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

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PHYSICAL AND CHEMICAL METHODS BRANCH
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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.

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ABSTRACT

The methods contained in this report describe the requirements for the analysis of drinking water and raw source water for 60 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) are 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. 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 April 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. Since the basic analytical procedure has not been technically changed since approved for trihalomethanes, accommodations have been made in the method for total trihalomethane measurements, if free chlorine quenching techniques are practiced. 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, as included, 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 procedures and a maximum holding time for the samples.

Method 504 is a relatively new method developed to measure low concentrations of 1,2-dichloroethane (EDB) and 1,2-dibromo-1-3-chloropropane (DBCP). The proposed monitoring requirement cites this method exclusively for these two compounds. Method 524.1 is a restricted 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 proposals and establishes preservation procedures and a maximum holding time for samples. Since the basic analytical procedure has not changed since approved for trihalomethanes, accommodations have been made in the method for total trihalomethane measurements if free chlorine quenching techniques are practiced. Although the Agency has not at this time proposed the method for approval in Part 141.30 such a proposal is under consideration.

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These methods have been 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. Jim Longbottom was responsible for preparing the combined methods package which is based upon earlier versions of Methods 502.1, 503.1 developed by Thomas Bellar, and Method 524 developed by Ann Alford-Stevens, James Eichelberger, and William Budde. New data on sample preservation and holding time, presented in this update, were developed by Thomas Bellar, Robert Slater, Jr., and Kent Sorrell.

METHOD 502.1. VOLATILE HALOGENATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY

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 method may be used to calculate total trihalomethane (TTHM) concentrations as defined and required in 40 CFR, Part 141.30, if a reducing agent is added as described in Sect. 7.1.2. 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
bis-2-Chloroisopropyl ether	108-60-1
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
Pentachloroethane	76-01-7
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-dichloroproane was included in the November 13, 1985 proposed monitoring regulation although supporting accuracy and precision data are not 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 if sufficient material is present.

3. INTERFERENCES

3.1 Samples may be contaminated during shipment or storage by diffusion of volatile organics through the sample bottle septum seal. Field reagent blanks (Sect. 9.1.1) must be analyzed to determine if contamination has occurred.

3.2 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 field reagent blanks (Sect. 9.1.1) and laboratory reagent blanks (Sect. 9.1.2) 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.

3.3 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. See Sect. 9.1.2.

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: carbon tetrachloride, bis-2-chloroisopropyl ether, 1,2-dichlorethane, 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 ≤ 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. A sample chromatogram obtained with Column 2 is presented in Figure 6.

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

5.4 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 - water meeting specifications in Sect. 9.1.2. 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.

6.3.5 Reducing agent - crystalline sodium thiosulfate, ACS Reagent Grade or sodium sulfite, ACS Reagent Grade.

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 Replicate field reagent 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 empty sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by field reagent blanks.

7.1.2 For samples collected to determine compliance with total trihalomethane regulations (40 CFR Part 141.30), add 2.5 to 3 mg reducing agent (Sect. 6.3.5) per 40 mL to the empty sample bottles and blanks just prior to shipping to the sampling site.

7.1.3 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.

7.1.4 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.

7.1.5 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 and the field reagent blanks to <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 and field reagent 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 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. Do not add less than 20 µL of an alcoholic standard to the reagent water or poor precision will result. Use a 25-µL 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.

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. 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:

$$S = 0.51\ (C)(V)\ \text{per liter}$$

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.

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 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 5 and 6) 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 MONITORING FOR INTERFERENCES

9.1.1 Field Reagent Blanks - A field reagent blank (Sect. 7.1.1) is a sealed bottle of reagent water that accompanies a set of sample bottles from the laboratory to a sampling site and back. Analyze a field reagent blank along with each sample set. If the field reagent blank contains a reportable level of any analyte, analyze a laboratory reagent blank as described in Sect. 9.1.2. If the contamination is not detected in the laboratory reagent blank, the sampling or transportation practices have caused the contamination. In this case, discard all samples in the set and resample the site.

9.1.2 Laboratory Reagent Blanks - A laboratory reagent blank is a 5-mL aliquot of reagent water analyzed as if it were a sample. Analyze a laboratory reagent blank each time fresh reagent water is prepared and as necessary to identify sources of contamination. The laboratory reagent blank should represent less than 0.01 µg/L response or less than 10% interference for those compounds that are monitored.

9.2 ASSESSING ACCURACY

9.2.1 At least quarterly, analyze a quality control check sample obtained from the U.S. Environmental Protection Agency,

Environmental Monitoring and Support Laboratory (EMSL), Quality Assurance Branch, Cincinnati. If measured analyte concentrations are not within acceptance limits provided with the sample, check the entire analytical procedure to locate and correct the problem source.

9.2.2 After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments and the laboratory control standard may not be used for calibration of the analytical system.

9.2.2.1 Laboratory Control Standard Concentrate - If internally prepared laboratory control standards are used to provide the routine assessment of accuracy, they should be prepared from a separate set of stock standards. From stock standards prepared as described in Section 6.4, add 500 µL of each stock standard to methanol in a 10-mL volumetric flask and adjust to volume.

9.2.2.2 Laboratory Control Standard - Add 20 µL of the control standard concentrate to 100 mL of reagent water in a 100-mL volumetric flask and mix well.

9.2.2.3 Analyze a 5-mL aliquot of the laboratory control standard as described in Sect. 10. For each analyte in the laboratory control standard, calculate the percent recovery (P_i) with the equation:

$$P_i = \frac{100\ S_i}{T_i}$$

where S_i = the analytical result from the laboratory control standard, in µg/L; and
T_i = the known concentration of the spike, in µg/L.

9.2.3 At least annually, the laboratory should participate in formal performance evaluation studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared.

9.3 ASSESSING PRECISION

9.3.1 Precision assessments for this method are based upon the analysis of field duplicates (Sect. 7.1). Analyze both sample bottles for at least 10% of all samples. To the extent practical, the samples for duplication should contain reportable levels of most of the analytes.

9.3.2 For each analyte in each duplicate pair, calculate the relative range (RR_i) with the equation:

$$RR_i = \frac{100\ R_i}{X_i}$$

where R_i = the absolute difference between the duplicate measurements X_1 and X_2, in µg/L

X_i = the average concentration found ($[X_1 + X_2]/2$), in µg/L.

9.3.3 Individual relative range measurements are pooled to determine average relative range or to develop an expression of relative range as a function of concentration.

10. PROCEDURE

10.1 INITIAL CONDITIONS - 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 (Figures 1 and 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

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

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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	Column 2	MDL (µg/L)
Chloromethane	90	317	0.01
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(c)	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 included in proposed monitoring requirement.
(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 ORGANOHALIDES 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
bis-2-Chloroisopropyl ether	0.40	125	21	0.11	28
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
Pentachloroethane	0.40	98	21	0.039	9.8
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

Table 2. (CONTINUED)

Analyte	Spike Level (µg/L)	Average Recovery %	Number or Samples	Standard Deviation (µg/L)	Relative Standard Deviation (%)
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	$0.10\bar{X} + 0.20$	$0.24\bar{X} + 1.25$	$1.02C - 1.81$
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

