METHODS FOR THE DETERMINATION OF ORGANIC COMPOUNDS IN FINISHED DRINKING WATER AND RAW SOURCE WATER

September 1986

PHYSICAL AND CHEMICAL METHODS BRANCH
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

Under authority of the Safe Drinking Water Act and the National Interim Primary Drinking Water Regulations, the U. S. Environmental Protection Agency establishes test procedures for monitoring contaminants in public water supplies. The test procedures in this document are designed to measure volatile organic compounds in such waters prior to or after final treatment.

Robert L. Booth, Director
Environmental Monitoring and Support Laboratory

ABSTRACT

The methods contained in this report describe the requirements for the analysis of drinking water and raw source water for 58 volatile organic compounds. The methods were prepared to be used for monitoring for volatile synthetic organic compounds (VOC) at low concentrations in such matrices, as proposed in 40 CFR 141.24. The methods may also be used for the proposed monitoring requirement for unregulated contaminants in 40 CFR 141.40. Included are sample collection and preservation procedures, instructions for preparation of standards, required operating conditions and quality control requirements.

PREFACE

On November 13, 1985, the U.S. Environmental Protection Agency published (50 FR 46902) proposed National Drinking Water Regulations for eight volatile synthetic organic chemicals (VOCs) and proposed monitoring requirements for these eight VOCs, tetrachloroethene and 51 other volatile compounds. Three methods in this report (Methods 502.1, 503.1, and 524.1) were proposed for use for the regulated contaminants and in conjunction with Method 504, for the proposed monitoring requirement.

The Agency is committed to avoid the needless proliferation of methods, however, the evolution of measurement technology and the timing of regulatory actions have resulted in a number of similar methods. To avoid confusion, the following discussion of the relationship of these methods to previous editions is provided.

Method 502.1 is the third generation method for volatile organohalides. It was produced originally as Method 501.1 for the measurement of total trihalomethanes as defined and required in 40 CFR Part 141.30. It was incorporated into 40 CFR Part 141.30 on November 29, 1979. The method was extended and formatted to its current broad scope as Method 502.1 in April 1981 and made available by the Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) to support the recommended maximum contaminant levels (RMCLs) for VOCs proposed on June 12, 1984. This current edition, which replaces the 1981 version of 502.1, focuses on the specific analytes in the VOC MCL and the monitoring proposals. The major changes in the method, reflected in this version, include a strictly prescribed preservation procedure and a maximum holding time for samples. The quality control requirements were modified in 1986 to reflect public comments on the November 1985 proposed rule, and two analytes were removed from the scope of the method. Although the Agency has not at this time proposed the method for approval in Part 141.30, such a proposal is under consideration.

Method 503.1 is a revision of the method prepared in April 1981 and made available by EMSL-Cincinnati to support the RMCL proposal for VOCs. The current revision, which replaces the 1981 version, focuses on the specific analytes in the VOC MCL and monitoring proposals and establishes preservation procedure and maximum holding time for the samples. It, too, has been revised to reflect public comments.

Method 504 was developed to measure low concentrations of 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP). Method 524.1 is a version of the general GC/MS procedure for volatiles described in Method 524 in February 1983, and subsequently approved for trihalomethane measurements. The principal changes incorporated in this method include a focus on the specific analytes in the VOC MCL and monitoring requirement and establishes the preservation procedure and maximum holding time for samples. The quality control section of the method has been revised to reflect public comment and the scope of the method has been reduced to

reflect the limitations of packed-column gas chromatography as defined by conventional practices. Although the Agency has not, at this time, proposed the method for approval in Part 141.30, such a proposal is under consideration.

Method 524.2 is introduced for the first time in this edition. It was developed in direct response to comments on the proposed rules. By approving capillary column techniques as described in this method, the Agency will be recognizing recently achieved technological advances in chromatography that permit separations to be achieved more completely and more rapidly and, thus, at lower cost than those established at the time of proposed rulemaking.

CONTENTS

ACKNOWLEDGMENTS

The methods in this document reflect public comments received on the November 1985 edition proposed on November 13, 1985 to support regulations for the U. S. Environmental Protection Agency's (USEPA) Office of Drinking Water (50 FR 46902). The revisions include one new method (Method 524.2) based upon work by Robert W. Slater, Jr. and Carol A. Madding. The remaining methods have been revised under the direction of an ad-hoc USEPA Work Group composed of the following: James J. Lichtenberg, James E. Longbottom, William L. Budde, Robert L. Graves, Robert W. Slater, Jr., Thomas A. Bellar, Ann Alford-Stevens, and Raymond J. Wesselman, of the Environmental Monitoring and Support Laboratory - Cincinnati; Herbert J. Brass, Robert F. Thomas, David J. Munch, Carol A. Madding, and Kent Sorrell of the Technical Support Division, Office of Drinking Water; and Alan A. Stevens of the Water Engineering Research Laboratory - Cincinnati.

The methods proposed in November 1985, were prepared by the staff of the Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) with the support and cooperation of the Office of Drinking Water, U. S. Environmental Protection Agency, Washington, D. C. Special acknowledgments are due for technical contributions during the preparation of these procedures to the staffs of the Technical Support Division, Office of Drinking Water, and of the Water Engineering Research Laboratory, Office of Research and Development, Cincinnati, Ohio. James E. Longbottom was responsible for preparing the combined methods package which was based upon earlier versions of Methods 502.1, 503.1 developed by Thomas A. Bellar, and Method 524 developed by Ann Alford-Stevens, James W. Eichelberger, and William L. Budde. Method 504 was prepared based upon the work of Theodore W. Winfield and Arnold L. Cohen. Data to support sample preservation and holding times were developed by Thomas A. Bellar, Robert W. Slater, Jr., and Kent Sorrell.

METHOD 502.1. VOLATILE HALOGENATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY (1985, Ed. Rev. 1986)

1. SCOPE AND APPLICATION

1.1 This method is applicable for the determination of various halogenated volatile compounds in finished drinking water, raw source water, or drinking water in any treatment stage. (1) The following compounds can be determined by this method:

Analyte	CAS No.
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-2
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7

Analyte	CAS No.
1,1-Dichloropropene	563-58-6
Methylene chloride	75-09-2
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl chloride	75-01-4

1.2 Single laboratory accuracy and precision data show that this procedure is useful for the detection and measurement of multi-component mixtures spiked into carbon filtered finished water and raw source water at concentrations between 0.20 and 0.40 µg/L with method detection limits (MDL) (2) generally less than 0.01 µg/L. Method detection limits for several of the listed analytes are presented in Table 1 (1). Some laboratories may not be able to achieve these detection limits since results are dependent upon instrument sensitivity and matrix effects. Determination of complex mixtures containing partially resolved compounds may be hampered by concentration differences larger than a factor of 10. This problem commonly occurs when finished drinking waters are analyzed because of the relatively high trihalomethane content. When such samples are analyzed, chloroform will affect the method detection limit for 1,2-dichloroethane.

1.3 Based upon similarities in structure with other analytes in the scope, 2,2-dichloropropane was included in the November 13, 1985 proposed monitoring regulation although supporting accuracy and precision data are not yet available for inclusion in this method.

1.4 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low µg/L level or by experienced technicians under the close supervision of a qualified analyst. It is also recommended for use only with a purge and trap system devoted to the analysis of low level samples.

2. SUMMARY OF METHOD

2.1 Organohalides and other highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with an inert gas to desorb trapped sample components onto a gas chromatography (GC) column. The gas chromatograph is temperature programmed to separate the method analytes which are then detected with a halogen specific detector.

2.2 A second chromatographic column is described that can be used to confirm GC identifications and measurements. Alternatively, confirmatory analyses may be performed by gas chromatography/mass-spectrometry (GC/MS) according to Method 524.1 or Method 524.2 if sufficient material is present.

3. INTERFERENCES

3.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks (Sect. 9.1.3) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst must eliminate the problem before analyzing samples. Subtracting blank values from sample results is not permitted.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, laboratory reagent blanks must be analyzed until system memory is reduced to an acceptable level.

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4. SAFETY

4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as

a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (3-5) for the information of the analyst.

4.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: carbon tetrachloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

5.1 SAMPLE CONTAINERS - 40-mL to 120-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

5.2 PURGE AND TRAP SYSTEM - The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

5.2.1 The all glass purging device (Figure 1) must be designed to accept 5-mL samples with a water column at least 3 cm deep. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point $\leq$ 5 mm from the base of the water column.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are

to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

5.2.3 The desorber must be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Figure 2 meets these criteria.

5.2.4 Figures 3 and 4 show typical flow patterns for the purge-sorb and desorb mode.

5.3 GAS CHROMATOGRAPHY SYSTEM

5.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. The column oven may need to be cooled to <30°C (Sect. 10.3); therefore, a subambient oven controller may be required.

5.3.2 Two gas chromatography columns are recommended. Column 1 is a highly efficient column that provides outstanding separations for a wide variety of organic compounds. Column 1 should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column 2 is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for the listed analytes on the two columns are presented in Table 1.

5.3.2.1 Column 1 - 1.5 to 2.5 m x 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent. The flow rate of the helium carrier gas is established at 40 mL/min. The column temperature is programmed to hold at 45°C for three min, increased to 220°C at 8°C/min, and held at 220°C for 15 min or until all expected compounds have eluted. During handling, packing, and programming, active sites can be exposed on the

Carbopack-B packing which can result in tailing peak geometry and poor resolution of many constituents. To protect the analytical column, pack the first 5 cm of the column with 3% SP-1000 on Chromosorb-W (60/80 mesh) followed by the Carbopack-B packing. Condition the precolumn and the Carbopack columns with carrier gas flow at 220°C overnight. Pneumatic shocks and rough treatment of packed columns will cause excessive fracturing of the Carbopack. If pressure in excess of 60 psi is required to obtain 40 mL/min carrier flow, the column should be repacked. A sample chromatogram obtained with Column 1 is presented in Figure 5.

5.3.2.2 Column 2 - 1.5 to 2.5 m long x 0.1 in ID stainless steel or glass, packed with n-octane chemically bonded on Porisil-C (100/120 mesh) or equivalent. The flow rate of the helium carrier gas is established at 40 mL/min. The column temperature is programmed to hold at 50°C for three min, increased to 170°C at 6°C/min, and held at 170°C for four min or until all expected compounds have eluted.

5.3.3 An electrolytic conductivity or microcoulometric detector is required. These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data shown in Tables 2 and 3. The operating conditions used to collect these data are as follow:

Reactor tube:	Nickel 1/16 in OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40mL/min
Carrier gas:	Helium at 40 mL/min

5.3.4 It is acceptable to insert a photoionization detector between the analytical column and the halide detector to simultaneously analyze for the regulated volatile organic compounds (VOC) that are aromatic or unsaturated (6). Most of the analytes listed in the Scope of Method 503.1 can be determined in this manner.

5.4 SYRINGE AND SYRINGE VALVES

5.4.1 Two 5-mL glass hypodermic syringes with Luer-Lok tip.

5.4.2 Three 2-way syringe valves with Luer ends.

5.4.3 One 25-µL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

5.4.4 Micro syringes - 10, 100 µL.

5.4.5 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

5.5 MISCELLANEOUS

5.5.1 Standard solution storage containers - 15-mL bottles with PTFE-lined screw caps.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 TRAP PACKING MATERIALS

6.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.1.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

6.1.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

6.1.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

6.2 COLUMN PACKING MATERIALS

6.2.1 1% SP-1000 on 60/80 mesh Carbopack-B or equivalent.

6.2.2 n-Octane chemically bonded on Porasil-C, 100/120 mesh (Durapak or equivalent).

6.2.3 3% SP-1000 on 60/80 mesh Chromosorb-W or equivalent.

6.3 REAGENTS

6.3.1 Methanol - demonstrated to be free of analytes.

6.3.2 Reagent water - Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

6.3.3 Hydrochloric acid (1+1) - Carefully add measured volume of conc. HCl to equal volume of reagent water.

6.3.4 Vinyl chloride - 99.9% pure vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm are available from several sources.

6.4 STANDARD STOCK SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

6.4.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

6.4.2 If the analyte is a liquid at room temperature, use a 100-uL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0 mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

6.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

6.4.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day.

6.5 SECONDARY DILUTION STANDARDS - Use standard stock solutions to prepare secondary dilution standard solutions that contain the analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions (Sect. 8.1) that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions for them. Storage times described for stock standard solutions in Sect. 6.4.4 also apply to secondary dilution standard solutions.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Collect all samples in duplicate. Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

7.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

7.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-quart container.

7.2 SAMPLE PRESERVATION

7.2.1 Adjust the pH of the duplicate samples <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume.(7) Seal the sample bottles, PFTE-face down, and shake vigorously for one minute.

7.2.2 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

7.3 SAMPLE STORAGE

7.3.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

7.3.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 CALIBRATION

8.1.1 A set of at least five calibration standards containing the method analytes is needed. More than one set of calibration standards may be required. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other standards should contain analytes at concentrations that define the range of the method.

8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of reagent water in a volumetric container or sample syringe. Use a microsyringe and rapidly inject the alcoholic standard into the water. Remove the needle as quickly as possible after injection. Aqueous standards are not stable and should be discarded after one hour unless sealed and stored as described in Sect. 7.2.2.

8.1.3 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 10 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

8.1.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Sect. 8.1.5.

8.1.5 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in methanol. The single point standards should be prepared at a concentration that produces a response close (±20%) to that of the unknowns.

8.1.6 As a second alternative to a calibration curve, internal standard calibration techniques may be used. The following organohalides are recommended for this purpose: 2-bromo-1-chloropropane or 1,4-dichlorobutane. The internal

standard is added to the sample just before purging. Check the validity of the internal standard calibration factors daily by analyzing a calibration standard.

8.1.7 Calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

8.1.7.1 Fill the purging device with 5.0 mL of reagent water or aqueous calibration standard.

8.1.7.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. Do not inject the standard through the aqueous sample inlet needle. Inject the gaseous standard before five min of the 11-min purge time have elapsed.

8.1.7.3 Determine the aqueous equivalent concentration of vinyl chloride standard injected with the equation:

$$S = 0.51\ (C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in ppm (v/v);
V = Volume of standard injected in milliliters.

8.2 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of reagent blanks, standards, duplicate samples, and the quality control check standard (Sect. 9.3.1).

8.2.1 All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing significantly in excess of that shown in the method chromatogram (Figure 5) must be corrected. Tailing problems are generally traceable to active sites on the GC column or the detector operation. If only the compounds eluting before chloroform give random responses or unusually wide peak widths, are poorly resolved, or are missing, the problem is usually traceable to the trap/desorber. If only brominated compounds show poor peak geometry or do not properly respond

at low concentrations, repack the trap. Excessive detector reactor temperatures can also cause low bromoform response. If negative peaks appear in the chromatogram, replace the ion exchange column and replace the electrolyte in the detector.

8.2.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially around the sample purger and detector reactor inlet and exit, electronic problems, or sampling and storage problems. Monitor the retention times for each organohalide using data generated from calibration standards and the laboratory control standard. If individual retention times vary by more than 10% over an 8-h period or do not fall within 10% of an established norm, the source of retention data variance must be corrected before acceptable data can be generated.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. A quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1.I) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

9.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.3. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed, but at least two samples per month.

9.1.5 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples. A procedure for low level check samples is described in Section 9.4.

9.1.6 The laboratory must maintain performance records to document the quality of data that is generated.

9.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

9.2.1 A quality control (QC) check sample concentrate is required containing each regulated analyte, and any additional analyte which is to be reported, at a concentration of 100 times the MCL or 1 µg/mL, whichever is smaller, in methanol. The QC check sample must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

9.2.2 Analyze seven 5-mL QC check samples at 1/5 MCL or 2 µg/L according to the method beginning in Sect. 10. Each sample is produced by injecting 10 µL of QC check sample concentrate into 5 mL of reagent water in a glass syringe through the syringe valve.

9.2.3 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L for each analyte using the seven results. Calculate the MDL for each analyte as specified in Ref. 2. The calculated MDL must be less than the spike level.

9.2.4 For each analyte, ($\bar{X}$) must be between 90% and 110% of the true value. Additionally, s must be $\leq$ 35% of $\bar{X}$. If s and $\bar{X}$ for all analytes meet the criteria, the system performance is acceptable and analysis of actual samples can begin. If any s exceeds the precision limit or any $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that analyte.
NOTE: The large number of analytes present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes are analyzed.

9.2.5 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 9.2.2 only for the analytes which failed the test.

9.3 The laboratory must demonstrate on a regular basis (See Section 9.1.4) that the measurement system is in control by analyzing a quality control sample for all analytes of interest at the MCL or 10 µg/L, whichever is smaller.

9.3.1 Prepare a QC check standard by adding 50 µL of QC check sample concentrate (Section 9.2.1) to 5 mL of regent water in a glass syringe.

9.3.2 Analyze the QC check according to Section 10, and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value.

9.3.3 If the recovery for any analyte falls outside the designated range, the analyte has failed the acceptance criteria. A check standard containing each analyte that failed must be re-analyzed.

9.4 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples.

9.4.1 Prepare a low level check sample by spiking 10 µL of QC check sample concentrate to 5 mL of reagent water and analyze according to the method in Sect. 10.

9.4.2 For each analyte, the recovery must be between 60% and 140% of the expected value.

9.4.3 When one or more analytes fail the test, the analyst must repeat the test only for those analytes which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 9.4.1.

9.5 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. PROCEDURE

10.1 INITIAL CONDITIONS

10.1.1 Recommended chromatographic conditions are summarized in Section 5.3.2. Estimated retention times and MDL that can be achieved under these conditions are given in Table 1. Other packed columns may be used if the requirements of Section 9.2 are met.

10.1.2 Calibrate the system daily as described in Section 8.1.4.

10.1.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

10.2 SAMPLE INTRODUCTION AND PURGING

10.2.1 Remove the plungers from two 5-mL syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample (or standard) bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If applicable, add the internal calibration standard to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

10.2.2 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 ± 0.1 min at ambient temperature (Figure 3).

10.3 SAMPLE DESORPTION - After the 11-min purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4) and initiate the temperature program sequence of the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 mL/min for 4.0 ± 0.1 min.

If rapid heating cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30°C (subambient temperature if poor peak geometry and random retention problems persist) instead of the initial operating temperature for analysis. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 5-mL flushes of reagent water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

10.4 TRAP RECONDITIONING - After desorbing the sample for four min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11. CALCULATIONS

11.1 Identify each organohalide in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory control standard (Sect. 8.2.2).

11.2 Determine the concentration of the unknowns by using the calibration curve or by comparing the peak height or area of the unknowns to the peak height or area of the standards as follows.

$$\text{Concentration of unknown } (\mu g/L) = \frac{\text{Peak height sample}}{\text{Peak height standard}} \times \text{Concentration of standard } (\mu g/L)$$

11.3 Report the results for the unknown samples in µg/L. Round off the results to the nearest 0.1 µg/L or two significant figures.

12. ACCURACY AND PRECISION

12.1 Single laboratory (EMSL-Cincinnati) accuracy and precision for the organohalides spiked in Ohio River water and carbon-filtered tap water are presented in Table 2.(1)

12.2 This method was tested by 20 laboratories using drinking water spiked with various organohalides at six concentrations between 8 and 505 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte. Linear equations to describe these relationships are presented in Table 3.(8)

13. REFERENCES

1. "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method, Method 502.1," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April, 1981.

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

3. "Carcinogens-Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August, 1977.

4. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. "Gas Chromatographic Analysis of Purgeable Halocarbon and Aromatic Compounds in Drinking Water Using Two Detectors in Series," Kingsley, B.A., Gin, C., Coulson, D.M., and Thomas, R.F., Water Chlorination, Environmental Impact and Health Effects, Volume 4, Ann Arbor Science.

