the GC column with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L) therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

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 Table 1 summarizes the estimated retention times on the two columns for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

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

7.4.5 Refer to Method 8000 for guidance on calculation of concentration.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each analyte of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria, for water samples, for this method. Table 4 gives method accuracy and precision as functions of concentration, for water samples, 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 recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

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 re-analyze the sample if any of the above checks reveal a problem.

- Re-extract and re-analyze 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 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 8.0-500 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte, and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

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

9.3 The method detection limits reported in Table 1 were generated under optimum analytical conditions by an Agency contractor (Ref. 6) as guidance, and may not be readily achievable by all laboratories at all times.

## 10.0 REFERENCES


1. Bellar, T.A.; Lichtenberg, J.J. J. Amer. Water Works Assoc. 1974, 66(12), pp. 739-744.

2. Bellar, T.A.; Lichtenberg, J.J., Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, Measurement of Organic Pollutants in Water and Wastewater; Van Hall, Ed.; ASTM STP 686, pp 108-129, 1979.

3. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane"; report for EPA Contract 68-03-2635.

4. 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.

5. "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)"; report for EPA Contract 68-03-2856.

6. Gebhart, J.E., S.V. Lucas, S.J. Naber, A.M. Berry, T.H. Danison and H.M. Burkholder, "Validation of SW-846 Methods 8010, 8015, and 8020"; Report for EPA Contract 68-03-1760, Work Assignment 2-15; US EPA, EMSL-Cincinnati, 1987.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
FOR HALOGENATED VOLATILE ORGANICS

| Compound | CAS Registry Number | Retention Time (minutes) Column 1 | Retention Time (minutes) Column 2 | Method Detection Limit[a] (µg/L) |
|---|---|---|---|---|
| Allyl chloride* | 107-05-1 | 10.17 | (b) | (b) |
| Benzyl chloride*,[c] | 100-44-7 | 30.29 | (b) | (b) |
| Bis(2-chloroethoxy)methane* | 111-91-1 | 38.60 | (b) | (b) |
| Bis(2-chloroisopropyl)ether* | 39638-32-9 | 34.79 | (b) | (b) |
| Bromobenzene | 108-86-1 | 29.05 | (b) | (b) |
| Bromodichloromethane | 75-27-4 | 15.44 | 14.62 | 0.002 |
| Bromoform* | 75-25-2 | 21.12 | 19.17 | 0.020 |
| Bromomethane* | 74-83-9 | 2.90 | 7.05 | 0.030 |
| Carbon tetrachloride* | 56-23-5 | 14.58 | 11.07 | 0.003 |
| Chloroacetaldehyde* | 107-20-0 | (b) | (b) | (b) |
| Chlorobenzene* | 108-90-7 | 25.49 | 18.83 | 0.001 |
| Chloroethane | 75-00-3 | 5.18 | 8.68 | 0.008 |
| Chloroform* | 67-66-3 | 12.62 | 12.08 | 0.002 |
| 1-Chlorohexane | 544-10-5 | 26.26 | (b) | (b) |
| 2-Chloroethyl vinyl ether* | 110-75-8 | 19.23 | (b) | 0.130 |
| Chloromethane* | 74-87-3 | 1.40 | 5.28 | 0.010 |
| Chloromethyl methyl ether* | 107-30-2 | 8.88 | (b) | (b) |
| 4-Chlorotoluene | 106-43-4 | 34.46 | (b) | (b) |
| Dibromochloromethane | 124-48-1 | 18.22 | 16.62 | (b) |
| 1,2-Dibromo-3-chloropropane* | 96-12-8 | 28.09 | (b) | 0.030 |
| Dibromomethane* | 74-95-3 | 13.83 | 14.92 | (b) |
| 1,2-Dichlorobenzene* | 95-50-1 | 37.96 | 23.52 | (b) |
| 1,3-Dichlorobenzene* | 541-73-1 | 36.88 | 22.43 | (b) |
| 1,4-Dichlorobenzene* | 106-46-7 | 38.64 | 22.33 | (b) |
| 1,4-Dichloro-2-butene* | 764-41-0 | 23.45 | (b) | (b) |
| Dichlorodifluoromethane*,[d] | 75-71-8 | 3.68 | (b) | (b) |
| 1,1-Dichloroethane* | 75-34-3 | 11.21 | 12.57 | 0.002 |
| 1,2-Dichloroethane* | 107-06-2 | 13.14 | 15.35 | 0.002 |
| 1,1-Dichloroethene* | 75-35-4 | 10.04 | 7.72 | 0.003 |
| trans-1,2-Dichloroethene* | 156-60-5 | 11.97 | 9.38 | 0.002 |
| Dichloromethane* | 75-09-2 | 7.56 | 10.12 | (b) |
| 1,2-Dichloropropane* | 78-87-5 | 16.69 | 16.62 | (b) |
| trans-1,3-Dichloropropene* | 10061-02-5 | 16.97[e] | 16.60 | 0.340 |
| Ethylene dibromide* | 106-93-4 | 19.59 | (b) | (b) |
| 1,1,2,2-Tetrachloroethane* | 79-34-5 | 23.12 | (b) | 0.010 |
| 1,1,1,2-Tetrachloroethane* | 630-20-6 | 21.10 | 21.70 | (b) |
| Tetrachloroethene* | 127-18-4 | 23.05 | 14.97 | 0.001 |
| 1,1,1-Trichloroethane | 71-55-6 | 14.48 | 13.10 | 0.003 |
| 1,1,2-Trichloroethane* | 79-00-5 | 18.27 | 18.07 | 0.007 |