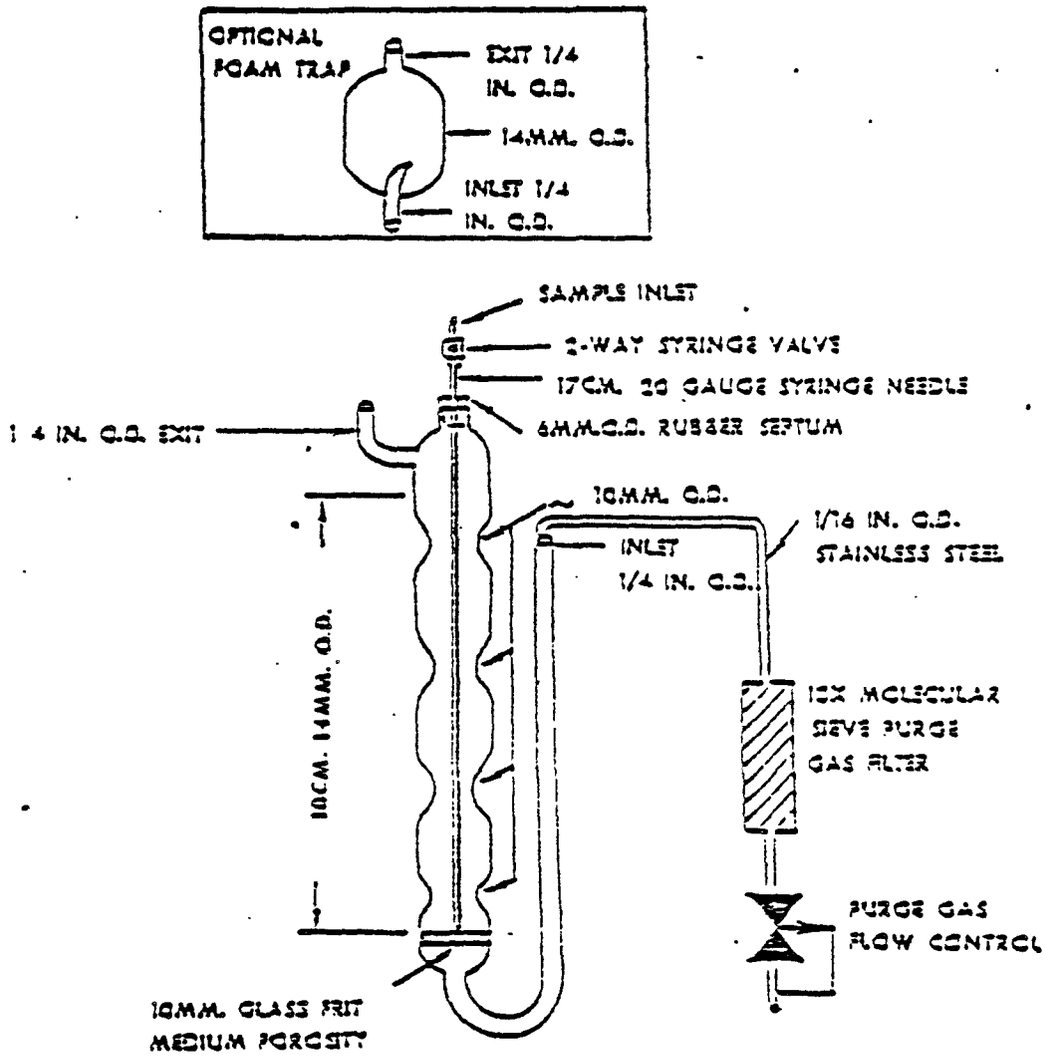


FIGURE 1. PURGING DEVICE

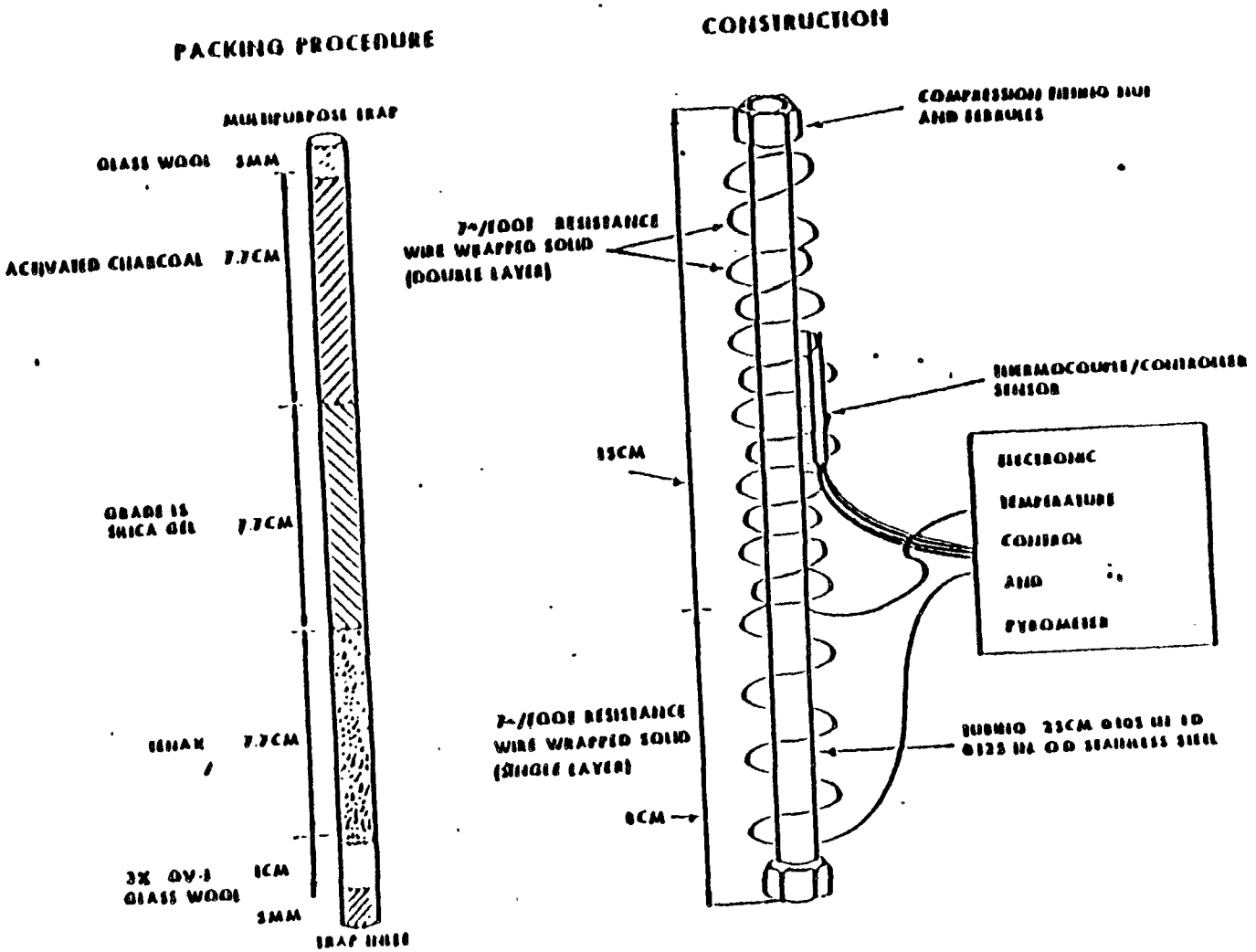


FIGURE 2 TRAP

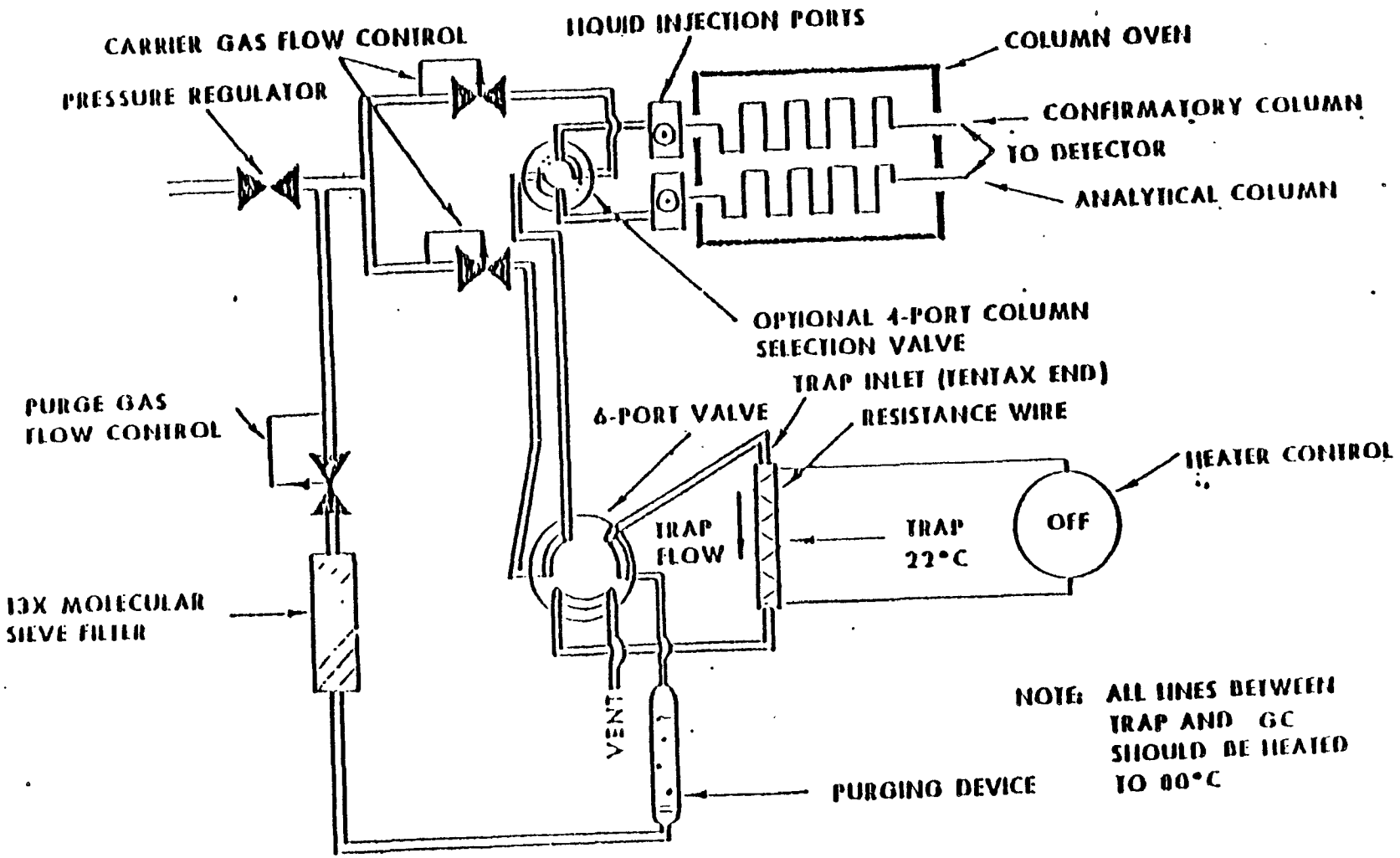