7. Bellar, T.A. and J.J. Lichtenberg, "The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8. "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

Table 1. RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR ORGANOHALIDES

Analyte	Retention Time (sec) Column 1	Retention Time (sec) Column 2	MDL (ug/L)
Chloromethane	90	317	0.01
Bromomethane	130	423	0.03
Dichlorodifluoromethane	157	(a)	(a)
Vinyl chloride	160	317	0.006
Chloroethane	200	521	0.008
Methylene chloride	315	607	(a)
Trichlorofluoromethane	431	(a)	(a)
1,1-Dichloroethene	476	463	0.003
Bromochloromethane	509	760	(a)
1,1-Dichloroethane	558	754	0.002
trans-1,2-Dichloroethene	605	563	0.002
cis-1,2-Dichloroethene	605	726	0.002
Chloroform	641	725	0.002
1,2-Dichloroethane	684	921	0.002
Dibromomethane	698	895	(a)
1,1,1-Trichloroethane	756	786	0.003
Carbon tetrachloride	781	664	0.003
Bromodichloromethane	819	877	0.002
Dichloroacetonitrile(b)	884	(a)	0.04
1,2-Dichloropropane	895	997	(a)
1,1-Dichloropropene	904	(a)	(a)
Trichloroethene	948	787	0.001
1,3-Dichloropropane	973	(a)	(a)
Dibromochloromethane	989	997	(a)
1,1,2-Trichloroethane	991	1084	0.007
1,2-Dibromoethane	1046	1131	0.03
2-Chloroethylethyl ether(b)	1056	(a)	0.02
2-Chloroethylvinyl ether(b)	1080	(a)	0.02
Bromoform	1154	1150	0.02
1,1,1,2-Tetrachloroethane	1163	1302	(a)
1,2,3-Trichloropropane	1279	(a)	(a)
Chlorocyclohexane(b)	1283	(a)	(a)
1,1,2,2-Tetrachloroethane	1297	(a)	0.01
Tetrachloroethene	1300	898	0.001
Pentachloroethane(6)	1300	(a)	(a)
1-Chlorocyclohexene(b)	1345	1186	(a)
Chlorobenzene	1451	1130	0.001
1,2-Dibromo-3-chloropropane	1560	(a)	0.03
Bromobenzene	1626	(a)	(a)
2-Chlorotoluene	1927	1320	(a)
bis-2-Chloroisopropyl ether	1931	(a)	(a)
1,3-Dichlorobenzene	2042	1346	(a)
1,2-Dichlorobenzene	2094	1411	(a)
1,4-Dichlorobenzene	2127	1340	(a)

(a) = Not determined.
(b) = Compound not a method analyte.
(c) = Pentachloroethane apparently decomposes to tetrachloroethene in the analytical system.

Table 1. (CONTINUED)

Column 1 Conditions: Carbopack B(60/80 mesh) coated with 1% SP-1000 packed in an 8 ft x 0.1 in ID stainless steel or glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 40°C for 3 min then programmed at 8°C/min to 220°C and held for 15 min.

Column 2 conditions: Porisil-C (100/120 mesh) coated with chemically bonded n-octane packed in a 6 ft x 0.1 in ID stainless steel or glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 50°C for 3 min then programmed at 6°C/min to 170°C and held for 4 min.

Table 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ORGANCHALIDES IN OHIO RIVER WATER AND DRINKING WATER

Analyte	Spike Level (µg/L)	Average Recovery %	Number or Samples	Standard Deviation (µg/L)	Relative Standard Deviation (%)
Bromobenzene	0.40	93	20	0.047	12
Bromochloromethane	0.40	90	19	0.038	9.5
Bromodichloromethane	0.20	100	17	0.013	6.5
Bromoform	0.20	95	17	0.030	15.0
Carbon tetrachloride	0.20	90	17	0.014	7.0
Chlorobenzene	0.40	88	18	0.037	9.3
Chlorocyclohexane(a)	0.40	93	21	0.033	8.3
1-Chlorocyclohexene(a)	0.40	93	21	0.051	12.8
Chloroethane	0.40	93	20	0.071	18
2-Chloroethylethyl ether(a)	0.40	95	18	0.030	7.5
Chloromethane	0.40	93	16	0.034	8.5
2-Chlorotoluene	0.40	85	20	0.037	9.3
Dibromochloromethane	0.20	95	17	0.014	7.0
1,2-Dibromoethane	0.40	93	18	0.050	12.5
Dibromomethane	0.40	100	5	0.032	8.0
1,2-Dichlorobenzene	0.40	95	21	0.053	13
1,3-Dichlorobenzene	0.40	95	21	0.033	8.3
1,4-Dichlorobenzene	0.40	90	20	0.051	13
Dichlorodifluoromethane	0.40	103	12	0.081	20
1,1-Dichloroethane	0.20	95	17	0.012	6.0
1,2-Dichloroethane	0.20	110	17	0.014	7.0
1,1-Dichloroethene	0.40	88	18	0.027	9.3
1,2-Dichloroethene(b)	0.40	88	20	0.028	7.0
1,2-Dichloropropane	0.40	95	20	0.014	3.5
1,3-Dichloropropane	0.40	98	21	0.026	6.5
1,1-Dichloropropene	0.40	88	18	0.037	9.3
Methylene chloride	0.20	85	17	0.024	12.0
1,1,1,2-Tetrachloroethane	0.40	93	20	0.032	8.0
1,1,2,2-Tetrachloroethane	0.40	95	18	0.036	9.0
Tetrachloroethene	0.20	90	17	0.019	9.5
1,1,1-Trichloroethane	0.40	93	20	0.032	8.0
1,1,2-Trichloroethane	0.40	95	15	0.024	6.0
Trichloroethene	0.20	94	17	0.012	6.0
Trichlorofluoromethane	0.40	90	21	0.037	9.3
1,2,3-Trichloropropane	0.40	100	20	0.038	9.5
Vinyl Chloride	0.20	110	12	0.029	15

(a) = Compound not included in proposed monitoring requirement.
(b) = Includes cis- and trans- isomers.

Table 3. SINGLE ANALYST PRECISION, OVERALL PRECISION, AND ACCURACY FOR ORGANOHALIDES IN DRINKING WATER

Analyte	Single Analyst Precision	Overall Precision	Accuracy as Mean Recovery($\bar{X}$)
Bromodichloromethane	$0.13\bar{X} + 1.41$	$0.18\bar{X} + 3.06$	$1.00C + 0.96$
Bromoform	$0.10\bar{X} + 0.20$	$0.24\bar{X} + 1.25$	$1.02C - 1.21$
Carbon Tetrachloride	$0.10\bar{X} + 1.57$	$0.20\bar{X} + 1.09$	$1.00C - 2.20$
Chlorobenzene	$0.07\bar{X} + 1.71$	$0.16\bar{X} + 1.43$	$1.00C - 1.39$
Chloroethane	$0.07\bar{X} + 0.65$	$0.19\bar{X} + 0.39$	$1.08C - 1.97$
Chloroform	$0.05\bar{X} + 5.58$	$0.09\bar{X} + 6.21$	$0.90C + 3.44$
Chloromethane	$0.28\bar{X} + 0.27$	$0.49\bar{X} + 1.51$	$0.91C - 0.99$
Dibromochloromethane	$0.10\bar{X} + 1.55$	$0.23\bar{X} + 0.91$	$0.98C + 2.89$
1,2-Dichlorobenzene	$0.12\bar{X} + 2.02$	$0.17\bar{X} + 2.26$	$0.91C + 1.12$
1,3-Dichlorobenzene	$0.15\bar{X} + 0.64$	$0.24\bar{X} + 1.48$	$0.91C - 0.13$
1,4-Dichlorobenzene	$0.09\bar{X} + 0.39$	$0.15\bar{X} + 0.39$	$0.91C + 0.26$
1,1-Dichloroethane	$0.09\bar{X} + 0.47$	$0.18\bar{X} + 1.13$	$0.93C - 2.04$
1,2-Dichloroethane	$0.06\bar{X} + 1.69$	$0.18\bar{X} + 1.21$	$1.03C - 0.41$
1,1-Dichloroethene	$0.12\bar{X} + 0.13$	$0.31\bar{X} - 0.71$	$1.03C - 1.16$
trans-1,2-Dichloroethene	$0.16\bar{X} + 0.29$	$0.24\bar{X} + 0.95$	$0.98C - 1.02$
1,2-Dichloropropane	$0.19\bar{X} - 0.61$	$0.27\bar{X} - 0.10$	$0.98C + 1.19$
Methylene Chloride	$0.08\bar{X} + 1.04$	$0.17\bar{X} + 2.43$	$0.97C - 1.50$
1,1,2,2-Tetrachloroethane	$0.09\bar{X} - 1.42$	$0.20\bar{X} + 1.65$	$0.92C - 0.82$
Tetrachloroethene	$0.17\bar{X} + 0.96$	$0.25\bar{X} + 0.58$	$0.96C + 0.35$
1,1,1-Trichloroethane	$0.14\bar{X} - 0.33$	$0.27\bar{X} - 0.76$	$0.92C + 0.02$
1,1,2-Trichloroethane	$0.06\bar{X} + 0.99$	$0.19\bar{X} + 0.69$	$0.84C + 0.83$
Trichloroethene	$0.13\bar{X} + 0.23$	$0.32\bar{X} - 0.57$	$0.92C - 0.10$
Trichlorofluoromethane	$0.22\bar{X} + 0.03$	$0.30\bar{X} + 0.64$	$0.92C + 1.21$
Vinyl Chloride	$0.14\bar{X} - 0.17$	$0.32\bar{X} + 0.07$	$1.06C - 1.86$

$\bar{X}$ = Mean recovery, in µg/L
C = True value for the concentration, in µg/L

METHOD 503.1. VOLATILE AROMATIC AND UNSATURATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY (1981, Ed. Rev. 1986)

1. SCOPE AND APPLICATION

1.1 This method is applicable for the determination of various volatile aromatic and unsaturated compounds in finished drinking water, raw source water, or drinking water in any treatment stage.(1) The following compounds can be determined by this method:

Analyte	CAS No.
Benzene	71-43-2
Bromobenzene	108-86-1
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Chlorobenzene	108-90-7
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
Trichloroethene	79-01-6
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 This method is not applicable to the determination of styrene in chlorinated drinking waters. The rapid oxidation rate of this compound prevents the effective use of a dechlorinating agent as a preservation technique for it.

1.3 Single laboratory accuracy and precision data show that this procedure is useful for the detection and measurement of multi-component mixtures spiked into finished water and raw source water at concentrations between 0.05 and 0.5 ug/L. The method detection limit (MDL) (2) for each analyte is presented in Table 1 (1). Some laboratories may not be able to achieve these detection limits since results are dependent upon instrument sensitivity and matrix effects. Individual aromatic compounds can be measured at concentrations up to 1500 ug/L. Determination of complex mixtures containing partially resolved compounds may be hampered by concentration differences larger than a factor of 10.

1.4 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low ug/L level or by experienced technicians under the close supervision of a qualified analyst.

2. SUMMARY OF METHOD

2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from a 5-mL sample by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing a suitable sorbent material. When purging is complete, the sorbent tube is heated and backflushed with an inert gas to desorb trapped sample components onto a gas chromatography (GC) column. The gas chromatograph is temperature programmed to separate the method analytes which are then detected with a photoionization detector.

2.2 A second chromatographic column is described that can be used to confirm GC identifications and measurements. Alternatively, confimatory analyses may be performed by gas chromatography/mass spectrometry (GC/MS) according to Method 524.1 or Method 524.2 if sufficient material is present.

3. INTERFERENCES

3.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks (Sect. 9.1.3) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Figure 1). Subtracting blank values from sample results is not permitted.

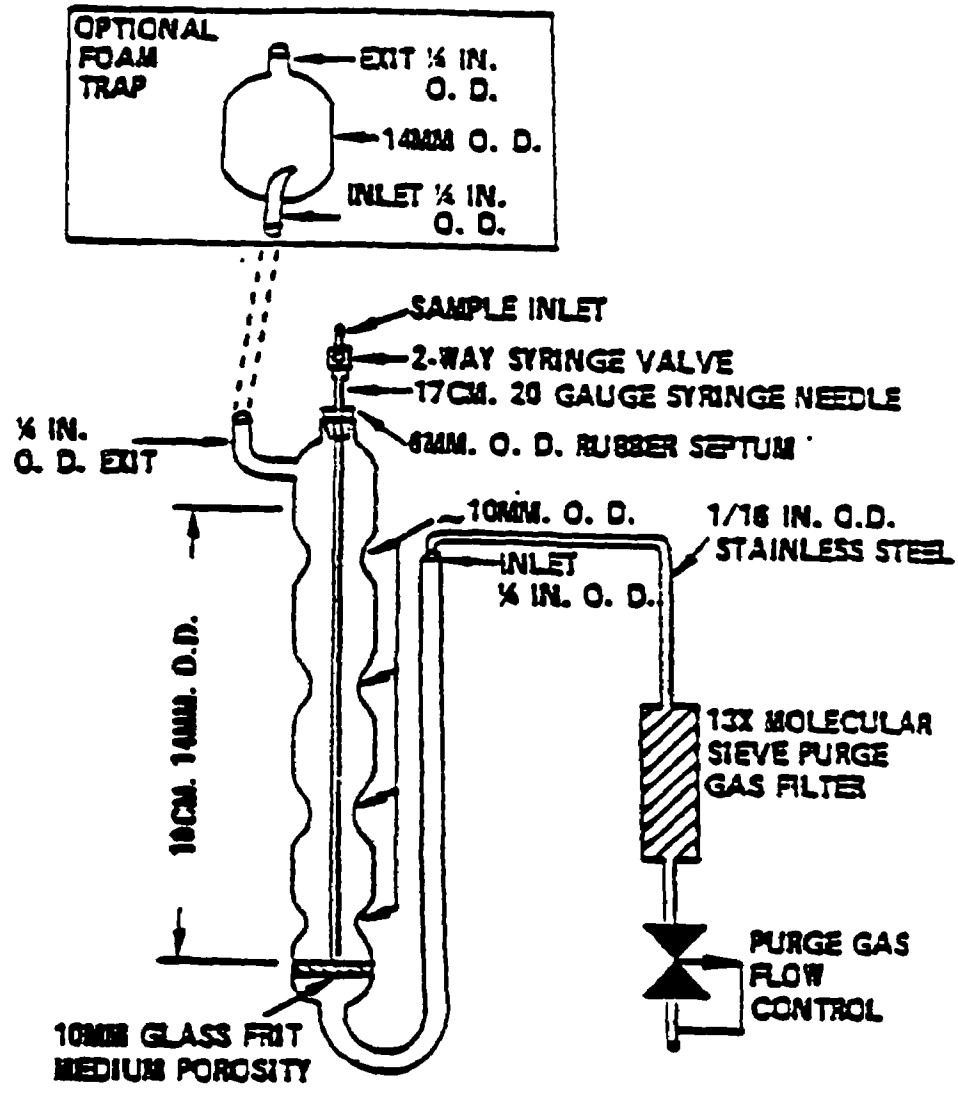

Figure 1. Purging device

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing hign concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of compounds being determined, it may be necessary to wash out the purging device with a soap solution, rinse it with distilled water, and then dry it in an oven at 105°C between analyses.

3.3 Excess water will cause a negative baseline deflection in the chromatogram. The method provides for a dry purge period to prevent this problem.

4. SAFETY

4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (3-5) for the information of the analyst.

4.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, 1,4-dichlorobenzene, hexachlorobutadiene, tetrachloroethene, and trichloroethene. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

5.1 SAMPLE CONTAINERS - 40-mL to 120-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

5.2 PURGE AND TRAP SYSTEM - The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

5.2.1 The all glass purging device (Figure 1) must be designed to accept 5-mL samples with a water column at least 3 cm deep. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point $\leq$ 5 mm from the base of the water column.

5.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. It is recommended that 1.0 cm of methyl silicone coated packing be added at the inlet end to prolong the life of the trap. Add a sufficient amount of 2,6-diphenylene oxide polymer to fill the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

5.2.3 The desorber must be capable of rapidly heating the trap to 180°C. The trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging. The desorber design illustrated in Figure 2 meets these criteria.

5.2.4 The purge and trap system may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3-5.

5.3 GAS CHROMATOGRAPHY SYSTEM

5.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and the temperature program.

5.3.2 Two gas chromatography columns are recommended. Column 1 is a highly efficient column that provides outstanding separations for a wide variety of organic compounds. Column 1 should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column 2 is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for the listed analytes on the two columns are presented in Table 1.

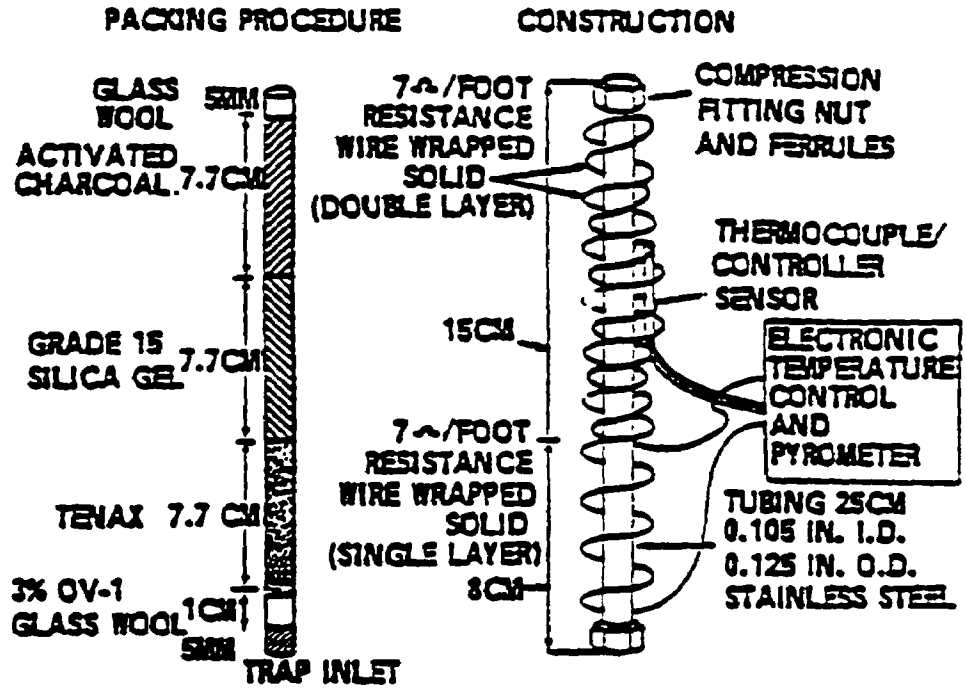

Figure 2. Trap packings and construction to include desorb capability

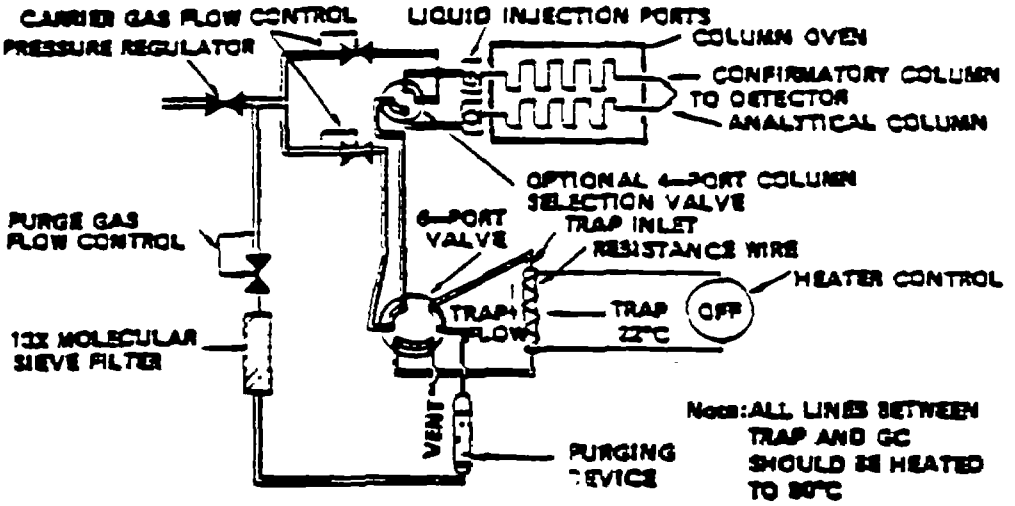

Figure 3. Purge and trap system - purge mode.