TABLE 1.
Continued

| Compound | CAS Registry Number | Retention Time (minutes) Column 1 | Retention Time (minutes) Column 2 | Method Detection Limit[a] (µg/L) |
|---|---|---|---|---|
| Trichloroethene* | 79-01-6 | 17.40 | 13.12 | 0.001 |
| Trichlorofluoromethane* | 75-69-4 | 9.26 | (b) | (b) |
| 1,2,3-Trichloropropane* | 96-18-4 | 22.95 | (b) | (b) |
| Vinyl Chloride* | 75-01-4 | 3.25 | 5.28 | 0.006 |

a = Using purge-and-trap method (Method 5030). See Sec. 9.3.
b = Not determined
* = Appendix VIII compounds
c = Demonstrated very erratic results when tested by purge-and-trap
d = See Sec. 4.10.2 of Method 5030 for guidance on selection of trapping material
e = Estimated retention time

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)
FOR VARIOUS MATRICES[a]

| Matrix | Factor |
|---|---|
| Ground water | 10 |
| Low-concentration soil | 10 |
| Water miscible liquid waste | 500 |
| High-concentration soil and sludge | 1250 |
| Non-water miscible waste | 1250 |

[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 listed herein are provided for guidance and may not always be achievable.

TABLE 3.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

| Analyte | Range for Q (µg/L) | Limit for S (µg/L) | Range for $\bar{x}$ (µg/L) | Range P, $P_s$ (%) |
|---|---|---|---|---|
| Bromodichloromethane | 15.2-24.8 | 4.3 | 10.7-32.0 | 42-172 |
| Bromoform | 14.7-25.3 | 4.7 | 5.0-29.3 | 13-159 |
| Bromomethane | 11.7-28.3 | 7.6 | 3.4-24.5 | D-144 |
| Carbon tetrachloride | 13.7-26.3 | 5.6 | 11.8-25.3 | 43-143 |
| Chlorobenzene | 14.4-25.6 | 5.0 | 10.2-27.4 | 38-150 |
| Chloroethane | 15.4-24.6 | 4.4 | 11.3-25.2 | 46-137 |
| 2-Chloroethylvinyl ether | 12.0-28.0 | 8.3 | 4.5-35.5 | 14-186 |
| Chloroform | 15.0-25.0 | 4.5 | 12.4-24.0 | 49-133 |
| Chloromethane | 11.9-28.1 | 7.4 | D-34.9 | D-193 |
| Dibromochloromethane | 13.1-26.9 | 6.3 | 7.9-35.1 | 24-191 |
| 1,2-Dichlorobenzene | 14.0-26.0 | 5.5 | 1.7-38.9 | D-208 |
| 1,3-Dichlorobenzene | 9.9-30.1 | 9.1 | 6.2-32.6 | 7-187 |
| 1,4-Dichlorobenzene | 13.9-26.1 | 5.5 | 11.5-25.5 | 42-143 |
| 1,1-Dichloroethane | 16.8-23.2 | 3.2 | 11.2-24.6 | 47-132 |
| 1,2-Dichloroethane | 14.3-25.7 | 5.2 | 13.0-26.5 | 51-147 |
| 1,1-Dichloroethene | 12.6-27.4 | 6.6 | 10.2-27.3 | 28-167 |
| trans-1,2-Dichloroethene | 12.8-27.2 | 6.4 | 11.4-27.1 | 38-155 |
| Dichloromethane | 15.5-24.5 | 4.0 | 7.0-27.6 | 25-162 |
| 1,2-Dichloropropane | 14.8-25.2 | 5.2 | 10.1-29.9 | 44-156 |
| cis-1,3-Dichloropropene | 12.8-27.2 | 7.3 | 6.2-33.8 | 22-178 |
| trans-1,3-Dichloropropene | 12.8-27.2 | 7.3 | 6.2-33.8 | 22-178 |