FIGURE 3 PURGE-TRAP SYSTEM (PURGE-SORB MODE)

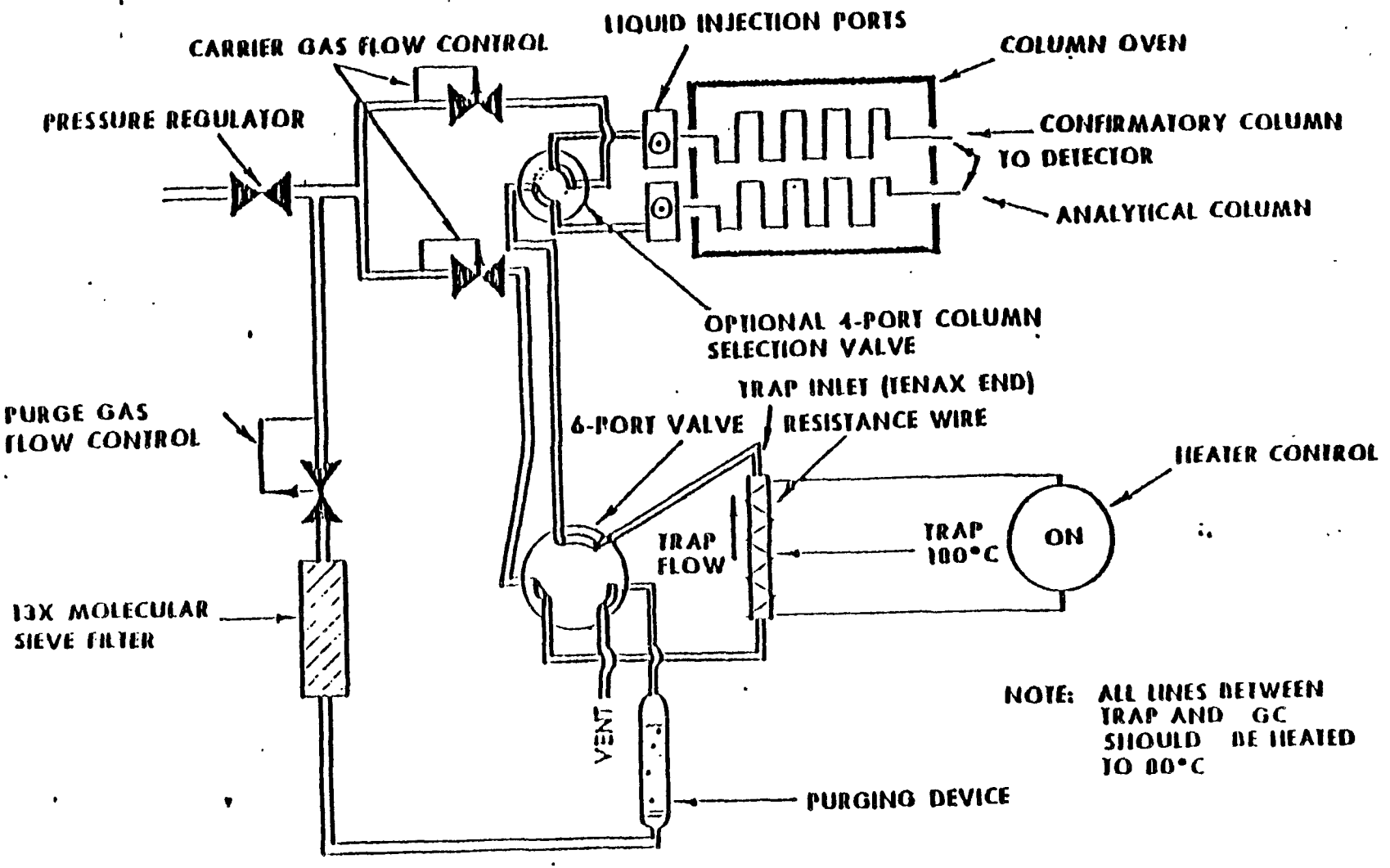
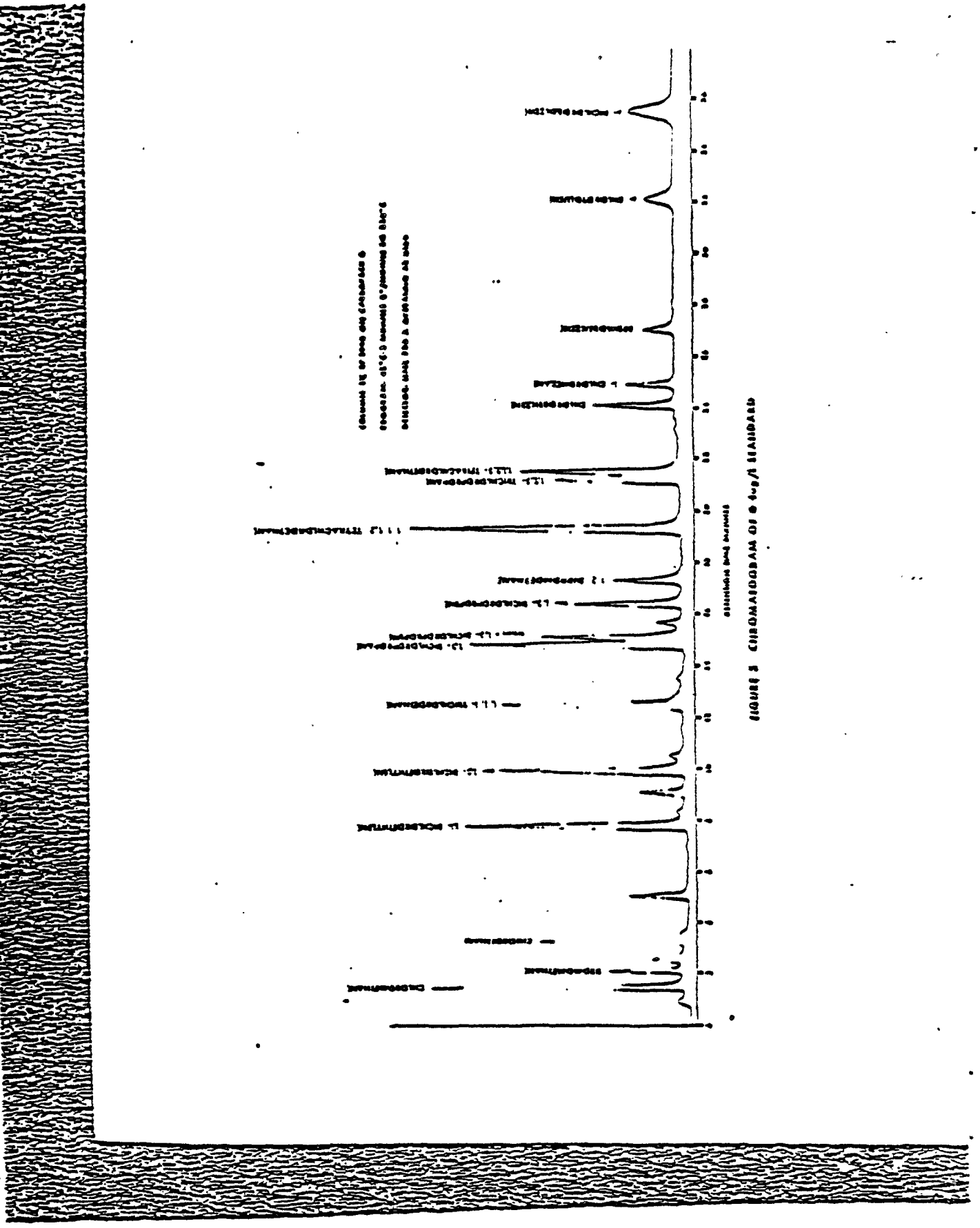