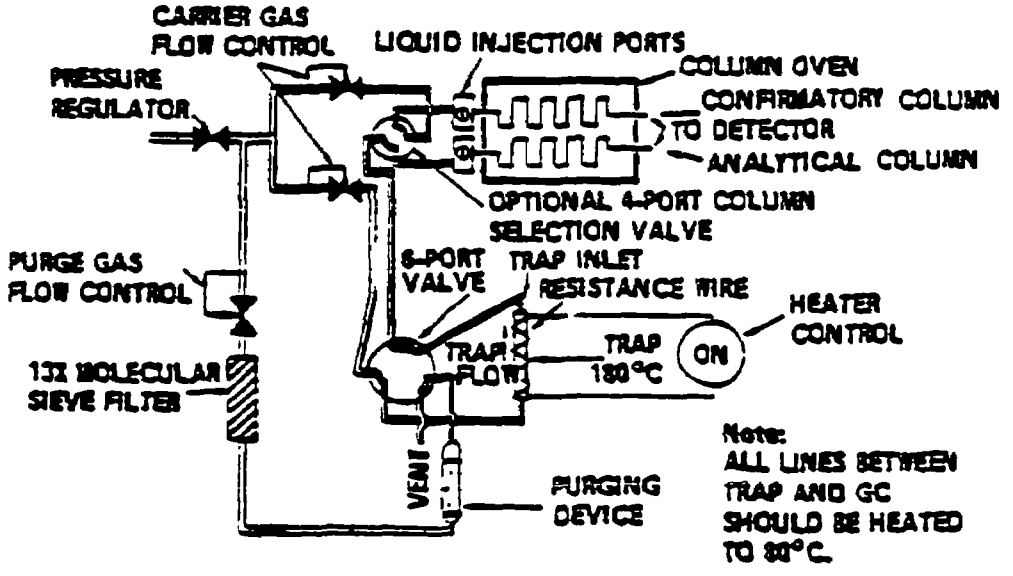

Figure 4. Schematic of purge and trap device - desorb mode

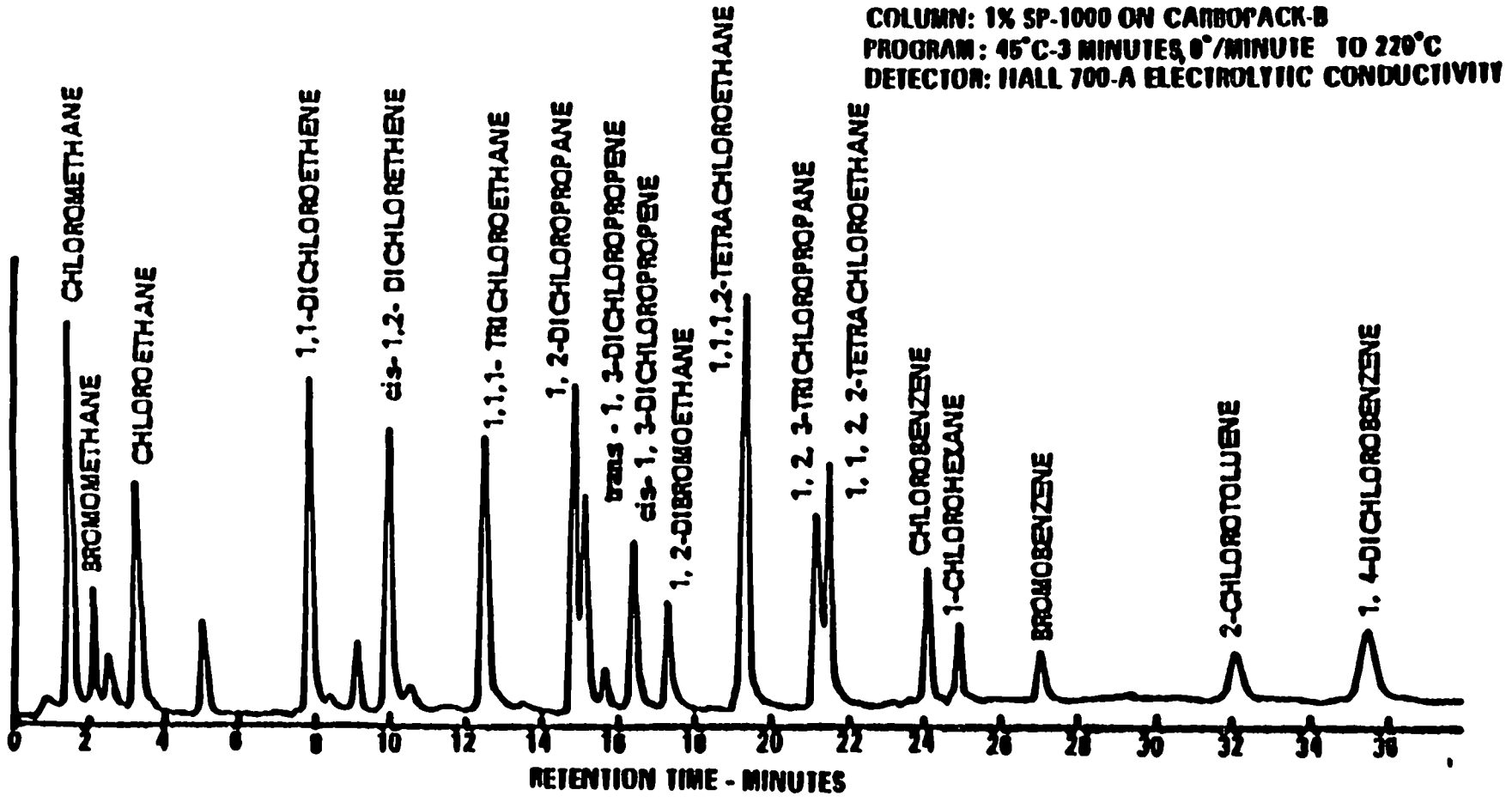

Figure 6. Gas chromatogram of purgeable halocarbons

5.3.2.1 Column 1 - 1.5 to 2.5 m x 0.085 in ID #304 stainless steel or glass, packed with 5% SP-1200 and 1.75% Bentone 34 on Supelcoport (80/100 mesh) or equivalent. The flow rate of the helium carrier gas must be established at 30 mL/min. The column temperature is held at 50°C for 2 min, then programmed at 3°C/min to 110°C and held at 110°C until all compounds have eluted. When not in use, maintain the column at 110°C. Condition new SP-1200/Bentone columns with carrier gas flow at 120°C for several days before connecting to the detector. A sample chromatogram obtained with Column 1 is presented in Figure 6.

5.3.2.2 Column 2 - 1.5 to 2.5 m long x 0.085 in ID # 304 stainless steel or glass, packed with 5% 1,2,3-tris(2-cyanoethoxy) propane on Chromosorb W (60/80 mesh) or equivalent. The flow rate of the helium carrier gas must be established at 30 mL/min. The column temperature must be programmed to hold at 40°C for 2 min, increase to 100°C at 2°C/min, and hold at 100°C until all expected compounds have eluted. A sample chromatogram obtained with Column 2 is presented in Figure 7.

5.3.3 A high temperature photoionization detector equipped with a 10.2 eV lamp is required (HNU Systems, Inc., Model PI-51-02 or equivalent).

5.4 SYRINGE AND SYRINGE VALVES

5.4.1 Two 5-mL glass hypodermic syringes with Luer-Lok tip.

5.4.2 Three 2-way syringe valves with Luer ends.

5.4.3 One 25-uL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

5.4.4 Micro syringes - 10, 100 uL.

5.5 MISCELLANEOUS

5.5.1 Standard solution storage containers - 15-mL bottles with PTFE-lined screw caps.

6. REAGENT AND CONSUMABLE MATERIALS

6.1 TRAP PACKING MATERIALS

6.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.1.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

6.2 COLUMN PACKING MATERIALS

6.2.1 5% SP-1200/1.75% Bentone 34 on 100/120 mesh Supelcoport or equivalent.

6.2.2 5% 1,2,3-tris(2-cyanoethoxy) propane on 60/80 mesh Chromosorb W or equivalent.

6.3 REAGENTS

6.3.1 Methanol - demonstrated to be free of analytes.

6.3.2 Reagent water - Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

6.3.3 Hydrochloric acid (1+1) - Carefully add measured volume of conc. HCl to equal volume of reagent water.

6.4 STANDARD STOCK SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

6.4.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

6.4.2 Using a 100-uL syringe, immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask.

6.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

6.4.4 Store stock standard solutions at 4°C in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions are stable for at least four weeks when stored at 4°C.

6.5 SECONDARY DILUTION STANDARDS - Use standard stock solutions to prepare secondary dilution standard solutions that contain the analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions (Sect. 8.1) that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions from them. Secondary dilution standard solutions must be replaced after one month.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Collect all samples in duplicate. Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

7.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

7.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-quart container.

7.2 SAMPLE PRESERVATION

7.2.1 Adjust the pH of the duplicate samples <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume. Seal the sample bottles, PFTE-face down, and shake vigorously for one minute.

7.2.2 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be $\leq$ 4°C on arrival at the laboratory.

7.3 SAMPLE STORAGE

7.3.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

7.3.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 CALIBRATION

8.1.1 A set of at least five calibration standards containing the method analytes is needed. More than one set of calibration standards may be required. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other standards should contain analytes at concentrations that define the range of the method.

8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of reagent water in a volumetric container. Use a microsyringe and rapidly inject the alcoholic standard into the water. Remove the needle as quickly as possible after injection. Aqueous standards are not stable and should be discarded after one hour unless preserved, sealed and stored as described in Sect. 7.2.2.

8.1.3 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 10 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

8.1.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Sect. 8.1.5.

8.1.5 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in methanol. The single point standards should be prepared at a concentration that produces a response close (±20%) to that of the unknowns. Do not use less than 20 µL of the secondary dilution standard to produce a single point calibration standard in reagent water.

8.1.6 As a second alternative to a calibration curve, internal standard calibration techniques may be used. α,α,α-Trifluorotoluene is recommended as an internal standard for this method. The internal standard is added to the sample just before purging. Check the validity of the internal standard calibration factors daily by analyzing a calibration standard.

8.2 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of reagent blanks, standards, duplicate samples, and the quality control check standard (Sect. 9.3).

8.2.1 All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing significantly in excess of that shown in the method chromatograms (Figures 6 and 7) must be corrected. If only the compounds eluting before ethylbenzene give random responses or unusually wide peak widths, are poorly resolved, or are missing, the problem is usually traceable to the trap/desorber. If negative peaks appear early in the chromatogram, increase the dry purge time to 5 min.

8.2.2 Check the precision between laboratory replicates. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially around the sample purger or to an improperly adjusted lamp intensity power. Monitor the retention times for each method analyte using data generated from calibration standards and the laboratory control standard. If individual retention times vary by more than 10% over an 8-h period or do not fall within 10% of an established norm, the source of retention data variance must be corrected before acceptable data can be generated.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to

document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. A quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

9.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.3. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples meet all specified quality control criteria.

9.1.5 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples. A procedure for low level check samples is described in Section 9.4.

9.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 9.5.

9.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

9.2.1 A quality control (QC) check sample concentrate is required containing each regulated analyte, and any additional analyte which is to be reported, at a concentration of 100 times the MCL or 1 µg/mL, whichever is smaller, in methanol. The QC check sample must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

9.2.2 Analyze seven 5-mL QC check samples at 1/5 MCL or 2 µg/L according to the method beginning in Sect. 10. Each sample

is produced by injecting 10 µL of QC check sample concentrate into 5 mL of reagent water in a glass syringe through the syringe valve.

9.2.3 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L for each analyte using the seven results. Calculate the MDL for each analyte as specified in Ref. 2. The calculated MDL must be less than the spike level.

9.2.4 For each analyte, ($\bar{X}$) must be between 90% and 110% of the true value. Additionally, s must be $\leq$ 35% of $\bar{X}$. If s and $\bar{X}$ for all analytes meet the criteria, the system performance is acceptable and analysis of actual samples can begin. If any s exceeds the precision limit or any $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that analyte.
NOTE: The large number of analytes present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes are analyzed.

9.2.5 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 9.2.2 only for the analytes which failed the test.

9.3 The laboratory must demonstrate on a regular basis that the measurement system is in control by analyzing a quality control sample for all analytes of interest at the MCL or 10 µg/L, whichever is smaller.

9.3.1 Prepare a QC check standard by adding 50 µL of QC check sample concentrate to 5 mL of regent water in a glass syringe.

9.3.2 Analyze the QC check according to Section 10, and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value.

9.3.3 If the recovery for any analyte falls outside the designated range, the analyte has failed the acceptance criteria. A check standard containing each analyte that failed must be re-analyzed.

9.4 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples.

9.4.1 Prepare a low level check sample by spiking 10 µL of QC check sample concentrate to 5 mL of reagent water and analyze according to the method in Sect. 10.

9.4.2 For each analyte, the recovery must be between 60% and 140% of the expected value.

9.4.3 When one or more analytes fail the test, the analyst must repeat the test only for those analytes which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 9.4.1.

9.5 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. PROCEDURE

10.1 INITIAL CONDITIONS

10.1.1 Recommended chromatographic conditions are summarized in Sect. 5.3.2. Estimated retention times and MDL that can be achieved under these conditions are given in Table 1. Other packed columns may be used if the requirements of Sect. 9.2 are met.

10.1.2 Calibrate the system daily as described in Sect. 8.1.4.

10.1.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

10.2 SAMPLE INTRODUCTION AND PURGING

10.2.1 Remove the plungers from two 5-mL syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample (or standard) bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If applicable, add the internal calibration standard to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

10.2.2 Attach the sample syringe valve to the syringe valve on the purging device. Open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 12.0 ± 0.1 min at ambient temperature (Figure 3).

10.3 TRAP DRY AND SAMPLE DESORPTION - After the 12-min purge, adjust the purge and trap system to the dry purge position (Figure 4) for four min. Empty the purging device using the sample syringe and wash the chamber with two 5-mL flushes of reagent water. After the 4-min dry purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 5) and initiate the temperature program sequence of the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 mL/min for 4.0 ± 0.1 min. The transfer is complete after approximately four min and the column is then rapidly heated to the initial operating temperature for analysis.

10.4 TRAP RECONDITIONING - After desorbing the sample for four min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11. CALCULATIONS

11.1 Identify each analyte in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory quality control check standard (Sect. 9.3).

11.2 Determine the concentration of the unknowns by using the calibration curve or by comparing the peak height or area of the unknowns to the peak height or area of the standards as follows.

$$\text{Concentration of unknown } (\mu g/L) = \frac{\text{Peak height sample}}{\text{Peak height standard}} \times \text{Concentration of standard } (\mu g/L)$$

11.3 Report the results for the unknown samples in ug/L. Round off the results to the nearest 0.1 ug/L or two significant figures.

12. ACCURACY AND PRECISION

12.1 Single laboratory (EMSL-Cincinnati) accuracy and precision for most of the analytes spiked in Ohio River water and chlorinated drinking water are presented in Table 2.(6)

12.2 This method was tested by 20 laboratories using drinking water spiked with various method analytes at six concentrations between

2.2 and 600 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte. Linear equations to describe these relationships are presented in Table 3 (7).

12.3 Multilaboratory studies have been conducted by the Quality Assurance Branch of EMSL-Cincinnati to evaluate the performance of various laboratories. Accuracy and precision data applicable to this method for several purgeable aromatics in reagent water are presented in Table 4 (8).

13. REFERENCES

1. "The Analysis of Aromatic Chemicals in Water by the Purge and Trap Method, Method 503.1," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April, 1981.

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

3. "Carcinogens-Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August, 1977.

4. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. Bellar, T.A., J.J. Lichtenberg, "The Determination of Volatile Aromatic Compounds in Drinking Water and Raw Source Water," unpublished report, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 1982.

7. "EPA Method Validation Study 24, Method 602 (Purgeable Aromatics)," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8. "Analytical Methods and Monitoring Issues Associated with Volatile Organics in Drinking Water," U.S. Environmental Protection Agency, Office of Drinking Water, Washington, D.C., June 1984.

Table 1. RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR METHOD ANALYTES

Analyte	Rentention Time (sec) Column 1	Column 2	MDL ug/L
Benzene	199	165	0.02
Trichloroethene	231	142	0.01
α,α,α-Trifluorotoluene(a)	296	168	0.02
Toluene	384	255	0.02
Tetrachloroethene	406	168	0.01
Ethylbenzene	606	375	0.002
1-Chlorocyclohexene (b)	637	345	0.008
p-Xylene	653	403	0.002
Chlorobenzene	689	481	0.004
m-Xylene	689	403	0.004
o-Xylene	738	518	0.004
Isopropylbenzene	768	455	0.005
Styrene	834	690	0.008
1,4-Bromofluorobenzene(b)	852	740	—
n-Propylbenzene	879	518	0.009
tert-Butylbenzene	975	595	0.006
2-Chlorotoluene	985	681	0.008
4-Chlorotoluene	990	—	—
Bromobenzene	999	807	0.002
sec-Butylbenzene	1027	595	0.02
1,3,5-Trimethylbenzene	1043	612	0.003
4-Isopropyltoluene	1090	681	0.009
1,2,4-Trimethylbenzene	1090	750	0.006
1,4-Dichlorobenzene	1152	975	0.006
1,3-Dichlorobenzene	1211	901	0.006
n-Butylbenzene	1211	765	0.02
Cyclopropylbenzene (b)	1211	—	—
2,3-Benzofuran (b)	1320	1460	0.03
1,2-Dichlorobenzene	1425	1161	0.02
Hexachlorobutadiene	1650	1011	0.02
1,2,4-Trichlorobenzene	1928	1535	0.03
Naphthalene	2545	2298	0.04
1,2,3-Trichlorobenzene	2631	1820	0.03

(a) = Recommended internal standard (Sect. 8.1.6).
(b) = Not a method analyte.

Table 1. (CONTINUED)

Column 1 conditions: Supelcoport (100/120 mesh) coated with 5% SP-1200/1.75% Bentone 34 packed in a 6 ft x 0.085 in ID stainless steel or glass column with helium carrier at 30 mL/min flowrate. Column temperature is held at 50°C for 2 min then programmed at 3°C/min to 110°C for a final hold.

Column 2 conditions: Chromosorb W(60/80 mesh) coated with 5% 1,2,3-tris(2-cyanoethoxy)propane packed in a 6 ft x 0.085 in ID stainless steel or glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held at 40°C for 2 min then programmed at 2°C/min to 100°C for a final hold.

Table 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR AROMATIC AND UNSATURATED ANALYTES IN CHLORINATED DRINKING WATER AND RAW SOURCE WATER

Analyte	Matrix Type (a)	Spike Level ug/L	Samples Analyzed	Average Recovery (%)	Relative Standard Deviation (%)
Benzene	A,B	0.40	13	100	2.8
Bromobenzene	A,B	0.50	19	93	6.2
n-Butylbenzene	A	0.40	7	78	15.[illegible]
sec-Butylbenzene	A	0.40	7	80	11.[illegible]
tert-Butylbenzene	A	0.40	7	88	8.7
Chlorobenzene	A,B	0.50	19	96	5.8
1-Chlorocyclohexene (b)	A,B	0.50	19	89	7.1
4-Chlorotoluene	A,B	0.50	17	91	5.0
1,2-Dichlorobenzene	A,B	0.50	18	92	7.1
1,3-Dichlorobenzene	A,B	0.50	19	91	8.5
1,4-Dichlorobenzene	A,B	0.50	19	95	6.4
Ethylbenzene	A	0.40	7	93	8.5
Hexachlorobutadiene	A	0.50	10	74	16.8
Isopropylbenzene	A	0.40	7	88	8.7
Naphthalene	A,B	0.50	16	92	14.8
n-Propylbenzene	A	0.40	7	83	9.3
Tetrachloroethene	A,B	0.50	19	97	7.8
Toluene	A,B	0.40	13	94	6.6
1,2,3-Trichlorobenzene	A,B	0.50	18	85	10.4
1,2,4-Trichlorobenzene	A,B	0.50	18	86	10.1
Trichloroethene	A,B	0.50	19	97	6.8
α,α,α-Trifluorotoluene(c)	A,B	0.50	18	88	9.7
1,2,4-Trimethylbenzene	A	0.40	7	75	8.7
1,3,5-Trimethylbenzene	A	0.50	10	92	8.7
m-Xylene	A	0.40	7	90	7.7
o-Xylene	A	0.40	7	90	7.2
p-Xylene	A	0.40	7	85	8.7

(a) = Matrix A is drinking water. Matrix B is raw source water.
(b) = Not a method analyte.
(c) = Recommended internal standard (Sect. 8.1.6).