| 1,1,2,2-Tetrachloroethane | 9.8-30.2 | 9.2 | 6.6-31.8 | 8-184 |
| Tetrachloroethene | 14.0-26.0 | 5.4 | 8.1-29.6 | 26-162 |
| 1,1,1-Trichloroethane | 14.2-25.8 | 4.9 | 10.8-24.8 | 41-138 |
| 1,1,2-Trichloroethane | 15.7-24.3 | 3.9 | 9.6-25.4 | 39-136 |
| Trichloroethene | 15.4-24.6 | 4.2 | 9.2-26.6 | 35-146 |
| Trichlorofluoromethane | 13.3-26.7 | 6.0 | 7.4-28.1 | 21-156 |
| Vinyl chloride | 13.7-26.3 | 5.7 | 8.2-29.9 | 28-163 |

Q = Concentration measured in QC check sample, in µg/L.

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 601 and were calculated assuming a QC check sample concentration of 20 µg/L.

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

| Analyte | Accuracy, as recovery, x' (µg/L) | Single analyst precision, $s_r$' (µg/L) | Overall precision, S' (µg/L) |
|---|---|---|---|
| Bromodichloromethane | 1.12C-1.02 | 0.11X+0.04 | 0.20X+1.00 |
| Bromoform | 0.96C-2.05 | 0.12X+0.58 | 0.21X+2.41 |
| Bromomethane | 0.76C-1.27 | 0.28X+0.27 | 0.36X+0.94 |
| Carbon tetrachloride | 0.98C-1.04 | 0.15X+0.38 | 0.20X+0.39 |
| Chlorobenzene | 1.00C-1.23 | 0.15X-0.02 | 0.18X+1.21 |
| Chloroethane | 0.99C-1.53 | 0.14X-0.13 | 0.17X+0.63 |
| 2-Chloroethyl vinyl ether[b] | 1.00C | 0.20X | 0.35X |
| Chloroform | 0.93C-0.39 | 0.13X+0.15 | 0.19X-0.02 |
| Chloromethane | 0.77C+0.18 | 0.28X-0.31 | 0.52X+1.31 |
| Dibromochloromethane | 0.94C+2.72 | 0.11X+1.10 | 0.24X+1.68 |
| 1,2-Dichlorobenzene | 0.93C+1.70 | 0.20X+0.97 | 0.13X+6.13 |
| 1,3-Dichlorobenzene | 0.95C+0.43 | 0.14X+2.33 | 0.26X+2.34 |
| 1,4-Dichlorobenzene | 0.93C-0.09 | 0.15X+0.29 | 0.20X+0.41 |
| 1,1-Dichloroethane | 0.95C-1.08 | 0.08X+0.17 | 0.14X+0.94 |
| 1,2-Dichloroethane | 1.04C-1.06 | 0.11X+0.70 | 0.15X+0.94 |
| 1,1-Dichloroethene | 0.98C-0.87 | 0.21X-0.23 | 0.29X-0.04 |
| trans-1,2-Dichloroethene | 0.97C-0.16 | 0.11X+1.46 | 0.17X+1.46 |
| Dichloromethane | 0.91C-0.93 | 0.11X+0.33 | 0.21X+1.43 |
| 1,2-Dichloropropane[b] | 1.00C | 0.13X | 0.23X |
| cis-1,3-Dichloropropene[b] | 1.00C | 0.18X | 0.32X |
| trans-1,3-Dichloropropene[b] | 1.00C | 0.18X | 0.32X |
| 1,1,2,2-Tetrachloroethane | 0.95C+0.19 | 0.14X+2.41 | 0.23X+2.79 |
| Tetrachloroethene | 0.94C+0.06 | 0.14X+0.38 | 0.18X+2.21 |
| 1,1,1-Trichloroethane | 0.90C-0.16 | 0.15X+0.04 | 0.20X+0.37 |
| 1,1,2-Trichloroethane | 0.86C+0.30 | 0.13X-0.14 | 0.19X+0.67 |
| Trichloroethene | 0.87C+0.48 | 0.13X-0.03 | 0.23X+0.30 |
| Trichlorofluoromethane | 0.89C-0.07 | 0.15X+0.67 | 0.26X+0.91 |
| Vinyl chloride | 0.97C-0.36 | 0.13X+0.65 | 0.27X+0.40 |