FIGURE 4 PURGE-TRAP SYSTEM (DESORB MODE)



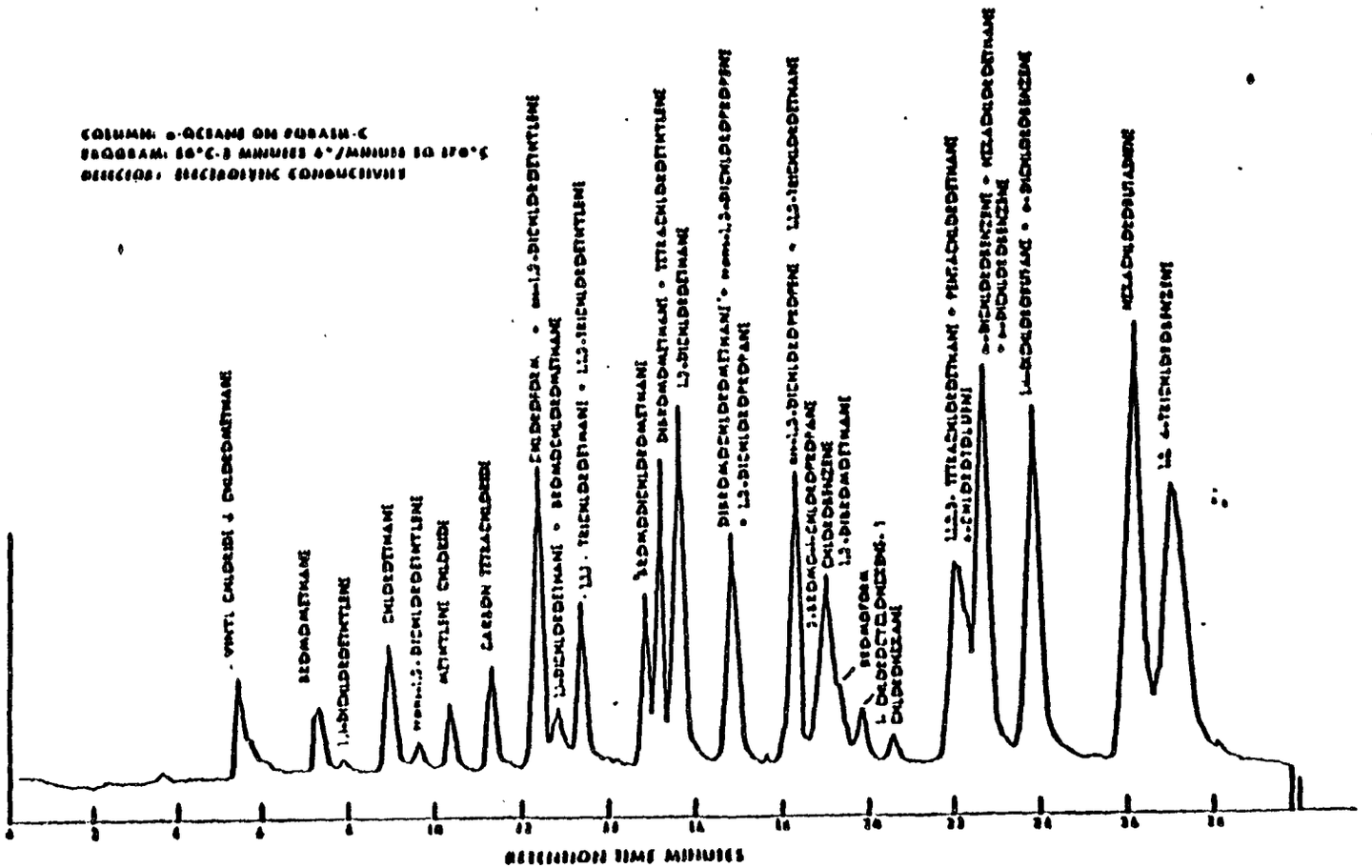


FIGURE 6 CHROMATOGRAM OF ORGANOHALIDES

METHOD 503.1. VOLATILE AROMATIC AND UNSATURATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY

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 µg/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 µg/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 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 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 if sufficient material is present.

3. INTERFERENCES

3.1 Samples may be contaminated during shipment or storage by diffusion of volatile organics through the sample bottle septum seal. Field reagent blanks (Sect. 9.1.1) must be analyzed to determine if contamination has occurred.

3.2 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 field reagent blanks (Sect. 9.1.1) and laboratory reagent blanks (Sect. 9.1.2) 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.

3.3 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 distilled water, and then dry it in an oven at 105°C between analyses.

3.4 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 3-6.

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.

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. Two temperature programs have been found to be useful and are described in Table 1. Program A optimizes separations for the early eluting analytes, while Program B optimizes the separation for the later eluting analytes. When not in use, maintain the column at the upper temperature (90°C or 110°C) of the program. Condition new SP-1200/Bentone columns with carrier gas flow at 120°C for several days before connecting to the detector. Sample chromatograms obtained with Column 1 are presented in Figures 7 and 8.

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 9.

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-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.

5.5 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 - water meeting specifications in Sect. 9.1.2. 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-µL 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 Replicate field reagent 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 empty sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by field reagent 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 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 and the field reagent blanks to <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 and field reagent 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 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. Do not add less than 20 µL of an alcoholic standard to the reagent water or poor precision will result. Use a 25-µL 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 in 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 laboratory control standard (Sect. 9.2.2).

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 7, 8, and 9) 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 MONITORING FOR INTERFERENCES

9.1.1 Field Reagent Blanks - A field reagent blank (Sect. 7.1.1) is a sealed bottle of reagent water that accompanies a set of sample bottles from the laboratory to a sampling site and back. Analyze a field reagent blank along with each sample set. If the field reagent blank contains a reportable level of any analyte, analyze a laboratory reagent blank as described in Sect. 9.1.2. If the contamination is not detected in the laboratory reagent blank, the sampling or transportation practices have caused the contamination. In this case, discard all samples in the set and resample the site.

9.1.2 Laboratory Reagent Blanks - A laboratory reagent blank is a 5-mL aliquot of reagent water analyzed as if it were a sample. Analyze a laboratory reagent blank each time fresh reagent water is prepared and as necessary to identify sources of contamination. The laboratory reagent blank should be below the method detection limit or represent less than 10% interference for those compounds that are monitored.