Table 3. SINGLE ANALYST PRECISION, OVERALL PRECISION, AND ACCURACY FOR PURGEABLE AROMATICS IN DRINKING WATER

Analyte	Single Analyst Precision (ug/L)	Overall Precision (ug/L)	Accuracy as Mean Recovery($\bar{X}$) (ug/L)
Benzene	$0.11\bar{X} - 0.06$	$0.22\bar{X} + 1.11$	$0.97C + 0.85$
Chlorobenzene	$0.10\bar{X} + 0.12$	$0.16\bar{X} + 0.36$	$0.94C + 0.12$
1,2-Dichlorobenzene	$0.10\bar{X} + 0.42$	$0.18\bar{X} + 0.28$	$0.91C + 0.44$
1,3-Dichlorobenzene	$0.08\bar{X} + 0.33$	$0.15\bar{X} + 0.33$	$0.93C + 0.21$
1,4-Dichlorobenzene	$0.09\bar{X} + 0.39$	$0.15\bar{X} + 0.39$	$0.91C + 0.26$
Ethylbenzene	$0.10\bar{X} + 0.18$	$0.20\bar{X} + 0.68$	$0.97C + 0.41$
Toluene	$0.10\bar{X} + 0.18$	$0.21\bar{X} + 0.16$	$0.94C + 0.17$

$\bar{X}$ = mean recovery (ug/L)
C = true value for the concentration (ug/L)

Table 4. ACCURACY AND PRECISION DATA FOR PURGEABLE AROMATICS FROM MULTILABORATORY PERFORMANCE EVALUATION STUDIES

Analyte	Spike Level (ug/L)	Number of Laboratories	Average Measured Concentrations (ug/L)	Relative Standard Deviation (%)	Average Recovery (%)
Benzene	94.1	9	91.9	18.6	98
	47.0	10	47.0	11.8	100
	18.8	8	18.7	16.4	100
	8.10	11	6.22	40.8	88
Chlorobenzene	41.4	5	39.8	6.20	96
	27.6	7	27.1	12.1	98
	13.8	6	14.3	6.73	104
	5.52	8	5.65	25.3	102
1,2-Dichlorobenzene	96.9	5	72.9	31.6	75
	19.4	4	16.5	18.8	85
1,4-Dichlorobenzene	68.6	5	62.5	22.8	91
	13.7	5	14.6	29.1	107
1,2,4-Trichlorobenzene	80.8	6	77.6	14.3	96
	6.7	6	8.46	30.7	126

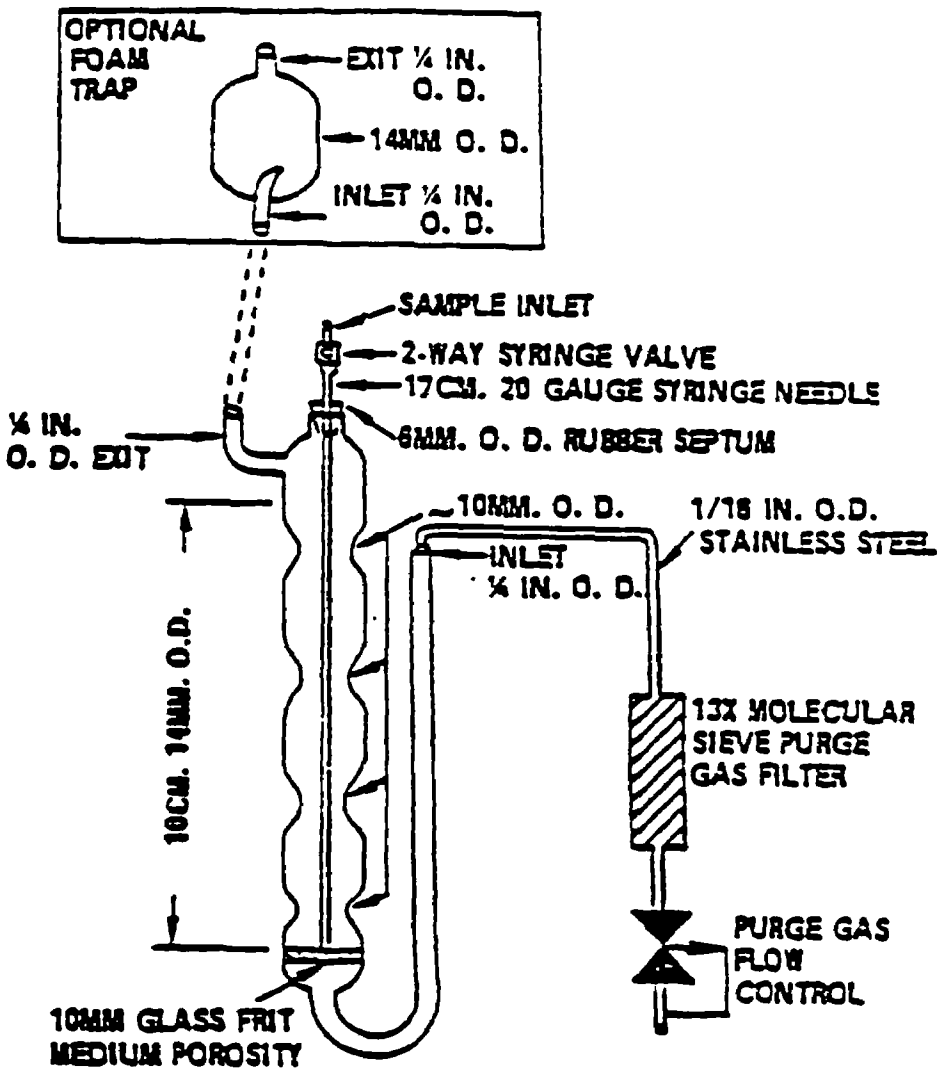

Figure 1. Purging device

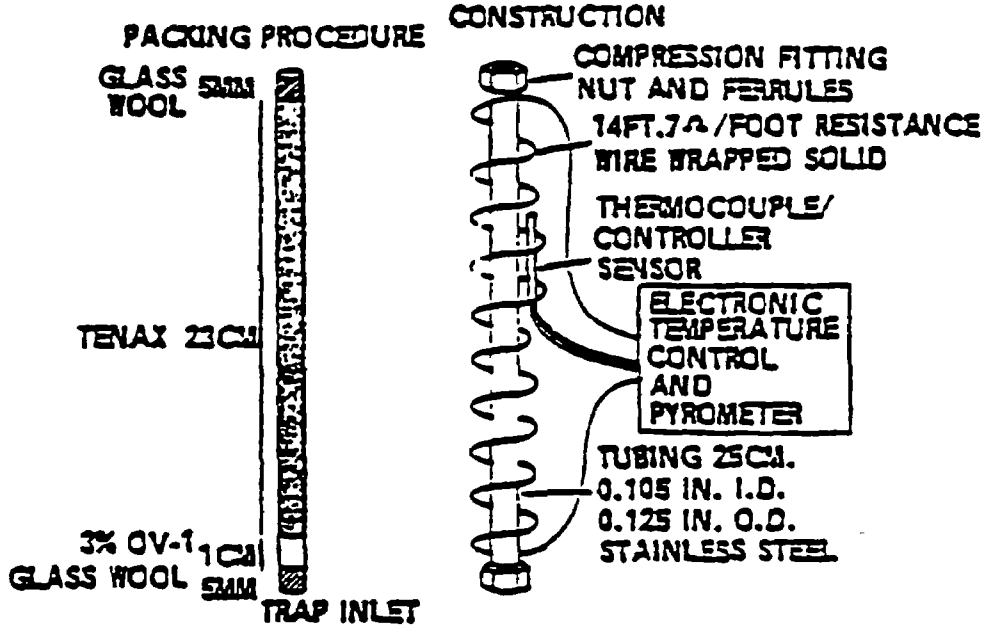

Figure 2. Trap packings and construction to include desorb capability

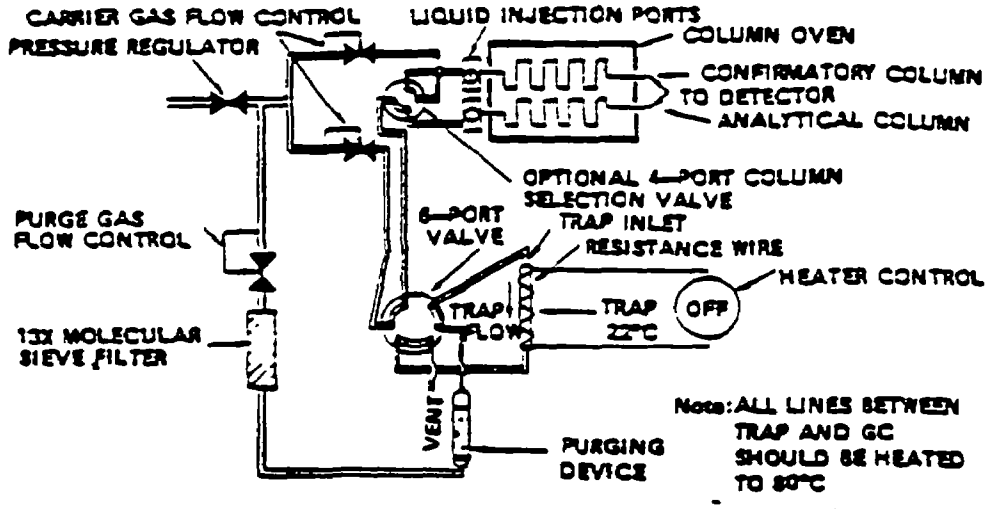

Figure 3. Purge and trap system - purge mode.

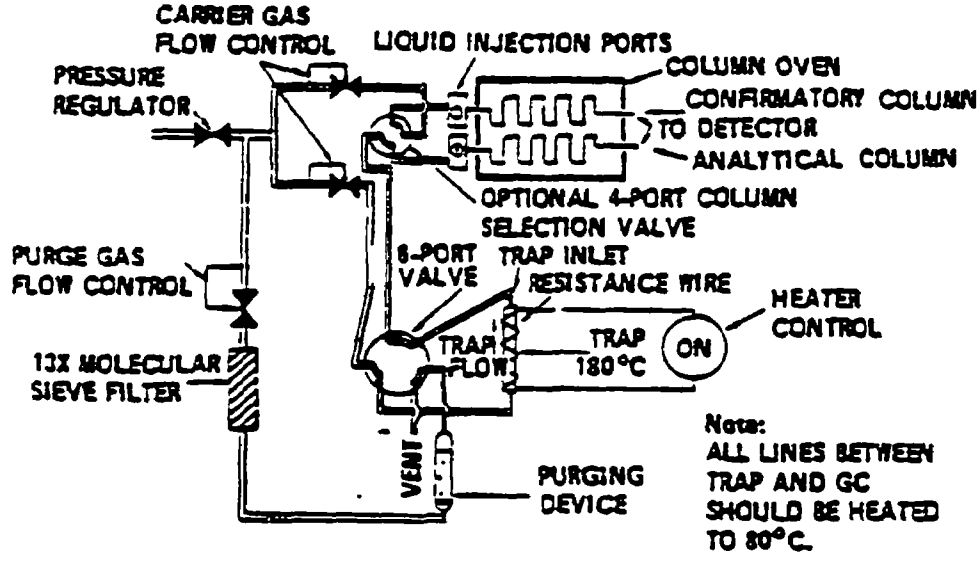

Figure 4. Schematic of purge and trap device - desorb mode

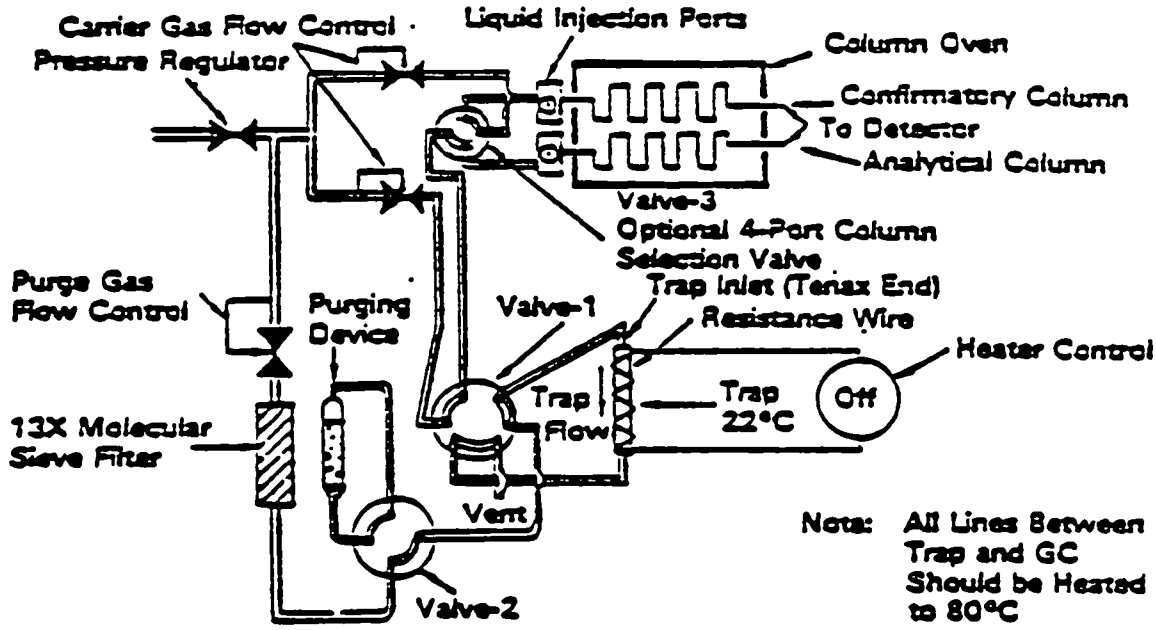

Figure 5. Purge and trap system-dry mode.

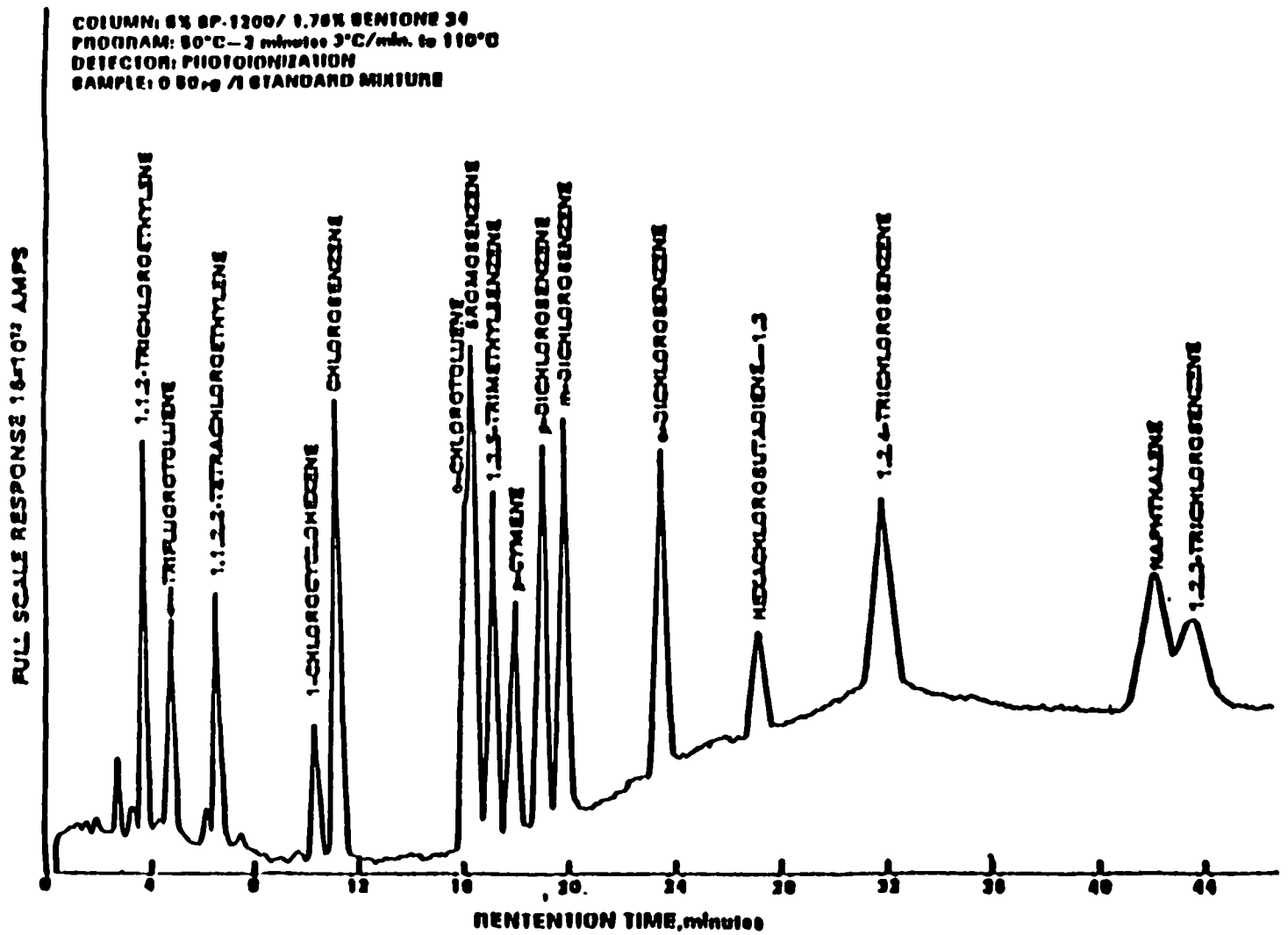

FIGURE 6. CHROMATOGRAM OF TEST MIXTURE

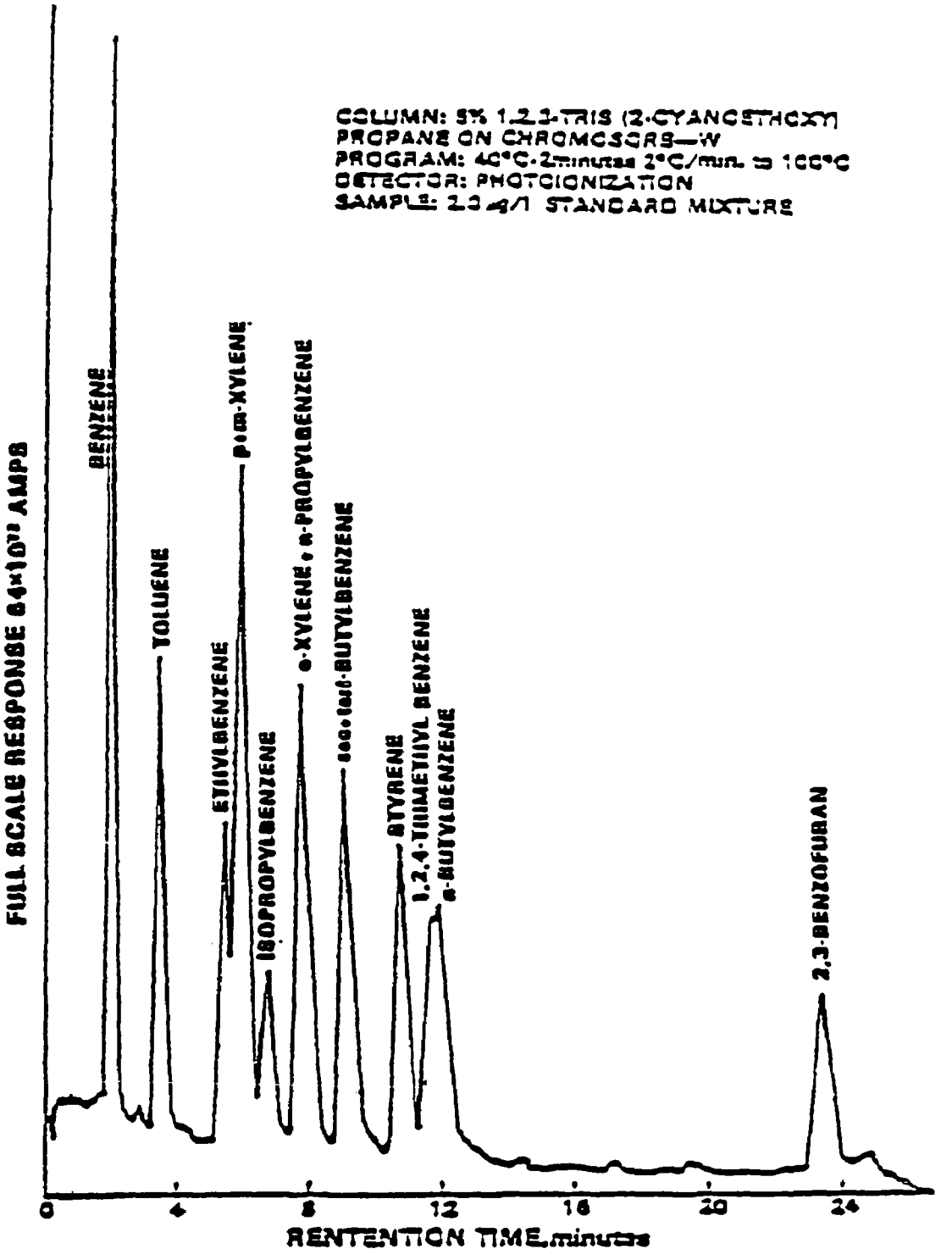

FIGURE 7. CHROMATOGRAM OF TEST MIXTURE

METHOD 504. 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY (1985, Ed. Rev. 1986)

1. SCOPE AND APPLICATION

1.1 This method (1,2,3) is applicable to the determination of the following compounds in finished drinking water and unfinished groundwater:

Analyte	CAS No.
1,2-Dibromoethane	106-93-4
1,2-Dibromo-3-Chloropropane	96-12-8

1.2 For compounds other than the above mentioned analytes, or for other sample sources, the analyst must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples (4) and provide qualitative confirmation of results by Gas Chromatography/Mass Spectrometry (GC/MS) (5).

1.3 The experimentally determined method detection limits (MDL) (6) for EDB and DBCP were calculated to be 0.01 ug/L. The method has been shown to be useful for these analytes over a concentration range from approximately 0.03 to 200 ug/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2. SUMMARY OF METHOD

2.1 Thirty-five mL of sample are extracted with 2 mL of hexane. Two uL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous calibration standards are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses.