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.

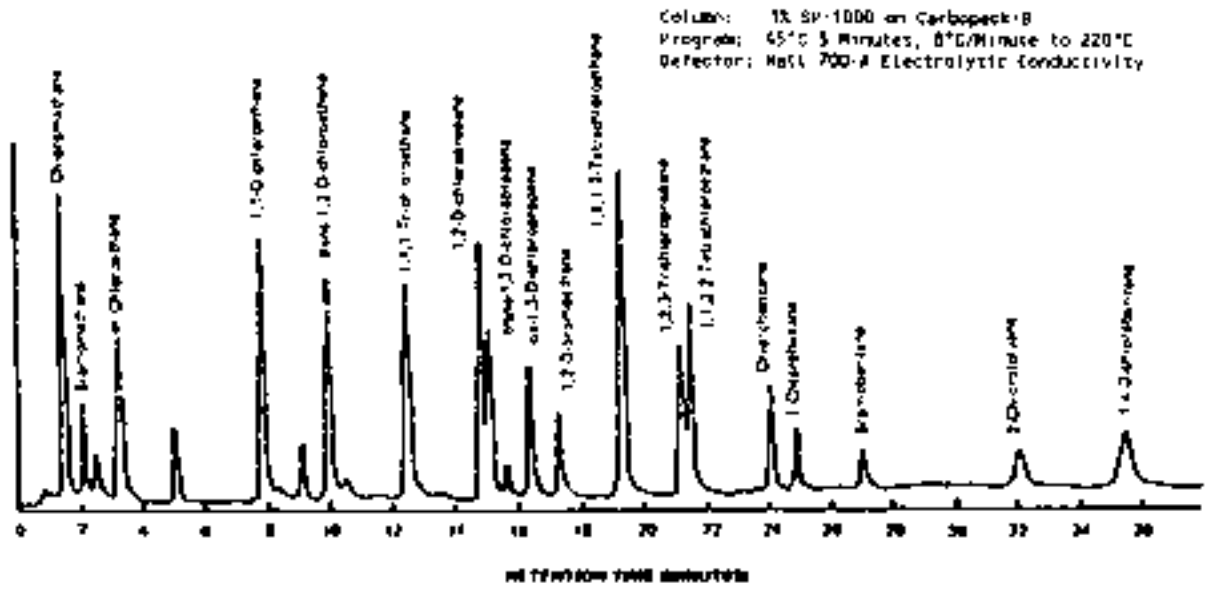
C = True value for the concentration, in µg/L.