9.2 ASSESSING ACCURACY

9.2.1 At least quarterly, analyze a quality control check sample obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (EMSL), Quality Assurance Branch, Cincinnati. If measured analyte concentrations are not within acceptance limits provided with the sample, check the entire analytical procedure to locate and correct the problem source.

9.2.2 After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments and the laboratory control standard may not be used for calibration of the analytical system.

9.2.2.1 Laboratory Control Standard Concentrate - If internally prepared laboratory control standards are used to provide the routine assessment of accuracy, they should be prepared from a separate set of stock standards. From stock standards prepared as described in Sect. 6.4, add 500 µL of each stock standard to methanol in a 10-mL volumetric flask and adjust to volume.

9.2.2.2 Laboratory Control Standard - Add 20 µL of the control standard concentrate to 100 mL of reagent water in a 100-mL volumetric flask and mix well.

9.2.2.3 Analyze a 5-mL aliquot of the laboratory control standard as described in Sect. 10. For each analyte in the laboratory control standard, calculate the percent recovery (P_i) with the equation:

$$P_i = \frac{100\ S_i}{T_i}$$

where S_i = the analytical result from the laboratory control standard, in µg/L; and
T_i = the known concentration of the spike, in µg/L.

9.2.3 At least annually, the laboratory should participate in formal performance evaluation studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared.

9.3 ASSESSING PRECISION

9.3.1 Precision assessments for this method are based upon the analysis of field duplicates (Sect. 7.1). Analyze both sample bottles for at least 10% of all samples. To the extent practical, the samples for duplication should contain reportable levels of most of the analytes.

9.3.2 For each analyte in each duplicate pair, calculate the relative range (RR_i) with the equation:

$$RR_i = \frac{100\ R_i}{X_i}$$

where R_i = the absolute difference between the duplicate measurements X_1 and X_2, in µg/L
X_i = the average concentration found ($[X_1 + X_2]/2$), in µg/L.

9.3.3 Individual relative range measurements are pooled to determine average relative range or to develop an expression of relative range as a function of concentration.

10. PROCEDURE

10.1 INITIAL CONDITIONS - 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 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 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 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 (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

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

Analyte	Retention Time (sec) Column 1 Program A	Column 1 Program B	Column 2	MDL µg/L
Benzene	199	199	165	0.02
Trichloroethene	223	231	142	0.01
α,α,α-Trifluorotoluene(a)	275	296	168	0.02
Toluene	340	384	255	0.02
Tetrachloroethene	360	406	168	0.01
Ethylbenzene	491	606	375	0.002
1-Chlorocyclohexene(b)	518	637	345	0.008
p-Xylene	518	653	403	0.002
Chlorobenzene	542	689	481	0.004
m-Xylene	542	689	403	0.004
o-Xylene	574	738	518	0.004
Isopropylbenzene	595	768	455	0.005
Styrene	644	834	690	0.008
1,4-Bromofluorobenzene(b)	664	852	740	—
n-Propylbenzene	681	879	518	0.009
tert-Butylbenzene	786	975	595	0.006
2-Chlorotoluene	804	985	681	0.008
4-Chlorotoluene	804	990	—	—
Bromobenzene	804	999	807	0.002
sec-Butylbenzene	829	1027	595	0.02
1,3,5-Trimethylbenzene	851	1043	612	0.003
4-Isopropyltoluene	909	1090	681	0.009
1,2,4-Trimethylbenzene	909	1090	750	0.006
1,4-Dichlorobenzene	999	1152	975	0.006
1,3-Dichlorobenzene	1082	1211	901	0.006
Cyclopropylbenzene(b)	1082	1211	—	—
n-Butylbenzene	1082	1211	765	0.02
2,3-Benzofuran(b)	1283	1320	1460	0.03
1,2-Dichlorobenzene	1528	1425	1161	0.02
Hexachlorobutadiene	2035	1650	1011	0.02
1,2,4-Trichlorobenzene	2690	1928	1535	0.03
Naphthalene	4280	2545	2298	0.04
1,2,3-Trichlorobenzene	4526	2631	1820	0.03

(a) = Recommended internal standard (Sect. 8.1.6).
(b) = Analyte not included in proposed monitoring requirement.

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 for Program A held at 50°C for 2 min then programmed at 6°C/min to 90°C for a final hold. Column temperature for Program B 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 µg/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	15.7
sec-Butylbenzene	A	0.40	7	80	11.0
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-Trichlorotoluene(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) = Analyte not included in proposed monitoring requirement.
(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 (µg/L)	Overall Precision (µg/L)	Accuracy as Mean Recovery($\bar{X}$) (µg/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 (µg/L)
C = true value for the concentration (µg/L)

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

Analyte	Spike Level (µg/L)	Number of Laboratories	Average Measured Concentrations (µg/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

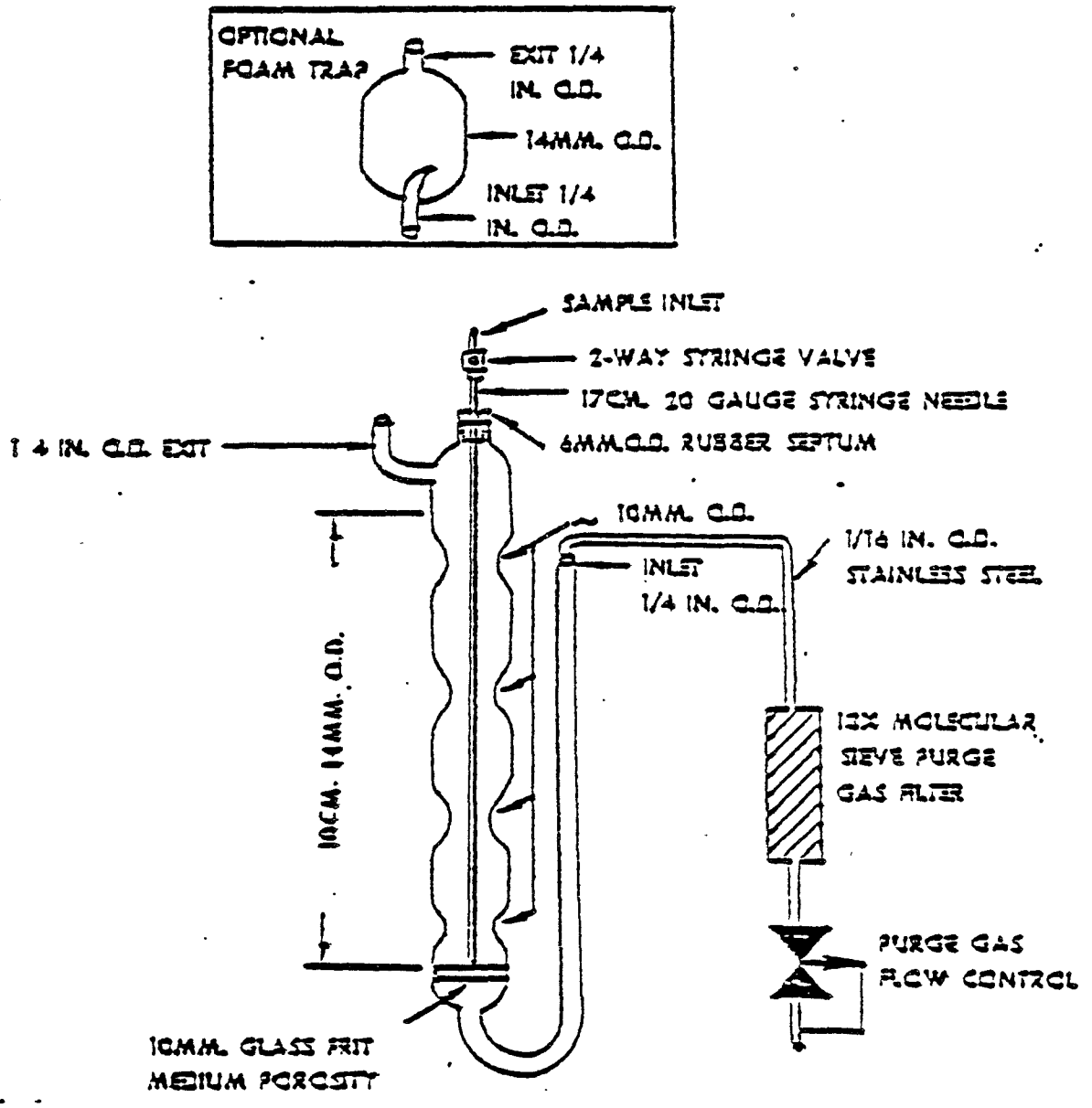

FIGURE 1. PURGING DEVICE.