2.2 The extraction and analysis time is 30 to 50 minutes per sample depending upon the analytical conditions chosen. (See Table 1 and Figure 1.)

2.3 Confirmatory evidence can be obtained using a dissimilar column (see Table 1). When component concentrations are sufficiently high (> 50 ug/L), Method 524.1 (7) may be employed for improved specificity.

3. INTERFERENCES

3.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be

analyzed on each new bottle of solvent before use. Indirect daily checks on the extracting solvent are obtained by monitoring the sample blanks (7.1.1). Whenever an interference is noted in the sample blank, the analyst should reanalyze the extracting solvent. Low level interferences generally can be removed by distillation or column chromatography (3); however, it is generally more economical to obtain a new source solvent. Interference-free solvent is defined as a solvent containing less than 0.1 ug/L individual analyte interference. Protect interference-free solvents by storing in an area known to be free of organochlorine solvents.

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal into the sample bottle during shipment and storage. The sample blank (7.1.1) is used to monitor for this problem.

3.3 This liquid/liquid extraction technique efficiently extracts a wide boiling range of non-polar organic compounds and, in addition, extracts polar organic components of the sample with varying efficiencies.

3.4 EDB at low concentrations may be masked by very high levels of dibromochloromethane (DBCM), a common chlorinated drinking water contaminant, when using the confirmation column (Sect. 5.8.2.2).

4. SAFETY

4.1 The toxicity and carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (8-10) for the information of the analyst.

4.2 EDB and DBCP have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

5.1 SAMPLE CONTAINERS - 40-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

5.2 VIALS, auto sampler, screw cap with PTFE-faced septa, 1.8 mL, Varian #96-000099-00 or equivalent.

5.3 MICRO SYRINGES - 10 and 100 µL.

5.4 MICRO SYRINGE - 25 µL with a 2-inch by 0.006-inch needle - Hamilton 702N or equivalent.

5.5 PIPETTES - 2.0 and 5.0 mL transfer.

5.6 VOLUMETRIC FLASKS - 10 and 100 mL, glass stoppered

5.7 STANDARD SOLUTION STORAGE CONTAINERS - 15-mL bottles with PTFE-lined screw caps.

5.8 GAS CHROMATOGRAPHY SYSTEM

5.8.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector.

5.8.2 Two gas chromatography columns are recommended. Column A is a highly efficient column that provides separations for EDB and DBCP without interferences from trihalomethanes (Sect. 3.4). Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for EDB and DBCP on these columns are presented in Table 1.

5.8.2.1 Column A - 0.32 mm ID x 30M long fused silica capillary with dimethyl silicone mixed phase (Durawax-DX3, 0.25 µm film, or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. The column temperature is programmed to hold at 40°C for 4 min, to increase to 190°C at 8°C/min, and hold at 190°C for 25 min or until all expected compounds have eluted. Injector temperature: 200°C. Detector temperature: 290°C. (See Figure 1 for a sample chromatogram and Table 1 for retention data).

5.8.2.2 Column B (confirmation column) - 0.32mm ID x 30M long fused silica capillary with methyl polysiloxane phase (DB-1, 0.25 µm film, or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. The column temperature is programmed to hold at 40°C for 4 min, to increase to 270°C at 10°C/minute, and hold at 270°C for 10 min or until all expected compounds have eluted. Injector temperature: 200°C. Detector temperature: 290°C. (See Table 1 for retention data).

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 REAGENTS

6.1.1 Hexane extraction solvent - UV Grade, Burdick and Jackson #216 or equivalent.

6.1.2 Methyl alcohol - ACS Reagent Grade, demonstrated to be free of analytes.

6.1.3 Sodium chloride, NaCl - ACS Reagent Grade - For pretreatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 minutes. Place in a bottle and cap.

6.2 STANDARD MATERIALS

6.2.1 1,2-Dibromoethane - 99%, available from Aldrich Chemical Company.

6.2.2 1,2-Dibromo-3-chloropropane - 99.4%, available from AMVAC Chemical Corporation, Los Angeles, California.

6.3 REAGENT WATER - Reagent water is defined as water free of interference when employed in the procedure described herein.

6.3.1 Reagent water can be generated by passing tap water through a filter bed containing activated carbon. Change the activated carbon whenever the criteria in Sect. 9.1.2 cannot be met.

6.3.2 A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.

6.3.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water at 100 mL/minute for 1 hour. While still hot, transfer the water to a narrow mouth screw cap bottle with a Teflon seal.

6.3.4 Test reagent water each day it is used by analyzing it according to Sect. 10.

6.4 STANDARD STOCK SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

6.4.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min and weigh to the nearest 0.1 mg.

6.4.2 Use a 100-µL syringe and immediately add two or more drops of standard material to the flask. Be sure that the standard material falls directly into the alcohol without contacting the neck of the flask.

6.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight.

6.4.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C.

6.5 SECONDARY DILUTION STANDARDS — Use standard stock solutions to prepare secondary dilution standard solutions that contain both analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Sect. 8.1.1) that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standard solutions in Sect. 6.4.4 also applies to secondary dilution standard solutions.

6.6 QUALITY CONTROL (QC) CHECK SAMPLE CONCENTRATE (0.25 µg/mL) — Prepare a QC check sample concentrate of 0.25 µg/mL of each analyte from the standard stock solutions prepared in Sect. 6.4.

6.7 MDL CHECK SAMPLE CONCENTRATE (0.05 µg/mL) — Dilute 2 mL QC check sample concentrate (Sect. 6.6) to 10 mL with methanol.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Replicate field blanks must be handled along with each sample set, which is composed of the samples collected from the same general sampling site at approximately the same time. At the laboratory, fill a minimum of two sample bottles with reagent water, seal, and ship to the sampling site along with sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by the field blanks.

7.1.2 Collect all samples in duplicate. Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

7.1.3 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized

(usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

7.1.4 When sampling from a well, fill a wide-mouth bottle or beaker with sample, and carefully fill duplicate 40-mL sample bottles.

7.2 SAMPLE PRESERVATION

7.2.1 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to insure that they will be below 4°C on arrival at the laboratory.

7.2.2 The addition of sodium thiosulfate as a dechlorinating agent and/or acidification to pH 2 with 1:1 HCl, common preservation procedures for purgeable compounds, have been shown to have no effect on EDB and DBCP and, therefore, their use is not recommended for samples to be analyzed for these analytes.

7.3 SAMPLE STORAGE

7.3.1 Store samples and field blanks together at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

7.3.2 Analyze all samples within 28 days of collection. Samples not analyzed within this period must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 CALIBRATION

8.1.1 At least three calibration standards are needed. One should contain EDB and DBCP at a concentration near to but greater than the method detection limit (Table 1) for each compound; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.02 µg/L, 0.10 µg/L, and 0.20 µg/L.

8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of reagent water in a volumetric flask. Do not add less than 20 µL of an alcoholic standard to the reagent water or poor precision will result. Use a 25-µL micro syringe and

rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask several times. Discard the contents contained in the neck of the flask. Aqueous standards should be prepared fresh daily unless sealed and stored without headspace as described in Sect. 7.

8.1.3 Analyze each calibration standard according to Sect. 10 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

8.1.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close (±20%) to that of the unknowns.

8.2 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of reagent blanks, standards, duplicate samples, and the laboratory control standard (Sect. 9.2.2).

8.2.1 Peak tailing significantly in excess of that shown in the method chromatogram must be corrected. Tailing problems are generally traceable to active sites on the GC column or the detector operation.

8.2.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory detection limits capability and an ongoing analysis of spiked samples to evaluate and document data quality. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method

performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1. The analyst must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable accuracy and precision with this method. This is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

9.1.4. The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.3. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed.

9.1.5 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples. The procedure for low level check samples is described in Sect. 9.4.

9.2 To establish the ability to achieve low detection limits and generate acceptable accuracy and precision, the analyst must perform the following operations:

9.2.1 Prepare seven MDL check samples at 0.05 µg/L by spiking 35 µg/L of the MDL check sample concentrate (Sect. 6.7) into 35-mL aliquots of reagent water in 40-mL bottles. Cap and mix well.

9.2.2 Analyze the well-mixed MDL check samples according to the method beginning in Section 10.

9.2.3 Calculate the average concentration found ($\overline{X}$) in µg/L, and the standard deviation of the concentrations (s) in µg/L, for each analyte using the seven results. Then calculate the MDL at 99% confidence level for seven replicates (6) as 3.143s.

9.2.4 For each analyte, $\overline{X}$ must be between 80% and 120% of the true value. Additionally, the MDL may not exceed the 0.05 µg/L spiked concentration. If both analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to

meet a criterian, repeat the test. It is recommended that the laboratory repeat the MDL determination on a regular basis.

9.3 The laboratory must demonstrate on a frequency equivalent to 10% of the sample load that the measurement system is in control by analyzing a QC check sample of both analytes at 0.25 ug/L.

9.3.1 Prepare a QC check sample (0.25 ug/L) by adding 35 uL of QC check sample concentrate (Sect. 6.6) to 35 mL of reagent water in a 40-mL bottle.

9.3.2 Analyze the QC check sample according to Sect. 10 and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value.

9.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second check standard containing each analyte that failed must be analyzed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test.

9.4 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples.

9.4.1 Prepare an MDL check sample (0.05 ug/L) as outlined in Sect. 9.2.1 and analyze according to the method in Sect. 10.

9.4.2 The instrument response must indicate that the laboratory's MDL is distinguishable from instrument background signal. If not, repeat the MDL test in Sect. 9.2.1. For each analyte, the recovery must be between 60% and 140% of the expected value. When either analyte fails the test, the analyst must repeat the test only for that analyte which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test.

9.5 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. PROCEDURE

10.1 SAMPLE PREPARATION

10.1.1 Remove samples and standards from storage and allow them to reach room temperature.

10.1.2 For samples and field blanks, contained in 40-mL bottles, remove the container cap. Discard a 5-mL volume using a 5-mL transfer pipette. Replace the container cap and weigh the container with contents to the nearest 0.1g and record this weight for subsequent sample volume determination (Sect. 10.3).

10.1.3 For calibration standards, QC check standards and reagent blank, measure a 35-mL volume using a 50-mL graduated cylinder and transfer it to a 40-mL sample container.

10.2 MICROEXTRACTION AND ANALYSIS

10.2.1 Remove the container cap and add 7g NaCl (Sect. 6.1.3) to the sample.

10.2.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 sec.

10.2.3 Remove the cap and, using a transfer pipette, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min. Allow the water and hexane phases to separate. (If stored at this stage, keep the container upside down.)

10.2.4 Remove the cap and carefully transfer 0.5 mL of the hexane layer into an autosampler using a disposable glass pipette.

10.2.5 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second autosampler vial. Reserve this second vial at 4°C for a reanalysis if necessary.

10.2.6 Transfer the first sample vial to an autosampler set up to inject 2.0 µL portions into the gas chromatograph for analysis. Alternately, 2 µL portions of samples, blanks and standards may be manually injected, although an autosampler is strongly recommended.

10.3 DETERMINATION OF SAMPLE VOLUME

10.3.1 For samples and field blanks, remove the cap from the sample container.

10.3.2 Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk wrist movements.

10.3.3 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g. This net weight is equivalent to the volume of water (in mL) extracted. (Sect. 11.3)

11. CALCULATIONS

11.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory control standard.

11.2 Use the calibration curve or calibration factor (Sect. 8.1.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g., calibration factor x response).

11.3 Calculate the sample volume (V_s) as equal to the net sample weight:

V_s = gross weight (Sect. 10.1.2) - bottle tare (Sect. 10.3.3).

11.4 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = C_i \times \frac{35}{V_s}$$

11.5 Report the results for the unknown samples in µg/L. Round off the results to the nearest 0.01 µg/L or two significant figures.

12. ACCURACY AND PRECISION

12.1 Single laboratory (EMSL-Cincinnati) accuracy and precision at several concentrations in tap water are presented in Table 2 (11). The method detection limits are presented in Table 1.

12.2 In a preservation study extending over a 4-week period, the average percent recoveries and relative standard deviations presented in Table 3 were observed for reagent water (acidified), tap water and groundwater. The results for acidified and non-acidified samples were not significantly different.

13. REFERENCES

1. Glaze, W.W., Lin, C.C., Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water, EPA-600/S4-83-052, January 1984.

2. Henderson, J.E., Peyton, G.R. and Glaze, W.H. (1976). In "Identifiction and Analysis of Organic Pollutants in Water" (L.H. Keith ed.), pp. 105-111. Ann Arbor Sci. Publ., Ann Arbor, Michigan.

3. Richard, J.J., G.A. Junk, "Liquid Extraction for Rapid Determination of Halomethanes in Water," Journal AWWA, 69, 62, January 1977.

4. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", EPA-600/4-79-019, U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Ohio 45268, March 1979.

5. Budde, W.L., J.W. Eichelberger, "Organic Analyses Using Gas Chromatography–Mass Spectrometry," Ann Arbor Science, Ann Arbor, Michigan 1979.

6. Glaser, J.A. et al., "Trace Analyses for Wastewaters," Environmental Science and Technology, 15, 1426 (1981).

7. "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, September 1986.

8. "Carcinogens–Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Publication No. 77-206, August, 1977.

9. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

10. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

11. Winfield, T.W., et al. "Analysis of Organohalide Pesticides in Drinking Water by Microextraction and Gas Chromatography." In preparation.

Table 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP)

Analyte	Retention Time, Min		MDL, ug/L
	Column A	Column B	
EDB	9.5	8.9	0.01
DBCP	17.3	15.0	0.01

Column A conditions: Durawax-DX 3 (0.25 µm film thickness) in a 30 m long x 0.32 mm ID fused silica capillary column with helium carrier gas at 25 cm/sec. Column temperature held isothermal at 40°C for 4 min, then programmed at 8°C/min to 180°C for final hold.

Column B conditions: DB-1 (0.25 µm film thickness) in a 30 m long x 0.32 mm ID fused silica capillary column with helium carrier gas at 25 cm/sec. Column temperature held isothermal at 40°C for 4 min, then programmed at 10°C/min to 270°C for final hold.

Table 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR EDB AND DBCP IN TAP WATER

Analyte	Number of Samples	Spike Level (ug/L)	Average Accuracy (%)	Relative Standard Deviation (%)
EDB	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
DBCP	7	0.03	90	11.4
	7	0.24	102	8.3
	7	50.0	94	4.8

Table 3. ACCURACY AND PRECISION AT 2.0 ug/L
OVER A 4-WEEK STUDY PERIOD

Analyte	Matrix[1]	Number of Samples	Average Accuracy (% Recovery)	Relative Std. Dev. (%)
EDB	RW-A	16	104	4.7
	GW	15	101	2.5
	GW-A	16	96	4.7
	TW	16	93	6.3
	TW-A	16	93	6.1
DBCP	RW-A	16	105	8.2
	GW	16	105	6.2
	GW-A	16	101	8.4
	TW	16	95	10.1
	TW-A	16	94	6.9

[1]Matrix Identities
RW-A = Reagent water at pH 2
GW = Groundwater, ambient pH
GW-A = Groundwater at pH 2
TW = Tap water, ambient pH
TW-A = Tap water at pH 2.

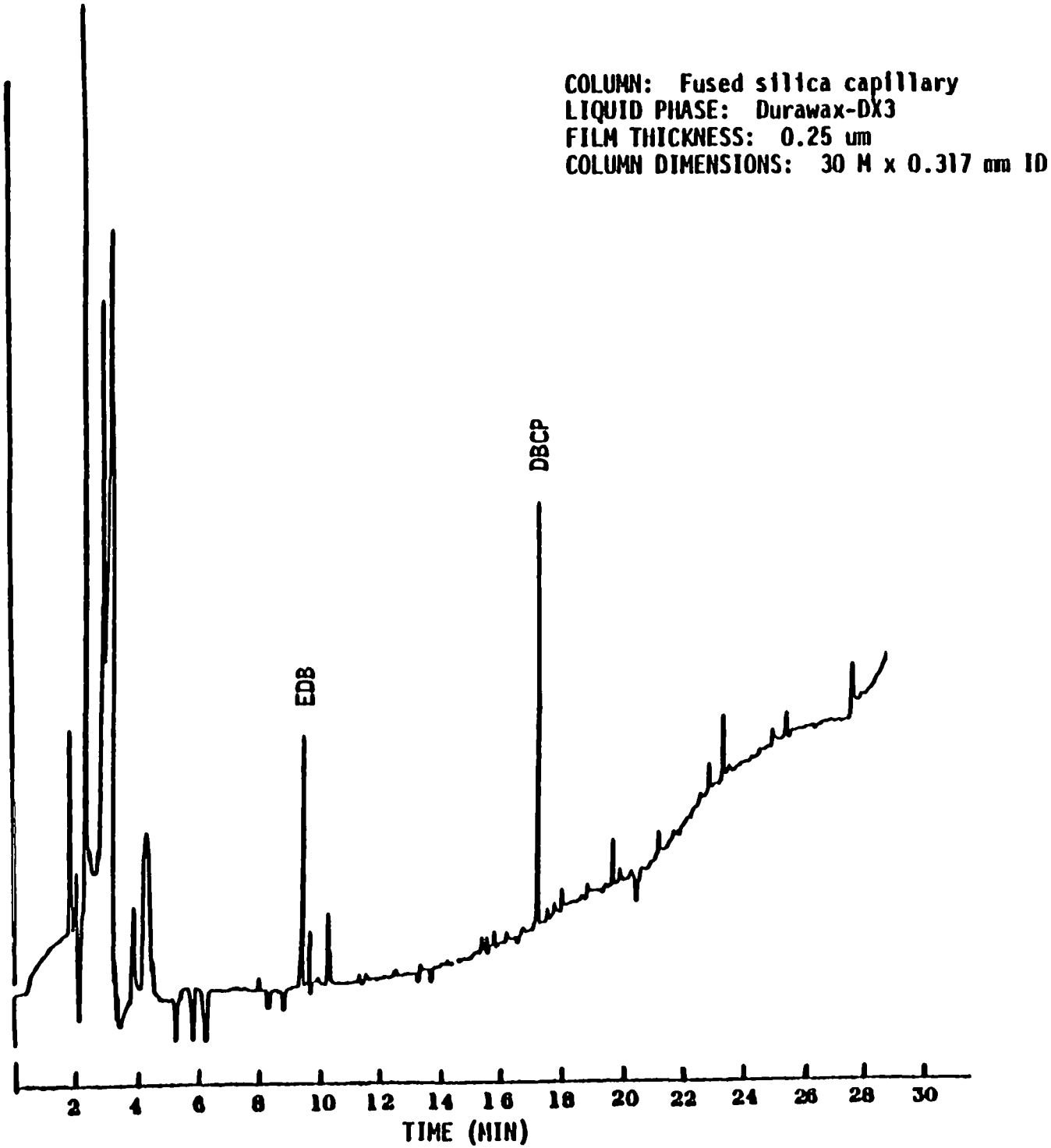

Figure 1. Extract of Reagent Water Spiked at 0.114 ug/L with EDB and DBCP

METHOD 524.1. VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY (Revised 1985)

1. SCOPE AND APPLICATION

1.1 This method is applicable for the determination of various volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage. (1) The following compounds can be determined by this method:

Analyte	Chemical Abstract Services Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4

Analyte	Chemical Abstract Services Registry Number
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
Methylene chloride	75-09-2
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 Method detection limits (MDLs) (2) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.2 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some geometrical isomers (i.e., xylenes) may be hampered by coelution.

1.3 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low µg/L level or by experienced technicians under the close supervision of a qualified analyst.

2. SUMMARY OF METHOD

2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is

complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components onto a gas chromatography (GC) column. The column is temperature programmed to separate the method analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph.

2.2 Tentative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is measured by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by a compound that is used as an internal standard.

3. INTERFERENCES

3.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks (Sect. 9.1.3) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Fig. 1). Subtracting blank values from sample results is not permitted.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of compounds being determined, it may be necessary to wash out the purging device with a soap solution, rinse it with reagent water, and then dry it in an oven at 105°C between analyses.

3.4 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from

stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4. SAFETY

4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (3-5) for the information of the analyst.

4.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

5.1 SAMPLE CONTAINERS - 60-mL to 120-mL screw cap vials (Pierce #19832 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12718 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

5.2 PURGE AND TRAP SYSTEM - The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

5.2.1 The all glass purging device (Fig. 1) must be designed to accept 25-mL samples with a water column at least 5 cm deep. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point $\leq$ 5 mm from the base of the water column.

5.2.2 The trap (Fig. 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. If it is not necessary to analyze for dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

5.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

5.2.4 The desorber must be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

5.2.5 Figures 3 and 4 show typical flow patterns for the purge-sorb and desorb mode.

5.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

5.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. The column oven may need to be cooled to <30°C (Sect. 10.3); therefore, a subambient oven controller may be required. The GC usually is interfaced to the MS with an all-glass enrichment device and an all-glass transfer line, but any enrichment device or transfer line can be used if the performance specifications described in Sect. 9.1 can be achieved.