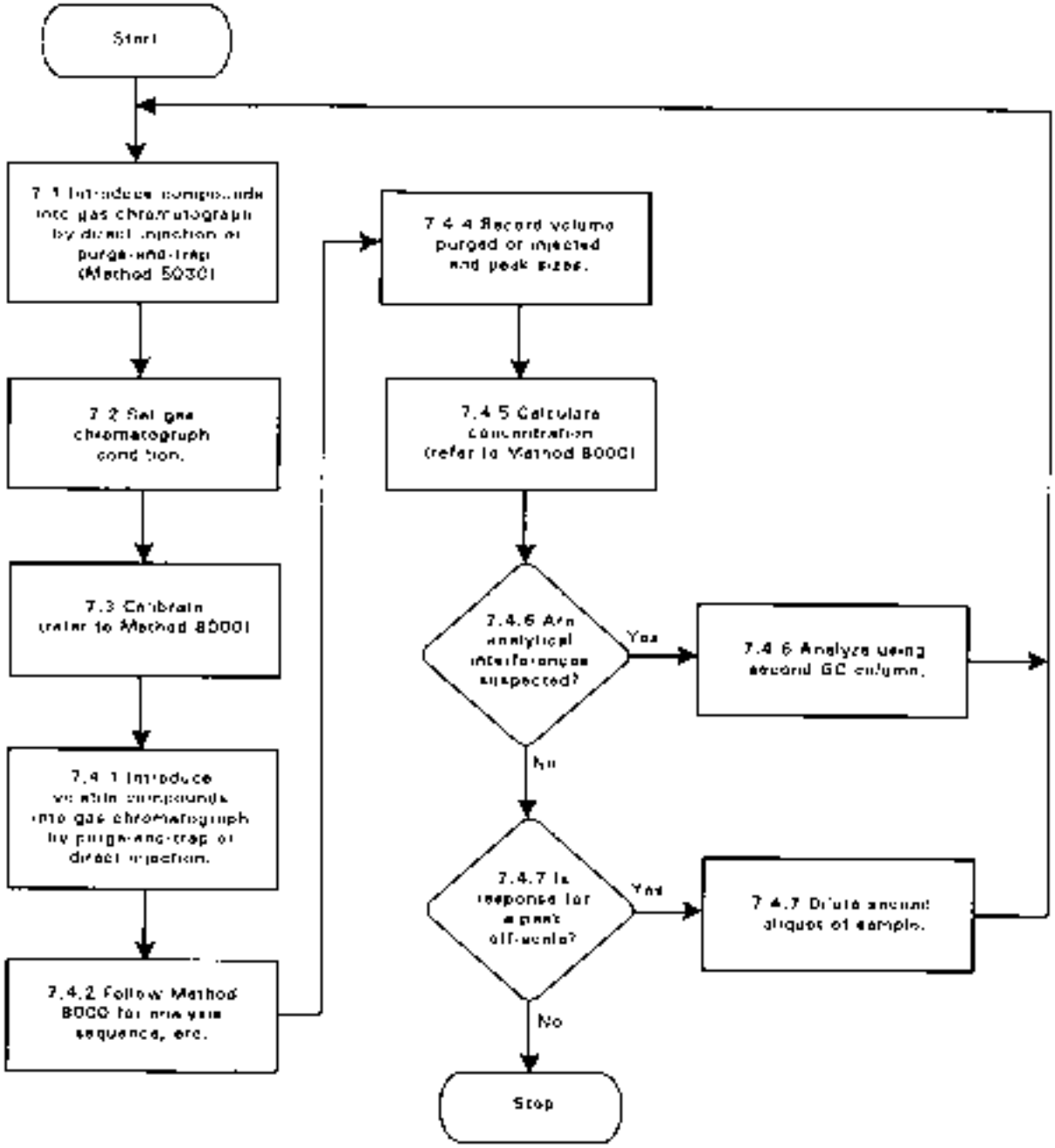
X = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

[a] From 40 CFR Part 136 for Method 601.

[b] Estimates based upon the performance in a single laboratory.

FIGURE 1.
GAS CHROMATOGRAM OF HALOGENATED VOLATILE ORGANICS




Start
7.1 Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
7.2 Set gas chromatograph condition.
7.3 Calibrate (refer to Method 8000)
7.4.1 Introduce volatile compounds into gas chromatograph by purge-and-trap or direct injection.
7.4.2 Follow Method 8000 for analysis sequence, etc.
7.4.4 Record volume purged or injected and peak sizes.
7.4.5 Calculate concentration (refer to Method 8000)
7.4.6 Are analytical interferences suspected?
Yes
7.4.6 Analyze using second GC column.
No
7.4.7 Is response for a given off-scale?
Yes
7.4.7 Dilute another aliquot of sample.
No
Stop