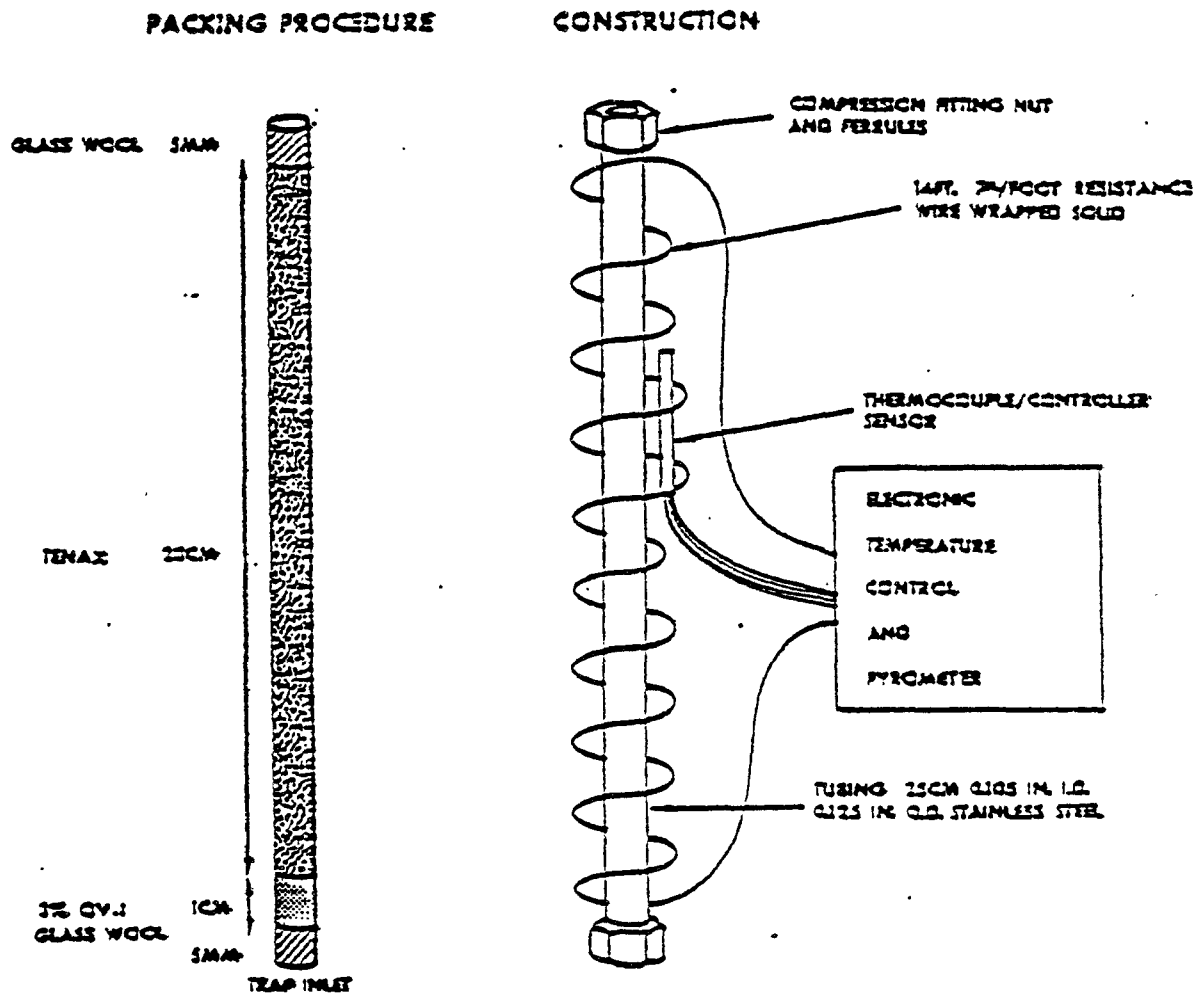

FIGURE 2. TRAP.

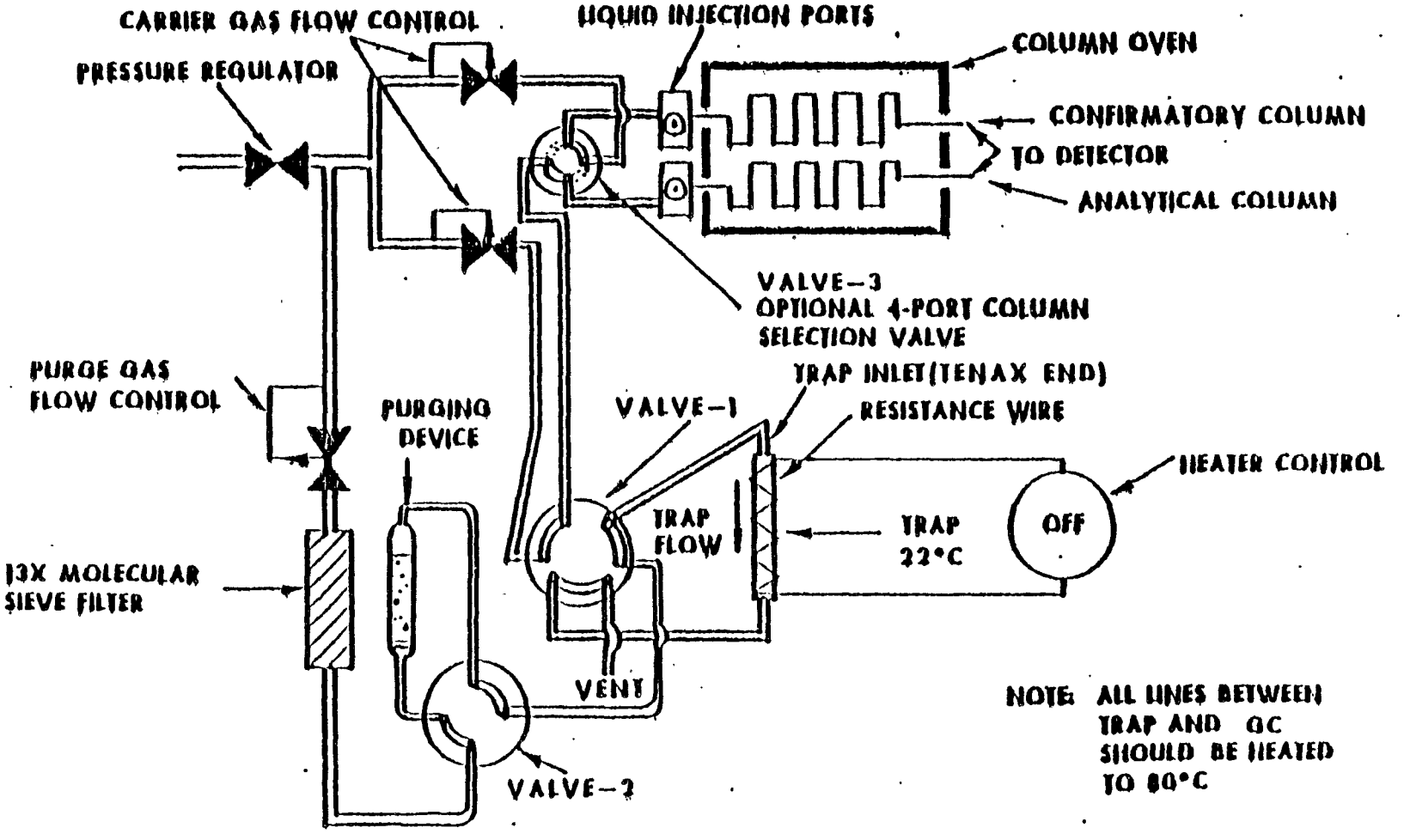

FIGURE 3. PURGE AND TRAP SYSTEM (PURGE-SORB MODE).