5.3.2 Gas Chromatographic Column - 1.5 to 2.5 m x 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent. The flow rate of the helium carrier gas is established at 40 mL/min. The column temperature is programmed to hold at 45°C for three min, increase to 220°C at 8°C/min, and hold at 220°C for 15 min or until all expected compounds have eluted. During handling, packing, and programming, active sites can be exposed on the Carbopack-B packing which can result in tailing peak geometry and poor resolution of many constituents. Pneumatic shocks and rough treatment of packed columns will cause excessive fracturing of the Carbopack. If pressure in excess of 60 psi is required to obtain 40 mL/min carrier flow, the column should be repacked. A sample chromatogram obtained with this column is presented in Fig. 5.

5.3.3 Mass spectral data are obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must be capable of scanning from 35 to 450 amu every 7s or less and must produce a mass spectrum that meets all criteria in Table 2 when 50 ng or less of 4-bromofluorobenzene is introduced into the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

5.3.4 An interfaced data system (DS) is required to acquire, store, reduce and output mass spectral data. The computer software must allow searching any GC/MS data file for ions of a specific mass and plotting ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also allow integrating the abundance in any EICP between specified time or scan number limits.

5.4 SYRINGE AND SYRINGE VALVES

5.4.1 Two 25-mL glass hypodermic syringes with Luer-Lok tip.

5.4.2 Three 2-way syringe valves with Luer ends.

5.4.3 One 25-uL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

5.4.4 Micro syringes - 10, 100 uL.

5.4.5 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

5.5 MISCELLANEOUS

5.5.1 Standard solution storage containers - 15-mL bottles with PTFE-lined screw caps.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 TRAP PACKING MATERIALS

6.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.1.2 Methyl silicone packing (optional) - OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

6.1.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

6.1.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

6.2 COLUMN PACKING MATERIALS

6.2.1 1% SP-1000 on 60/80 mesh Carbopack-B or equivalent.

6.3 REAGENTS

6.3.1 Methanol - Demonstrated to be free of analytes.

6.3.2 Reagent water - Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

6.3.3 Hydrochloric acid (1+1) - Carefully add measured volume of conc. HCl to equal volume of reagent water.

6.3.4 Vinyl chloride - 99.9% pure vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm are available from several sources.

6.4 STANDARD STOCK SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

6.4.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

6.4.2 If the analyte is a liquid at room temperature, use a 100-µL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

6.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

6.4.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day.

6.5 SECONDARY DILUTION STANDARDS - Use standard stock solutions to prepare secondary dilution standard solutions that contain the analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions (Sect. 8.1) that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions for them. Storage times described for stock standard solutions in Sect. 6.4.4 also apply to secondary dilution standard solutions.

6.6 INTERNAL STANDARD SPIKING SOLUTION — Prepare a spiking solution containing fluorobenzene, and 1,2-dichlorobenzene-d_4 in methanol using the procedures described in Sect. 6.4 and 6.5. It is recommended that the secondary dilution standard be prepared at a concentration of 25 µg/mL of each internal standard compound. The addition of 10 µL of such a standard to 25.0 mL of sample or calibration standard would be equivalent to 10 µg/L.

6.7 BFB STANDARD — Prepare a 25-µg/mL solution of bromofluorobenzene in methanol.

6.8 LABORATORY QUALITY CONTROL STANDARD CONCENTRATE - Using standard stock solutions, prepare a solution containing each analyte of interest of a concentration of 500 times the MCL in methanol.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Collect all samples in duplicate. Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

7.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

7.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-quart container.

7.2 SAMPLE PRESERVATION

7.2.1 Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume.(6) Seal the sample bottles, PFTE-face down, and shake vigorously for one minute.

7.2.2 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

7.3 SAMPLE STORAGE

7.3.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

7.3.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 PREPARATION OF CALIBRATION STANDARDS

8.1.1 A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method.

8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be discarded after one hour unless sealed and stored as described in Sect. 7.2.2.

8.2 CALIBRATION

8.2.1 After meeting the BFB criteria in Sect. 10.1, analyze each calibration standard according to Sect. 10, adding 10 µL of internal standard spiking solution directly to the syringe. Tabulate area response of the characteristic m/z versus the concentration for each analyte and internal standard. Calculate response factors (RF) for each analyte using Equation 1:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Equation 1}$$

where:

A_s = Area of the characteristic m/z for the analyte to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard, in µg/L.

C_s = Concentration of the analyte to be measured, in µg/L.

The choice of which internal standard is used for an analyte is left to the analyst. Normally all aromatics are compared to 1,2-dichlorobenzene-d_4 and all other analytes are

compared to the internal standard having the closest relative retention time.

8.2.2 The results are used to prepare a calibration curve for each analyte. Alternatively, if the RF for an analyte is constant (less than 10% RSD) over the working range, the average RF can be used for that analyte.

8.2.3 The working calibration curve or average response factor must be verified on each working day by the measurement of one or more calibration standards. If the quantitation ion area for any analyte varies from the response determined for that standard concentration from the calibration curve or average RF established in Sect. 8.2.2 by more than ±20%, repeat steps 8.2.1 and 8.2.2.

8.2.4 Calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

8.2.4.1 Fill the purging device with 25.0 mL of reagent water or aqueous calibration standard.

8.2.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. Do not inject the standard through the aqueous sample inlet needle. Inject the gaseous standard before five min of the 11-min purge time have elapsed.

8.2.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with the equation:

$$S = 0.102\ (C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in ppm (v/v);
V = Volume of standard injected in milliliters.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this

program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. A quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.2.2) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

9.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.3. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but at least two samples per month.

9.1.5 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples. A procedure for low level check samples is described in Section 9.4.

9.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 9.5.

9.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

9.2.1 A quality control (QC) check sample concentrate is required containing each regulated analyte, and any additional analyte which is to be reported, at a concentration of 500 times the MCL or 5 µg/mL, whichever is smaller, in methanol. The QC check sample must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

9.2.2 Analyze seven 25-mL QC check samples at 1/5 MCL or 2 µg/L according to the method beginning in Sect. 10. Each sample is produced by injecting 10 µL of QC check sample concentrate into 25 mL of reagent water in a glass syringe through the syringe valve.

9.2.3 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L for each analyte using the seven results. Calculate the MDL for each analyte as specified in Ref. 2. The calculated MDL must be less than the spike level.

9.2.4 For each analyte, ($\bar{X}$) must be between 90% and 110% of the true value. Additionally, s must be $\leq$ 35% of $\bar{X}$. If s and $\bar{X}$ for all analytes meet the criteria, the system performance is acceptable and analysis of actual samples can begin. If any s exceeds the precision limit or any $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that analyte.
NOTE: The large number of analytes present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes are analyzed.

9.2.5 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 9.2.2 only for the analytes which failed the test.

9.3 The laboratory must demonstrate on a regular basis as outlined in Sect. 9.1.4 that the measurement system is in control by analyzing a quality control check sample for all analytes of interest at the MCL or 10 µg/L, whichever is smaller.

9.3.1 Prepare a QC check standard by adding 50 µL of QC check sample concentrate to 25 mL of regent water in a glass syringe.

9.3.2 Analyze the QC check according to Section 10, and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value.

9.3.3 If the recovery for any analyte falls outside the designated range, the analyte has failed the acceptance criteria. A check standard containing each analyte that failed must be re-analyzed.

9.4 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples.

9.4.1 Prepare a low level check sample by spiking 10 µL of QC check sample concentrate to 25 mL of reagent water and analyze according to the method in Sect. 10.

9.4.2 For each analyte, the recovery must be between 60% and 140% of the expected value.

9.4.3 When one or more analytes fail the test, the analyst must repeat the test only for those analytes which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 9.4.1.

9.5 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. PROCEDURE

10.1 DAILY GC/MS PERFORMANCE TESTS

10.1.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for BFB (7). The performance test must be passed before any samples, blanks, or standards are analyzed.

10.1.2 At the beginning of each day, inject 2 µL (50 ng) of BFB solution directly on the column. Alternatively, add 2 µL of BFB solution to 25.0 mL of reagent water or calibration standard and analyze the solution according to Sect. 10. Obtain a background-corrected mass spectrum of BFB and confirm that all the key m/z criteria in Table 2 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

10.2 INITIAL CONDITIONS

10.2.1 Acquire GC/MS data for performance tests, standards and samples using the following instrumental analytes:

Electron Energy:	70 V (nominal)
Mass Range:	35 to 300 amu
Scan Time:	To give at least 5 scans per peak but not to exceed 7 s per scan.

10.2.2 The operating conditions for the gas chromatograph are summarized under Section 5.3.2. Table 1 lists the retention times and MDL that can be achieved under these conditions. Examples of separations achieved with this method are shown in Figures 5. Other columns or chromatographic conditions may be used if the requirements of Section 9 are met.

10.3 SAMPLE INTRODUCTION AND PURGING

10.3.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

10.3.2 Remove the plungers from two 25-mL syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample (or standard) bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0 mL. Add 10 µL of the internal standard spiking solution (Section 6.5) to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

10.3.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 ± 0.1 min at ambient temperature (Fig. 3).

10.4 SAMPLE DESORPTION - After the 11-min purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Fig. 4) and initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 15 mL/min for 4.0 ± 0.1 min. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 25-mL flushes of reagent

water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

10.5 GAS CHROMATOGRAPHY - Hold the column temperature at 45°C for 3 min, then program at 8°C/min to 220°C and hold until all analytes elute.

10.6 TRAP RECONDITIONING - After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.7 TERMINATION OF DATA ACQUISITION - When sample components have eluted from the GC, terminate MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate EICPs. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11. QUALITATIVE IDENTIFICATION

11.1 IDENTIFICATION PROCEDURES CRITERIA — Tentatively identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in a collection. Use the following criteria to confirm a tentative identification:

11.1.1 The GC retention time of the sample component must be within 30 s of the time observed for that same compound when a calibration solution was analyzed.

11.1.2 All ions that are present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample component and should agree within absolute 10%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 20 to 40%.

11.1.3 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley

between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining EICPs of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria described in Section 11.1.2 can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.1.4 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

12. CALCULATIONS

12.1 When an analyte has been identified, the quantitation of that analyte should be based on the integrated abundance from the EICP of the primary characteristic m/z given in Table 4. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate. Instrument calibration for secondary ions is performed, as necessary, using the data and procedures described in Sect. 8.2.

12.2 Calculate the concentration in the sample using the calibration curve or average response factor (RF) determined in Sect. 8.2.2 and Equation 2:

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(C_{is})}{(A_{is})(RF)} \qquad \text{Equation 2.}$$

where:

A_s = Area of the characteristic m/z for the analyte to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard, in µg/L.

12.3 Report results in µg/L. All QC data obtained should be reported with the sample results.

13. ACCURACY AND PRECISION

13.1 This method was tested in a single laboratory using reagent water spiked at concentrations between 1 and 5 µg/L. (8) Single operator precision and accuracy data are presented for some selected analytes in Table 3.

13.2 Method detection limits have been calculated for some analytes from data collected in three laboratories. (1,8,9) These data are summarized in Table 1.

14. REFERENCES

1. A. Alford-Stevens, J.W. Eichelberger, W.L. Budde, "Purgeable Organic Compounds in Water by Gas Chromatography/ Mass Spectrometry, Method 524." Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1983.

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

3. "Carcinogens-Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August, 1977.

4. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. Bellar, T.A. and J.J. Lichtenberg, "The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, January 1985.

7. Budde, W.L. and Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

8. Slater, R.W., "Method Detection Limits for Drinking Water Volatiles," Unpublished report, March 1985.

9. Sorrell, R.K., Private Communication, May 1985.

Table 1. CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON WIDE BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (mins)		MDL (µg/L)
	Column 1[a]	Column 2[b]	
Dichlorodifluoromethane	1.55	0.70	0.10
Chloromethane	1.63	0.73	0.13
Vinyl chloride	1.71	0.79	0.17
Bromomethane	2.01	0.96	0.11
Chloroethane	2.09	1.02	0.10
Trichlorofluoromethane	2.27	1.19	0.08
1,1-Dichloroethene	2.89	1.57	0.12
Methylene Chloride	3.60	2.06	0.03
trans-1,2-Dichloroethene	3.98	2.36	0.06
1,1-Dichloroethane	4.85	2.93	0.04
2,2-Dichloropropane	6.01	3.80	0.35
cis-1,2-Dichloroethene	6.19	3.90	0.12
Chloroform	6.40	4.80	0.03
Bromochloromethane	6.74	4.38	0.04
1,1,1-Trichloroethane	7.27	4.84	0.08
Carbon Tetrachloride	7.61	5.26	0.21
1,1-Dichloropropene	7.68	5.29	[illegible]
Benzene	8.23	5.67	[illegible]
1,2-Dichloroethane	8.40	5.83	0.06
Trichloroethene	9.59	7.27	0.19
1,2-Dichloropropane	10.09	7.66	0.04
Bromodichloromethane	10.59	8.49	0.08
Dibromomethane	10.65	7.93	0.24
Toluene	12.43	10.00	0.11
1,1,2-Trichloroethane	13.41	11.05	0.10
Tetrachloroethene	13.74	11.15	0.14
1,3-Dichloropropane	14.04	11.31	0.04
Dibromochloromethane	14.39	11.85	0.05
1,2-Dibromoethane	14.73	11.83	0.06
1-Chlorohexane	15.46	13.29	0.05
Chlorobenzene	15.76	13.01	0.04
1,1,1,2-Tetrachloroethane	15.94	13.33	0.05
Ethylbenzene	15.99	13.39	0.06
p-Xylene	16.12	13.69	0.13
m-Xylene	16.17	13.68	0.05
o-Xylene	17.11	14.52	0.11
Styrene	17.31	14.60	0.04
Bromoform	17.93	14.88	0.12
Isopropylbenzene	18.06	15.46	0.15
1,1,2,2-Tetrachloroethane	18.72	16.35	0.04
Bromobenzene	18.95	15.86	0.03

Table 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS

Analyte	Retention Time[1] (min)	Method Detection Limits (µg/L) Ref. 1	Ref. 8	Ref. 9
Vinyl chloride	3.8	—[2]	0.31	—
Dichlorodifluoromethane	3.8	—	0.33	—
Methylene chloride	6.4	0.25	0.13	—
Trichlorofluoromethane	8.3	—	0.21	—
1,1-Dichloroethene	9.0	0.27	0.19	—
Bromochloromethane	9.3	—	—	—
1,1-Dichloroethane	10.1	—	0.17	—
trans-1,2-Dichloroethene	10.8	1.7	0.19	0.2
Chloroform	11.4	0.20	0.24	0.1
Dibromomethane	12.1	—	0.30	—
1,2-Dichloroethane	12.1	0.35	0.22	0.2
2,2-Dichloropropane	12.7	—	—	—
1,1,1-Trichloroethane	13.4	0.13	0.26	0.2
Carbon tetrachloride	13.7	0.13	0.28	0.2
Bromodichloromethane	14.3	0.29	0.28	0.2
1,2-Dichloropropane	15.7	—	0.17	—
1,1-Dichloropropene	16.0	—	—	—
Trichloroethene	16.5	0.18	0.36	0.2
Benzene	17.0	0.21	0.10	0.2
Dibromochloromethane	17.1	0.34	0.30	0.2
1,2-Dibromoethane	17.9	—	0.36	—
1,3-Dichloropropane	18.4	—	0.10	—
Bromoform	19.8	0.34	0.66	0.5
1,1,2,2-Tetrachloroethane	22.1	0.28	0.41	—
Tetrachloroethene	22.2	0.07	0.29	0.2
Toluene	23.5	0.08	0.12	0.2
Chlorobenzene	24.6	0.09	0.14	0.2
1,2-Dibromo-3-chloropropane	25.8	—	1.8	—
Bromobenzene	26.7	—	0.12	—
Isopropylbenzene	28.5	—	—	—
m-Xylene	29.5	—	—	—
Styrene	29.7	1.3	0.20	—
n-Propylbenzene	30.7	—	—	—
o-Xylene	30.9	—	0.20	—
p-Xylene	30.9	0.18	0.13	—
t-Butylbenzene	31.5	—	—	—

Table 1. (Continued)

ANALYTE	RETENTION TIME (mins)		MDL (µg/L)
	Column 1[a]	Column 2[b]	
1,2,3-Trichloropropane	19.02	16.23	0.32
n-Propylbenzene	19.06	16.41	0.04
2-Chlorotoluene	19.34	16.42	0.04
1,3,5-Trimethylbenzene	19.47	16.90	0.05
4-Chlorotoluene	19.50	16.72	0.06
tert-Butylbenzene	20.28	17.57	0.14
1,2,4-Trimethylbenzene	20.34	17.70	0.13
sec-Butylbenzene	20.79	18.09	0.13
p-Isopropyltoluene	21.20	18.52	0.12
1,3-Dichlorobenzene	21.22	18.14	0.12
1,4-Dichlorobenzene	21.55	18.39	0.03
n-Butylbenzene	22.22	19.49	0.11
1,2-Dichlorobenzene	22.52	19.17	0.03
1,2-Dibromo-3-Chloropropane	24.53	21.08	0.26
1,2,4-Trichlorobenzene	26.55	23.08	0.04
Hexachlorobutadiene	26.99	23.68	0.11
Naphthalene	27.17	23.52	0.04
1,2,3-Trichlorobenzene	27.78	24.18	0.03
INTERNAL STANDARDS/SURROGATES			
Fluorobenzene	8.81	6.45	
p-Bromofluorobenzene	18.63	15.71	
1,2-Dichlorobenzene-d_4	22.26	19.14	

[a]Column 1 - 60 meter x 0.75mm ID VOCOL capillary. Hold at 10°C for 5 min, then program to 160°C at 6°/min.

[b]Column 2 - 30 meter x 0.53mm ID DB-624 mega-bore capillary. Hold at 10°C for 5 min, then program to 160°C at 6°/min.

Table 1. (Continued)

Analyte	Retention Time[1] (min)	Method Detection Limits (µg/L) - Ref. 1	Ref. 8	Ref. 9
2-Chlorotoluene	31.5	—	—	—
Hexachlorobutadiene	32.0	—	—	—
4-Chlorotoluene	32.5	—	—	—
sec-Butylbenzene	32.5	—	—	—
1,2-Dichlorobenzene	35.0	—	1.0	—
1,4-Dichlorobenzene	35.3	0.3	2.0	0.1

1 Column Conditions: 2 m x 2 mm ID glass column packed with Carbopack B (60-80 mesh) coated with 1% SP-1000. Carrier gas - Helium at flow of 30 mL/min. Column temperature held at 45°C for 3 min, then programmed at 8°C/min to 220°C and held until all analytes elute.

2 Not Determined

Table 2. CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON NARROW BORE CAPILLARY COLUMN

ANALYTE	RETENTION TIME (mins) Column 3	MDL (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.06
Chloroethane	1.45	0.02
Trichlorofluoromethane	1.77	0.07
1,1-Dichloroethene	2.33	0.05
Methylene Chloride	2.66	0.09
trans-1,2-Dichloroethene	3.54	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon Tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.10
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10

Table 2. (Continued)

ANALYTE	RETENTION TIME (mins)	MDL (µg/L)
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-Chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14
INTERNAL STANDARD		
Fluorobenzene	8.81	6.45

Column - 30 meter x 0.32mm ID DB-5 capillary with µm film thickness

Table 2. BFB KEY m/z ABUNDANCE CRITERIA

Mass	m/z Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

Table 3. SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER

Analyte	Conc. Tested ug/L	Number of Samples	Average Conc. Measured ug/L	Standard Deviation ug/L	Percent Rel. Std. Dev.
Benzene	1.0	8	0.97	0.036	3.6
Bromobenzene	1.0	8	0.92	0.042	4.6
Bromodichloromethane	1.5	8	1.43	0.096	6.7
Bromoform	2.5	8	2.36	0.23	9.7
Carbon tetrachloride	1.0	8	0.88	0.098	11.1
Chlorobenzene	1.0	8	1.02	0.047	4.6
Chloroform	1.0	8	1.03	0.086	8.4
Dibromochloromethane	1.5	8	1.49	0.10	7.0
1,2-Dibromo-3-chloropropane	3.0	8	3.4	0.63	18.2
1,2-Dibromoethane	1.0	8	0.93	0.13	13.6
Dibromomethane	1.0	8	0.94	0.11	11.4
1,2-Dichlorobenzene	5.0	8	4.95	0.35	7.1
1,4-Dichlorobenzene	5.0	8	5.27	0.72	13.6
Dichlorodifluoromethane	1.0	8	0.96	0.11	11.9
1,1-Dichloroethane	1.0	8	1.05	0.060	5.9
1,2-Dichloroethane	1.0	8	0.97	0.077	7.9
1,1-Dichloroethene	1.0	8	1.09	0.066	6.1
trans-1,2-Dichloroethene	1.0	8	0.98	0.066	6.8
1,2-Dichloropropane	1.0	8	1.01	0.060	5.9
1,3-Dichloropropane	1.0	8	1.00	0.033	3.4
Methylene chloride	1.0	7	0.99	0.045	4.5
Styrene	1.0	8	1.06	0.066	6.2
1,1,2,2-Tetrachloroethane	1.0	8	1.11	0.14	12.8
Tetrachloroethene	1.0	8	0.93	0.10	10.9
Toluene	1.0	8	1.05	0.043	4.1
1,1,1-Trichloroethane	1.0	8	1.05	0.093	8.8
Trichloroethene	1.0	8	0.90	0.12	13.6
Trichlorofluoromethane	1.0	7	1.09	0.072	6.6
Vinyl chloride	1.0	8	0.98	0.11	10.8
o-Xylene	1.0	8	1.02	0.068	6.7
p-Xylene	1.0	8	1.11	0.047	4.2

Table 3. BFB KEY m/z ABUNDANCE CRITERIA

Mass	m/z Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

Table 4. SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER DETERMINED WITH A WIDE BORE CAPILLARY COLUMN

Analyte	Conc. Range, µg/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Benzene	0.1 - 10	31	97	5.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichloroethane	0.5 - 10	24	96	5.1	5.3
1,2-Dichloroethane	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2 Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.5
p-Isopropyltoluene	0.1 - 10	23	99	6.7	5.7

Table 4. CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANICS COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ions
Benzene	78	-
Bromobenzene	156	77,158
Bromochloromethane	128	49,130
Bromodichloromethane	83	85,127
Bromoform	173	175,254
Bromomethane	94	96
n-Butylbenzene	91	92,134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91,134
Carbon tetrachloride	117	119
Chlorobenzene	112	77,114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-Chloropropane	75	155,157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109,188
Dibromomethane	93	95,174
1,2-Dichlorobenzene	146	111,148
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65,83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61,63
cis-1,2-Dichloroethene	96	61,98
trans-1,2-Dichloroethene	96	61,98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110,77
Ethylbenzene	91	106
Hexachlorobutadiene	225	223,227
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134,91
Methylene chloride	84	86,49
Naphthalene	128	-
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133,119

Table 4. (Continued)

Analyte	Conc. Range, µg/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Methylene chloride	0.1 - 10	30	95	5.0	5.3
Naphthalene	0.1 - 100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 - 100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

a. Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

b. Standard deviation was calculated by pooling data from three levels.

Table 4. (Continued)

Analyte	Primary Ion	Secondary Ions
1,1,2,2-Tetrachloroethane	83	131,85
Tetrachloroethene	166	168,129
Toluene	92	
1,1,1-Trichloroethane	97	99,61
1,1,2-Trichloroethane	83	97,85
Trichloroethene	95	130,132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
Vinyl Chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
Fluorobenzene	96	70
1,2-Dichlorobenzene-d_4	150	115,152
p-Bromofluorobenzene	95	174,176

Table 5. SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER DETERMINED ON A NARROW BORE CAPILLARY COLUMN

Analyte	Conc, µg/L	Number of Samples	Recovery,[a] %	Standard Deviation	Percent Rel. Std. Dev.
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2 Dichloroethene	0.1	7	100	3.7	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5

Table 5. (Continued)

Analyte	Conc, µg/L	Number of Samples	Recovery,[a] %	Standard Deviation	Percent Rel. Std. Dev.
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

a. Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

Table 6. CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANICS COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ions
Benzene	78	-
Bromobenzene	156	77,158
Bromochloromethane	128	49,130
Bromodichloromethane	83	85,127
Bromoform	173	175,254
Bromomethane	94	96
n-Butylbenzene	91	92,134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91,134
Carbon tetrachloride	117	119
Chlorobenzene	112	77,114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-Chloropropane	75	155,157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109,188
Dibromomethane	93	95,174
1,2-Dichlorobenzene	146	111,148
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65,83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61,63
cis-1,2-Dichloroethene	96	61,98
trans-1,2-Dichloroethene	96	61,98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110,77
Ethylbenzene	91	106
Hexachlorobutadiene	225	223,227
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134,91
Methylene chloride	84	86,49
Naphthalene	128	-
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133,119

Table 6. (Continued)

Analyte	Primary Ion	Secondary Ions
1,1,2,2-Tetrachloroethane	83	131,85
Tetrachloroethene	166	168,129
Toluene	92	91
1,2,3-Trichlorobenzene	180	182,145
1,2,4-Trichlorobenzene	180	182,145
1,1,1-Trichloroethane	97	99,61
1,1,2-Trichloroethane	83	97,85
Trichloroethene	95	130,132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl Chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
Fluorobenzene	96	70
1,2-Dichlorobenzene-d_4	150	115,152
p-Bromofluorobenzene	95	174,176

METHOD 524.2. VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY (August, 1986)

1. SCOPE AND APPLICATION

1.1 This method is applicable for the determination of various volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage. (1) The following compounds can be determined by this method:

Analyte	Chemical Abstract Services Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4

Analyte	Chemical Abstract Services Registry Number
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
Methylene chloride	75-09-2
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 Method detection limits (MDLs) (2) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some geometrical isomers (i.e., xylenes) may be hampered by coelution.

1.3 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low µg/L level or by experienced technicians under the close supervision of a qualified analyst.

2. SUMMARY OF METHOD

2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through a 25 mL aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis. The column is temperature programmed to separate the method analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph.

Wide-bore capillary columns generally require a jet separator, whereas narrow-bore capillaries can be directly interfaced to the ion source.

2.2 Tentative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is measured by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by a compound that is used as an internal standard.

3. INTERFERENCES

3.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks (Sect. 9.1.3) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Fig. 1). Subtracting blank values from sample results is not permitted.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of compounds being determined, it may be necessary to wash out the purging device with a soap solution, rinse it with reagent water, and then dry it in an oven at 105°C between analyses.

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4. SAFETY

4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (3-5) for the information of the analyst.

4.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

5.1 SAMPLE CONTAINERS - 60-mL to 120-mL screw cap vials (Pierce #19832 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12718 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

5.2 PURGE AND TRAP SYSTEM - The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

5.2.1 The all glass purging device (Fig. 1) must be designed to accept 25-mL samples with a water column at least 5 cm deep. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point $\leq$ 5 mm from the base of the water column.

5.2.2 The trap (Fig. 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

5.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the adsorbent from aerosols, and also of insuring that the adsorbent is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

5.2.4 The desorber must be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

5.2.5 Figures 3 and 4 show typical flow patterns for the purge-sorb and desorb modes.

5.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

5.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. The column oven must be cooled to <30°C, therefore, a subambient oven controller is required. The GC usually is interfaced to the MS with an all-glass enrichment device and an all-glass transfer line, but any enrichment device or transfer line can be used if the performance specifications described in Sect. 9.2.5 can be achieved.

5.3.2 Gas Chromatographic Column 1 - 60m long x 0.75mm ID VOCOL (Supelco, Inc.) wide-bore capillary column with 1.5 µm film thickness. The flow rate of helium carrier gas is established at 15 mL/min. The column temperature is held for 5 minutes at 10°C, then programmed to 160°C at 6°C/min, and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Fig. 5. This column was used to develop the method performance statements in Section 13.

5.3.3 Gas Chromatographic Column 2 - 30m long x 0.53mm ID DB-624 Mega-Bore (J&W Scientific, Inc.) column with 3 µm film thickness. Helium carrier gas flow is 15 mL/min. The column temperature is held for 5 minutes at 10°C, then programmed to 160°C at 6°C/min. A sample chromatogram obtained with this column is presented in Fig. 6.

5.3.4 Gas Chromatographic Column 3 - 30 meter long x 0.32mm ID fused silica capillary column coated with Durabond DB-5 (J&W Scientific, Inc.) with a 1um film thickness. Helium carrier gas flow is 4.0 mL/min. The column is maintained at 10°C for 5 mins, then programmed at 6°/min for 10 min than 15°/min for 5 min to 145°C. A sample chromatogram obtained with this column is presented in Fig. 7.

5.3.5 Mass spectral data are obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must be capable of scanning from 35 to 300 amu every 2s or less and must produce a mass spectrum that meets all criteria in Table 3 when 50 ng or less of 4-bromofluorobenzene is introduced into the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

5.3.6 An interfaced data system (DS) is required to acquire, store, reduce and output mass spectral data. The computer software must allow searching any GC/MS data file for ions of a specific mass and plotting ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also allow integrating the abundance in any EICP between specified time or scan number limits.

5.4 CAPILLARY INTERFACE - The device interfaces the purge and trap concentrator to the capillary gas chromatograph. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused silica capillary pre-column. When the interface is flash heated the sample is transferred to the analytical capillary column.

5.4.1 Under a stream of liquid nitrogen, the temperature of the fused silica in the interface is maintained at -150°C during the cryofocusing step. After the desorption period, the interface must be capable of rapid heating to +250°C in 15 sec. or less to complete the transfer of analytes.

5.5 SYRINGE AND SYRINGE VALVES

5.5.1 Two 25-mL glass hypodermic syringes with Luer-Lok tip.

5.5.2 Three 2-way syringe valves with Luer ends.

5.5.3 Micro syringes - 10, 25, 100 µL.

5.5.4 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

5.6 MISCELLANEOUS

5.6.1 Standard solution storage containers - 15-mL bottles with PTFE-lined screw caps.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 TRAP PACKING MATERIALS

6.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.1.2 Methyl silicone packing (optional) - OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

6.1.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

6.1.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

6.2 REAGENTS

6.2.1 Methanol - Demonstrated to be free of analytes.

6.2.2 Reagent water - Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

6.2.3 Hydrochloric acid (1+1) - Carefully add measured volume of conc. HCl to equal volume of reagent water.

6.2.4 Vinyl chloride - 99.9% pure vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

6.3 STANDARD STOCK SOLUTIONS

These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

6.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

6.3.2 If the analyte is a liquid at room temperature, use a 100-uL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

6.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

6.3.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day.

6.4 SECONDARY DILUTION STANDARDS - Use standard stock solutions to prepare secondary dilution standard solutions that contain the analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions (Sect. 8.1) that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions from them. Storage times described for stock standard solutions in Sect. 6.3.4 also apply to secondary dilution standard solutions.

6.5 INTERNAL STANDARD SPIKING SOLUTION — Prepare a spiking solution containing fluorobenzene, and 1,2-dichlorobenzene-d_4 in methanol using the procedures described in Sect. 6.3 and 6.4. It is recommended that the secondary dilution standard be prepared at a concentration of 25 ug/mL of each internal standard compound. The addition of 10 uL of such a standard to 25.0 mL of sample or calibration standard would be equivalent to 10 ug/L.

6.6 BFB STANDARD — Prepare a 25-ug/mL solution of bromofluorobenzene in methanol.

6.7 LABORATORY QUALITY CONTROL STANDARD CONCENTRATE - Using standard stock solutions, prepare a solution containing each analyte of interest at a concentration of 500 times the MCL in methanol.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Collect all samples in duplicate. Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

7.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

7.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the container.

7.2 SAMPLE PRESERVATION

7.2.1 Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume.(6) Seal the sample bottles, PFTE-face down, and shake vigorously for one minute.

7.2.2 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

7.3 SAMPLE STORAGE

7.3.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

7.3.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 PREPARATION OF CALIBRATION STANDARDS

8.1.1 A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method.

8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be discarded after one hour unless sealed and stored as described in Sect. 7.2.

8.2 CALIBRATION

8.2.1 After meeting the BFB criteria in Sect. 10.1, analyze each calibration standard according to Sect. 10, adding 10 µL of internal standard spiking solution directly to the syringe. For each analyte, select a significant characteristic ion. When feasible, use the most intense ion in the mass spectrum; when a less intense ion is more characteristic and sufficiently intense to provide necessary sensitivity, use that ion to avoid possible interferences. Tabulate area response of the characteristic m/z versus the concentration for each analyte and internal standard. Calculate response factors (RF) for each analyte using Equation 1:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Equation 1}$$

where:

A_s = Area of the characteristic m/z for the analyte to be measured;

A_{is} = Area of the characteristic m/z for the internal standard;

C_{is} = Concentration of the internal standard, in µg/L.
C_s = Concentration of the analyte to be measured, in µg/L.

The choice of which internal standard to use for an analyte is left to the analyst.

8.2.2 Prepare a calibration curve for each analyte. Alternatively, if the RF for an analyte is constant (less than 10% RSD) over the working range, the average RF can be used for that analyte.

8.2.3 The working calibration curve or average response factor must be verified on each working day by the measurement of one or more calibration standards. If the quantitation ion area for any analyte varies from the response determined for that standard concentration from the calibration curve or average RF established in Sect. 8.2.2 by more than ±20%, repeat steps 8.2.1 and 8.2.2.

8.2.4 Calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

8.2.4.1 Fill the purging device with 25.0 mL of reagent water or aqueous calibration standard.

8.2.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. Do not inject the standard through the aqueous sample inlet needle. Inject the gaseous standard before five min of the 11-min purge time have elapsed.

8.2.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with the equation:

$$S = 0.102\ (C)(V) \qquad \text{Equation 2}$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in ppm;
V = Volume of standard injected in milliliters.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. A quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.2.2) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

9.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.3. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but at least two samples per month.

9.1.5 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples. A procedure for low level check samples is described in Section 9.4.

9.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 9.5.

9.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

9.2.1 A quality control (QC) check sample concentrate is required containing each regulated analyte, and any additional analyte which is to be reported, at a concentration of 500 times the MCL or 5 µg/mL, whichever is smaller, in methanol. The QC check sample must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

9.2.2 Analyze seven 25-mL QC check samples at 1/5 MCL or 2 µg/L according to the method beginning in Sect. 10. Each sample is produced by injecting 10 µL of QC check sample concentrate into 25 mL of reagent water in a glass syringe through the syringe valve.

9.2.3 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L for each analyte using the seven results. Calculate the MDL for each analyte as specified in Ref. 2. The calculated MDL must be less than the spike level.

9.2.4 For each analyte, ($\bar{X}$) must be between 90% and 110% of the true value. Additionally, s must be $\leq$ 35% of $\bar{X}$. If s and $\bar{X}$ for all analytes meet the criteria, the system performance is acceptable and analysis of actual samples can begin. If any s exceeds the precision limit or any $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that analyte.
NOTE: The large number of analytes present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes are analyzed.

9.2.5 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 9.2.2 only for the analytes which failed the test.

9.3 The laboratory must demonstrate on a regular basis as outlined in Section 9.1.4 that the measurement system is in control by analyzing a quality control check sample for all analytes of interest at the MCL or 10 µg/L, whichever is smaller.

9.3.1 Prepare a QC check standard by adding 50 µL of QC check sample concentrate to 25 mL of regent water in a glass syringe.

9.3.2 Analyze the QC check according to Section 10, and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value.

9.3.3 If the recovery for any analyte falls outside the designated range, the analyte has failed the acceptance criteria. A check standard containing each analyte that failed must be re-analyzed.

9.4 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples.

9.4.1 Prepare a low level check sample by spiking 10 uL of QC check sample concentrate to 25 mL of reagent water and analyze according to the method in Sect. 10.

9.4.2 For each analyte, the recovery must be between 60% and 140% of the expected value.

9.4.3 When one or more analytes fail the test, the analyst must repeat the test only for those analytes which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 9.4.1.

9.5 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. PROCEDURE

10.1 DAILY GC/MS PERFORMANCE TESTS

10.1.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for BFB (7). The performance test must be passed before any samples, blanks, or standards are analyzed.

10.1.2 At the beginning of each day, inject 2 uL (50 ng) of BFB solution directly on the column. Alternatively, add 2 uL of BFB solution to 25.0 mL of reagent water or calibration standard and analyze the solution according to Sect. 10. Obtain a background-corrected mass spectrum of BFB and confirm that all the key m/z criteria in Table 3 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

10.2 INITIAL CONDITIONS

10.2.1 Acquire GC/MS data for performance tests, standards and samples using the following instrumental analytes:

Electron Energy:	70 V (nominal)
Mass Range:	35 to 300 amu
Scan Time:	To give at least 5 scans per peak but not to exceed 2 s per scan.

10.2.2 The operating conditions for the gas chromatograph are summarized under Sections 5.3.2 through 5.3.4.. Tables 1 and 2 list the retention times and MDL that can be achieved under these conditions. Examples of separations achieved with this method are shown in Figures 5–7. Other columns or chromatographic conditions may be used if the requirements of Section 9 are met.

10.3 SAMPLE INTRODUCTION AND PURGING

10.3.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

10.3.2 Remove the plungers from two 25-mL syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample (or standard) bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0 mL. Add 10 µL of the internal standard spiking solution (Section 6.5) to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

10.3.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 ± 0.1 min at ambient temperature (Fig. 3).

10.4 SAMPLE DESORPTION - The mode of sample desorption is determined by the type of capillary column employed for the analysis. When using a wide-bore capillary column, follow the desorption conditions of Sect. 10.4.1. The conditions for using narrow bore columns is described in Sect. 10.4.2.

10.4.1 Sample Desorption for Wide-Bore Capillary Column

Under most conditions, this type of column must be interfaced to the MS through an all-glass jet separator.

10.4.1.1 After the 11-min purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Fig. 4) and initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 15 mL/min for 4.0 * 0.1 min. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 25-mL flushes of reagent water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

10.4.1.2 Gas Chromatography - Hold the column temperature at 10°C for 5 min, then program at 6°C/min to 160°C and hold until all analytes elute.

10.4.1.3 Trap Reconditioning - After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.4.2 Sample Desorption for Narrow-Bore Capillary Column

Under normal operating conditions, most narrow-bore capillary columns can be interfaced directly to the MS without a jet separator.

10.4.2.1 Sample Desorption - After the 11 min purge, attach the trap to the cryogenically cooled interface at -150°C and adjust the purge and trap system to the desorb mode (Fig. 4). Introduce the trapped materials to the interface by rapidly heating the trap to 180°C while backflushing the trap with an

inert gas at 4 mL/min for 5.0 ± 0.1 min. While the extracted sample is being introduced into the interface, empty the purging device using the sample syringe and rinse the chamber with two 25-mL flushes of reagent water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle. After desorbing for 5 min, flash heat the interface to 250°C and quickly introduce the sample on the chromatographic column. Start the temperature program sequence, and initiate data acquisition.

10.4.2.2 Gas Chromatography - Hold the column temperature at 10°C for 5 min, then program at 6°C/min to 70°C and then at 15°/min to 145°C.

10.3.2.3 Trap Reconditioning - After desorbing the sample for 5 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.5 TERMINATION OF DATA ACQUISITION - When sample components have eluted from the GC, terminate MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate EICPs. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11. QUALITATIVE IDENTIFICATION

11.1 IDENTIFICATION PROCEDURES CRITERIA — Tentatively identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in a collection. Use the following criteria to confirm a tentative identification:

11.1.1 The GC retention time of the sample component must be within 10 s of the time observed for that same compound when a calibration solution was analyzed.

11.1.2 All ions that are present above 10% relative abundance in the mass spectrum of the standard must be present in the

mass spectrum of the sample component and should agree within absolute 10%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 20 to 40%.

11.1.3 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining EICPs of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria described in Section 11.1.2 can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.1.4 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

12. CALCULATIONS

12.1 When an analyte has been identified, the quantitation of that analyte should be based on the integrated abundance from the EICP of the primary characteristic m/z given in Table 6. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate. Instrument calibration for secondary ions is performed, as necessary, using the data and procedures described in Sect. 8.2.

12.2 Calculate the concentration in the sample using the calibration curve or average response factor (RF) determined in Sect. 8.2.2 and Equation 3:

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(C_{is})}{(A_{is})(RF)} \qquad \text{Equation 3.}$$

where:

A_s = Area of the characteristic m/z for the analyte to be measured;
A_{is} = Area of the characteristic m/z for the internal standard;
C_{is} = Concentration of the internal standard, in µg/L.

12.3 Report results in µg/L. All QC data obtained should be reported with the sample results.

13. ACCURACY AND PRECISION

13.1 This method has been tested in a single laboratory using spiked reagent water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L (8). Single laboratory accuracy and precision data are presented for the method analytes in Table 4. Calculated MDLs are presented in Table 1.

13.2 The method was tested using reagent water spike at 0.1 to 0.5 µg/L and analyzed on a cryofocused narrow-bore column. The accuracy and precision data for these compounds are presented in Table 5 (9). MDL values were also calculated from these data and are presented in Table 2.

14. REFERENCES

1. A. Alford-Stevens, J.W. Eichelberger, W.L. Budde, "Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry, Method 524." Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1983.

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

3. "Carcinogens-Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August, 1977.

4. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. Bellar, T.A. and J.J. Lichtenberg, "The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, January 1985.

7. Budde, W.L. and Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

8. Slater, R.W., "Method Detection Limits for Drinking Water Volatiles," Unpublished report, June 1986.

9. Madding, C., Memorandum to H. Brass, June 1986.

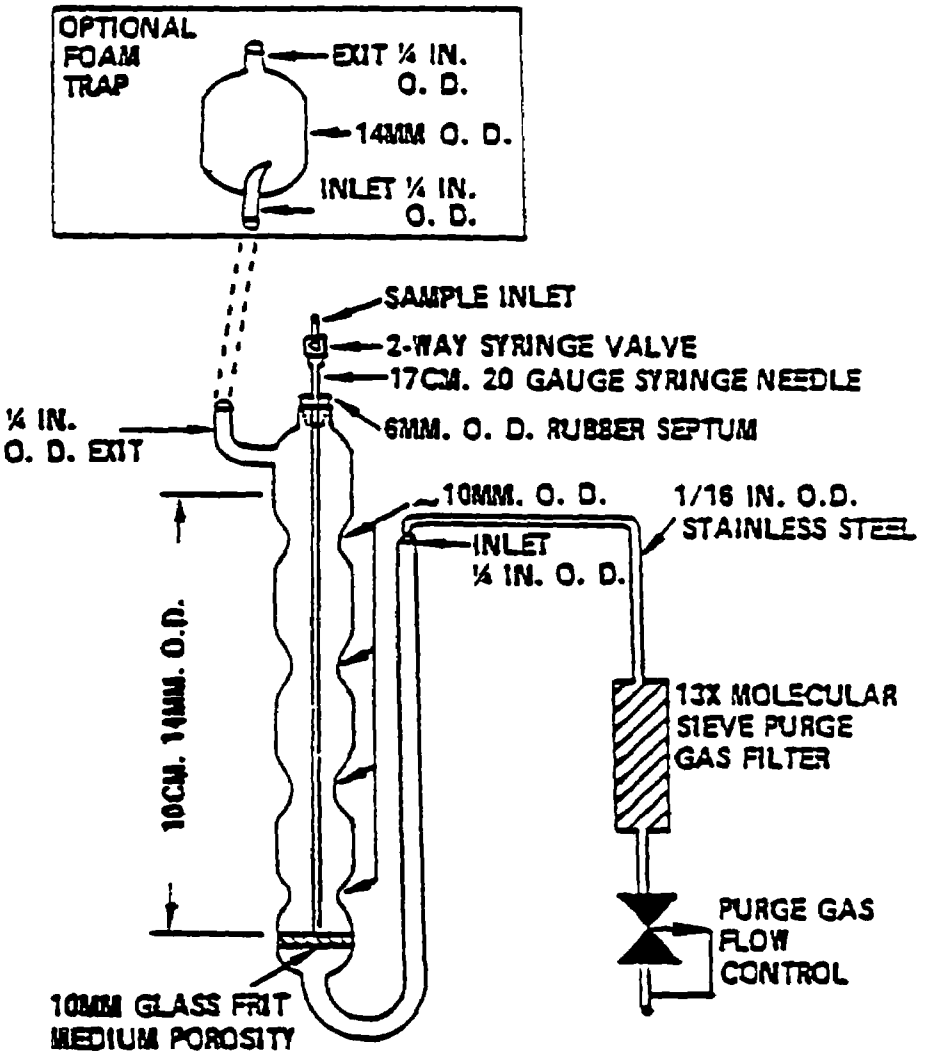

Figure 1. Purging device

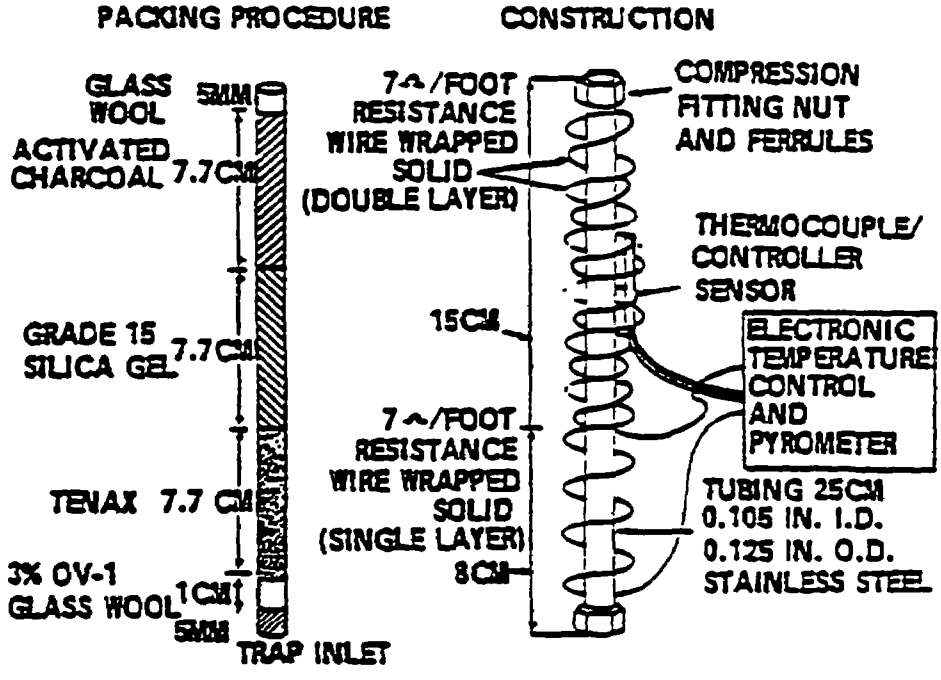

Figure 2. Trap packings and construction to include desorb capability

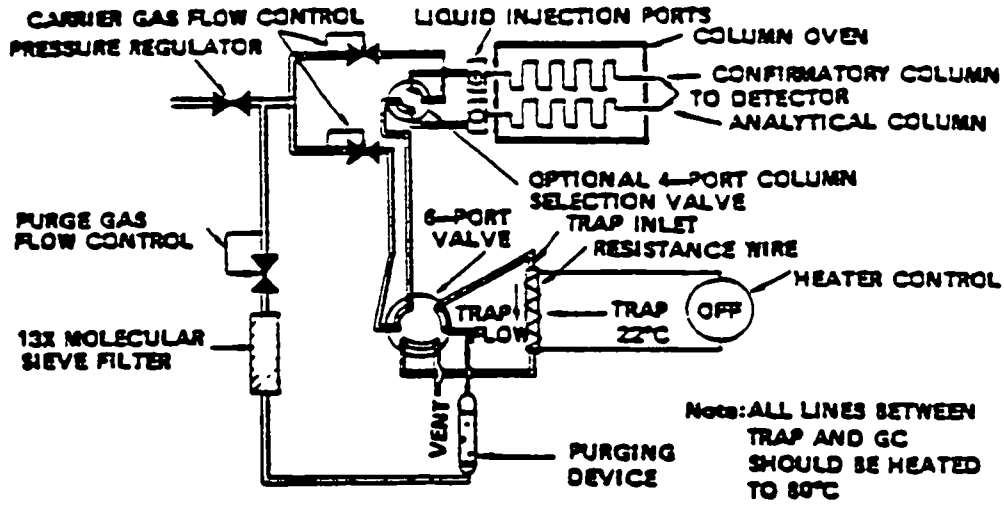

Figure 3. Purge and trap system - purge mode.

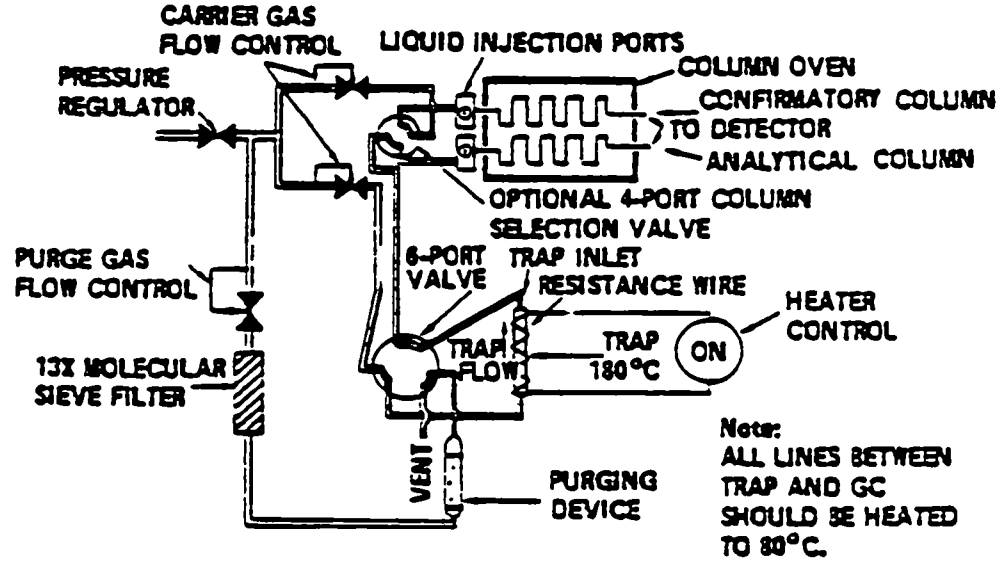

Figure 4. Schematic of purge and trap device - desorb mode

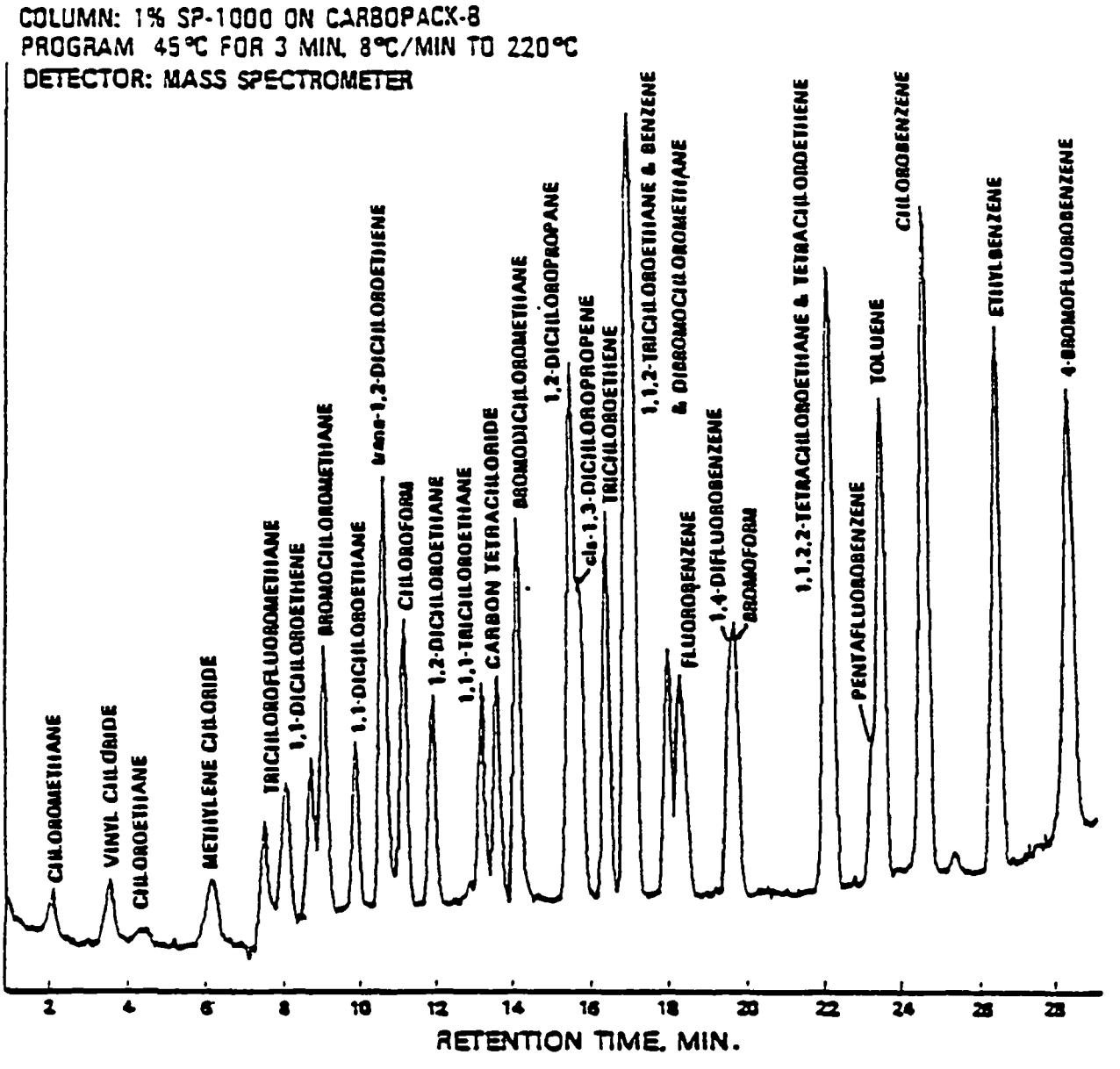

Figure 5. Gas chromatogram of volatile organics.

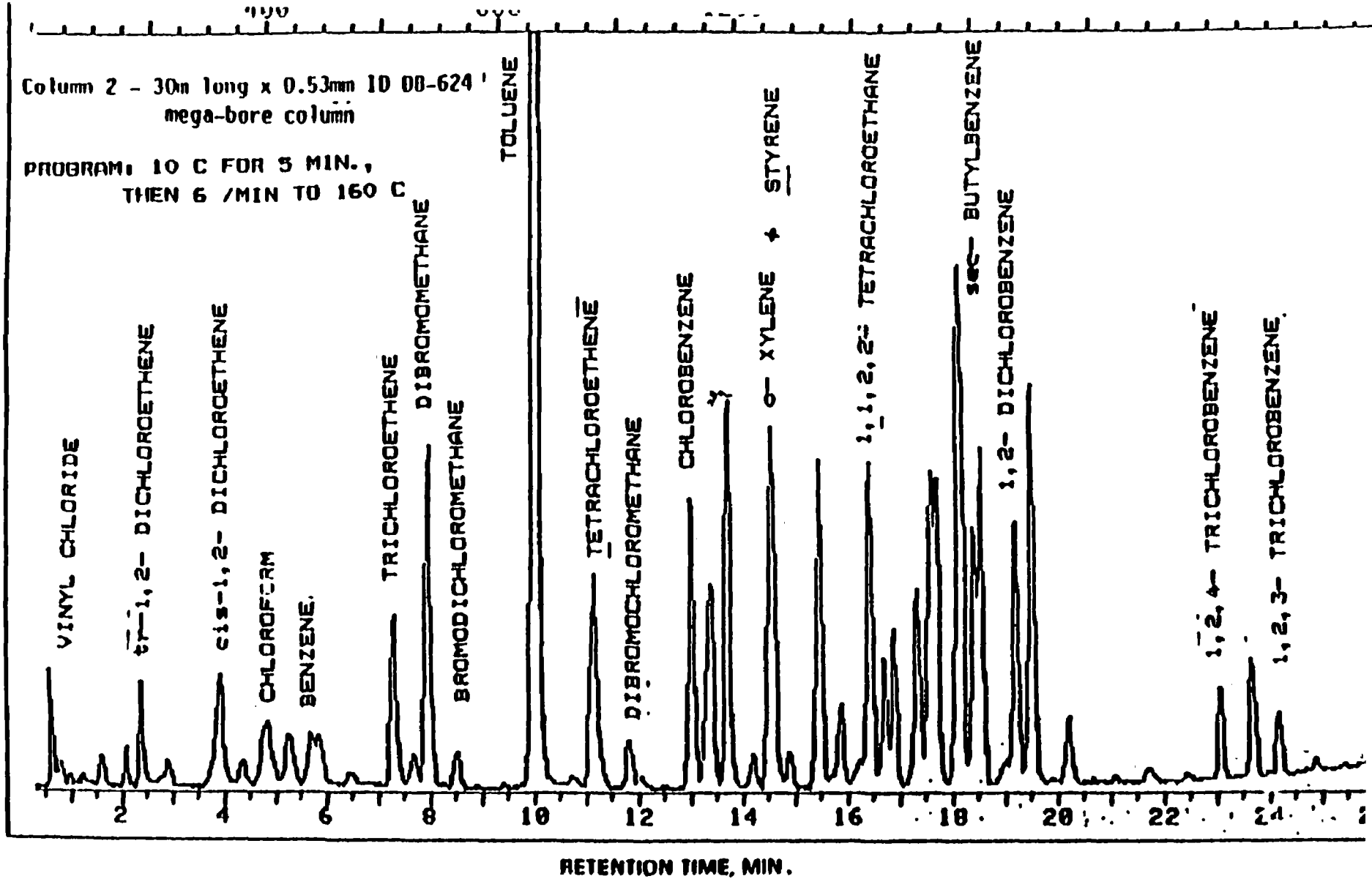

Figure 6. Gas chromatogram of volatile organics.

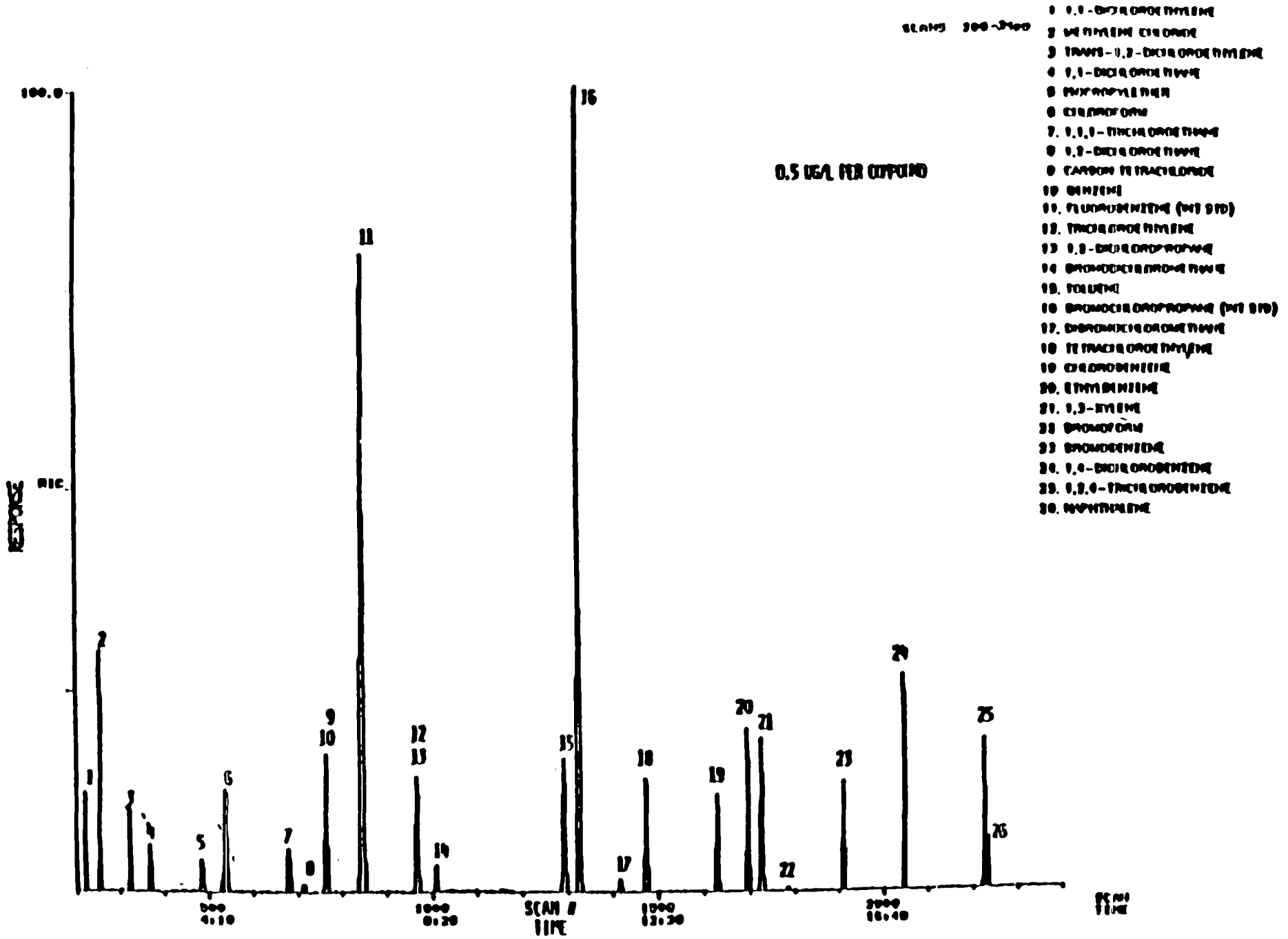

Figure 7. CHROMATOGRAM OF TEST MIXTURE