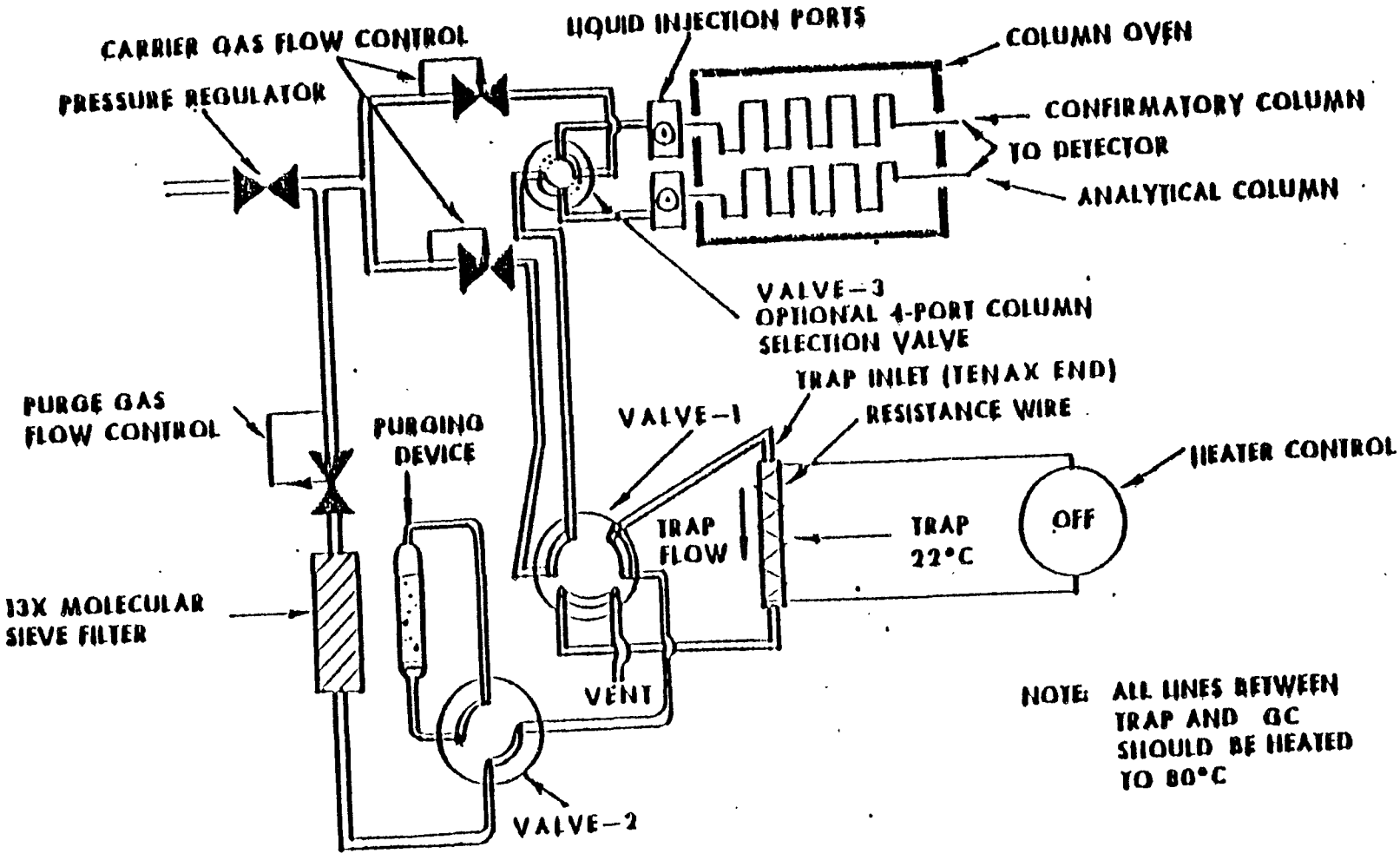

FIGURE 4. PURGE AND TRAP SYSTEM (TRAP-DRY MODE).

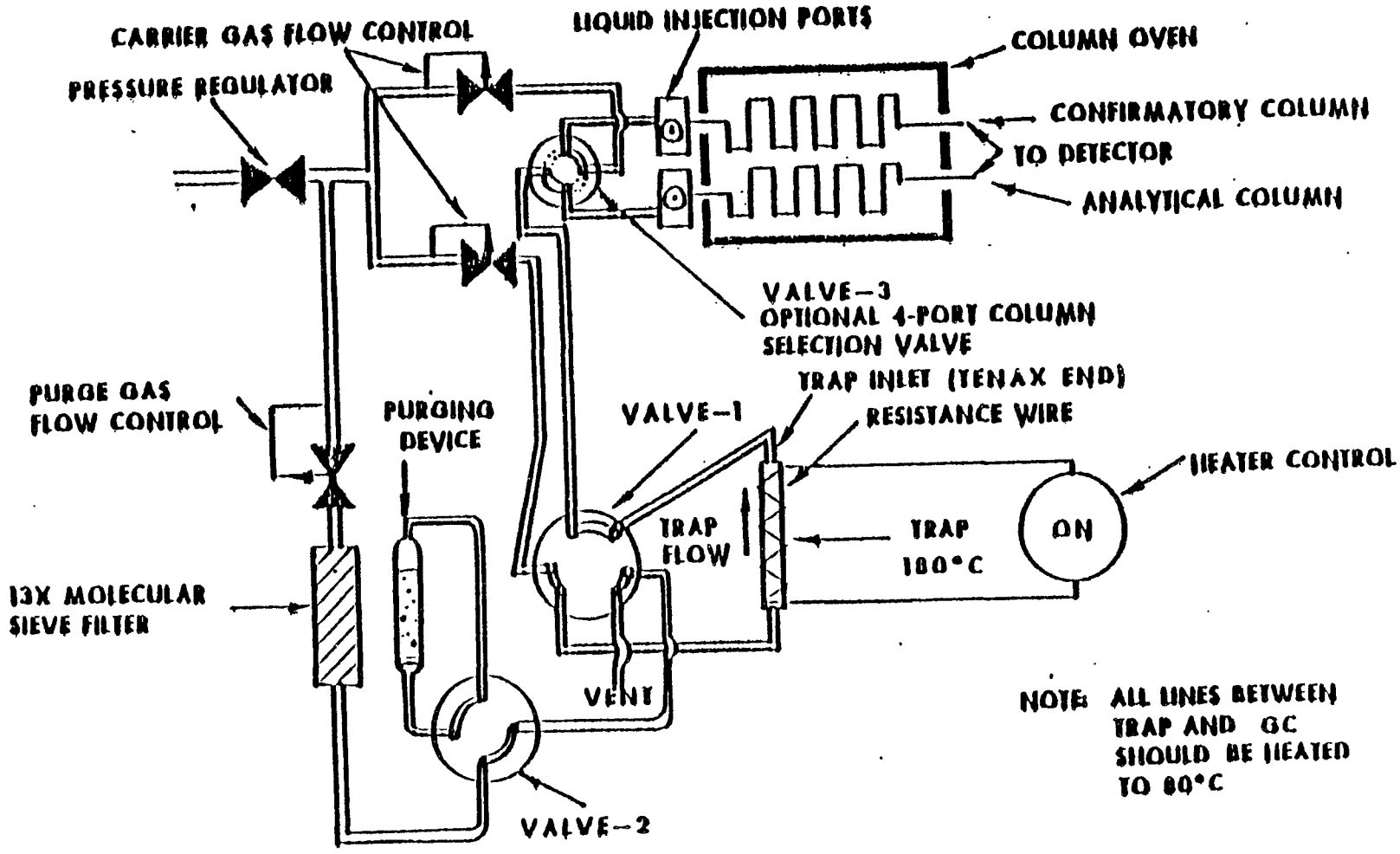

FIGURE 5. PURGE AND TRAP SYSTEM (DESORB MODE)

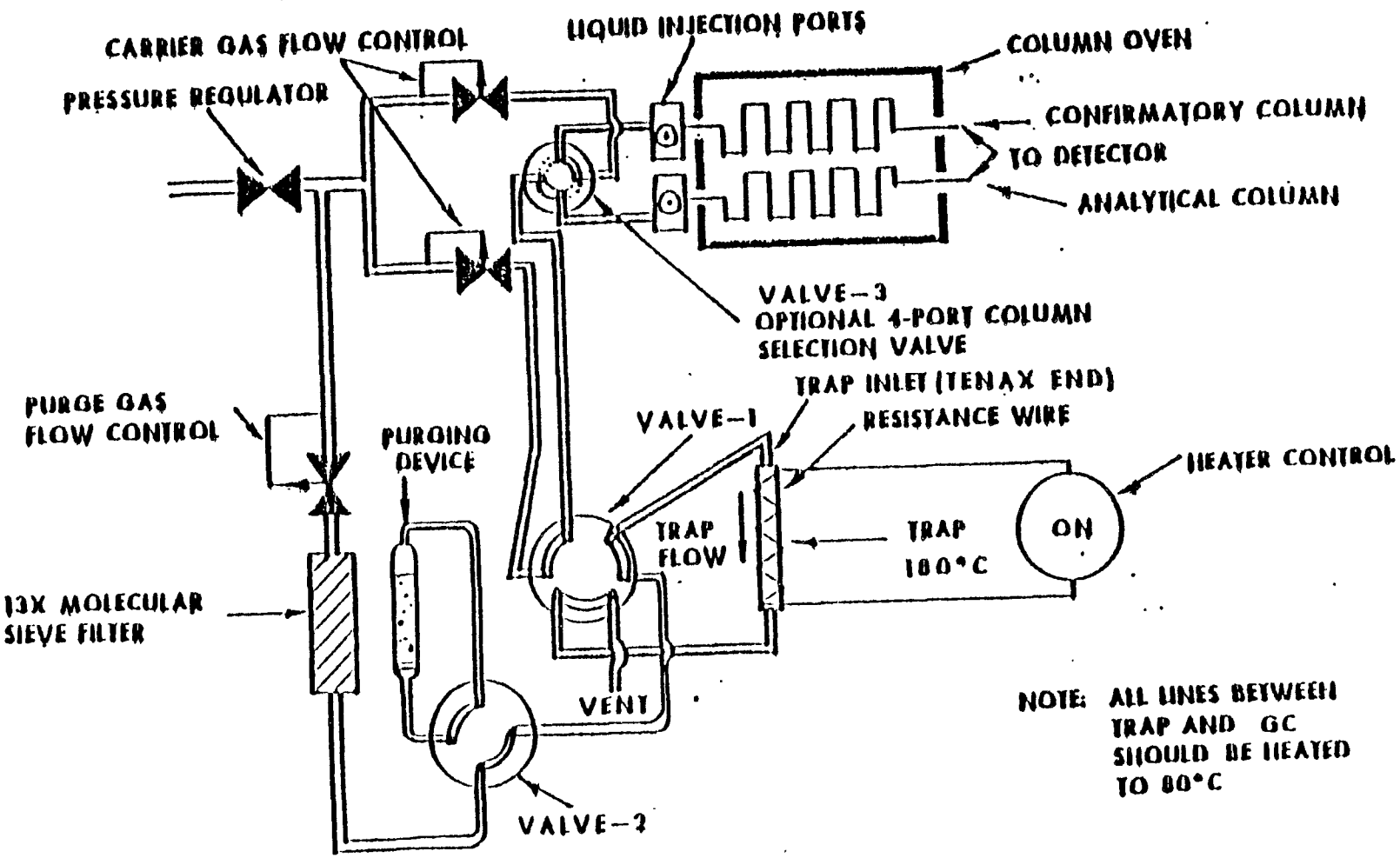

FIGURE 6. PURGE AND TRAP SYSTEM (TRAP-CONDITION MODE).

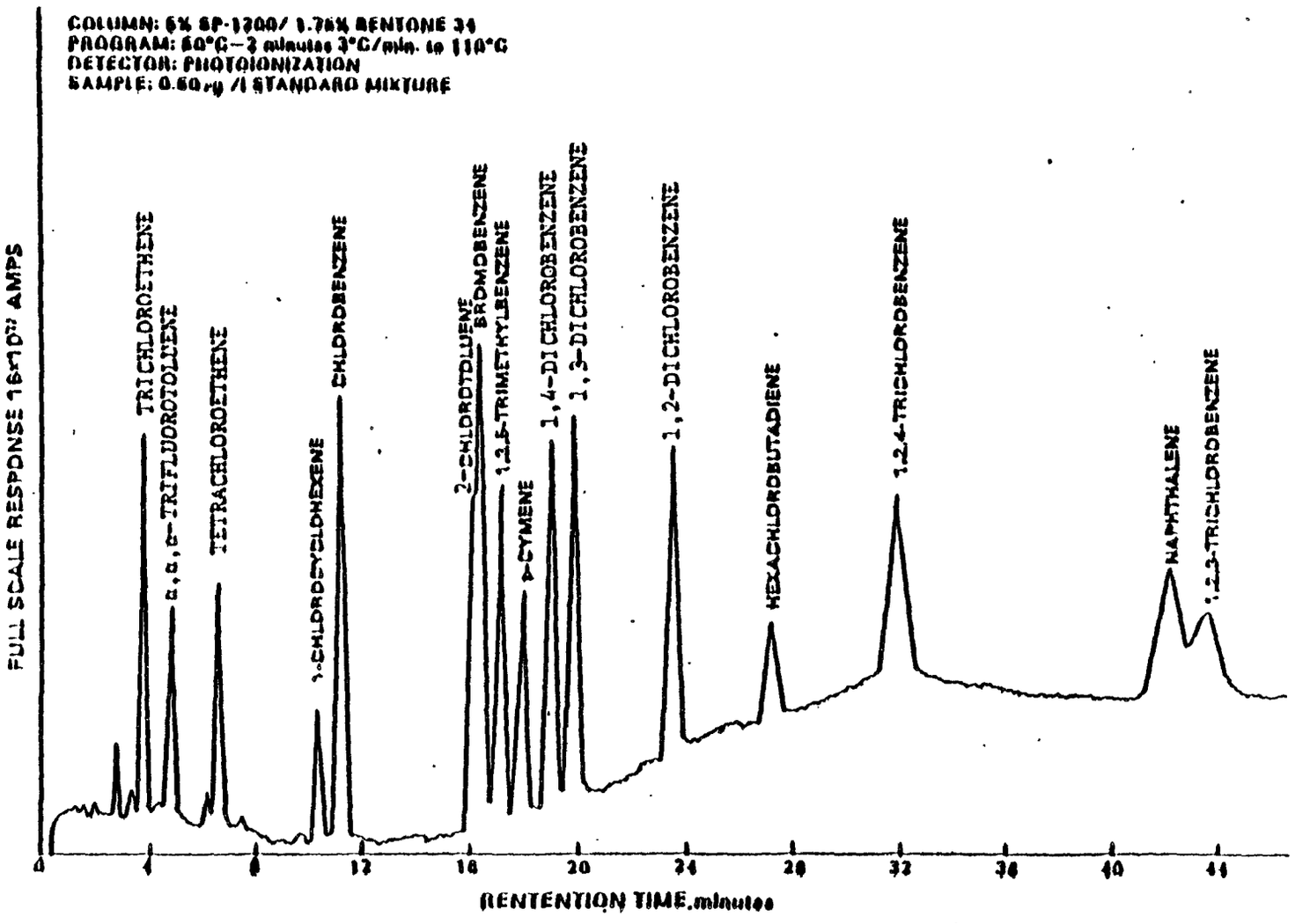

FIGURE 7. CHROMATOGRAM OF TEST MIXTURE.

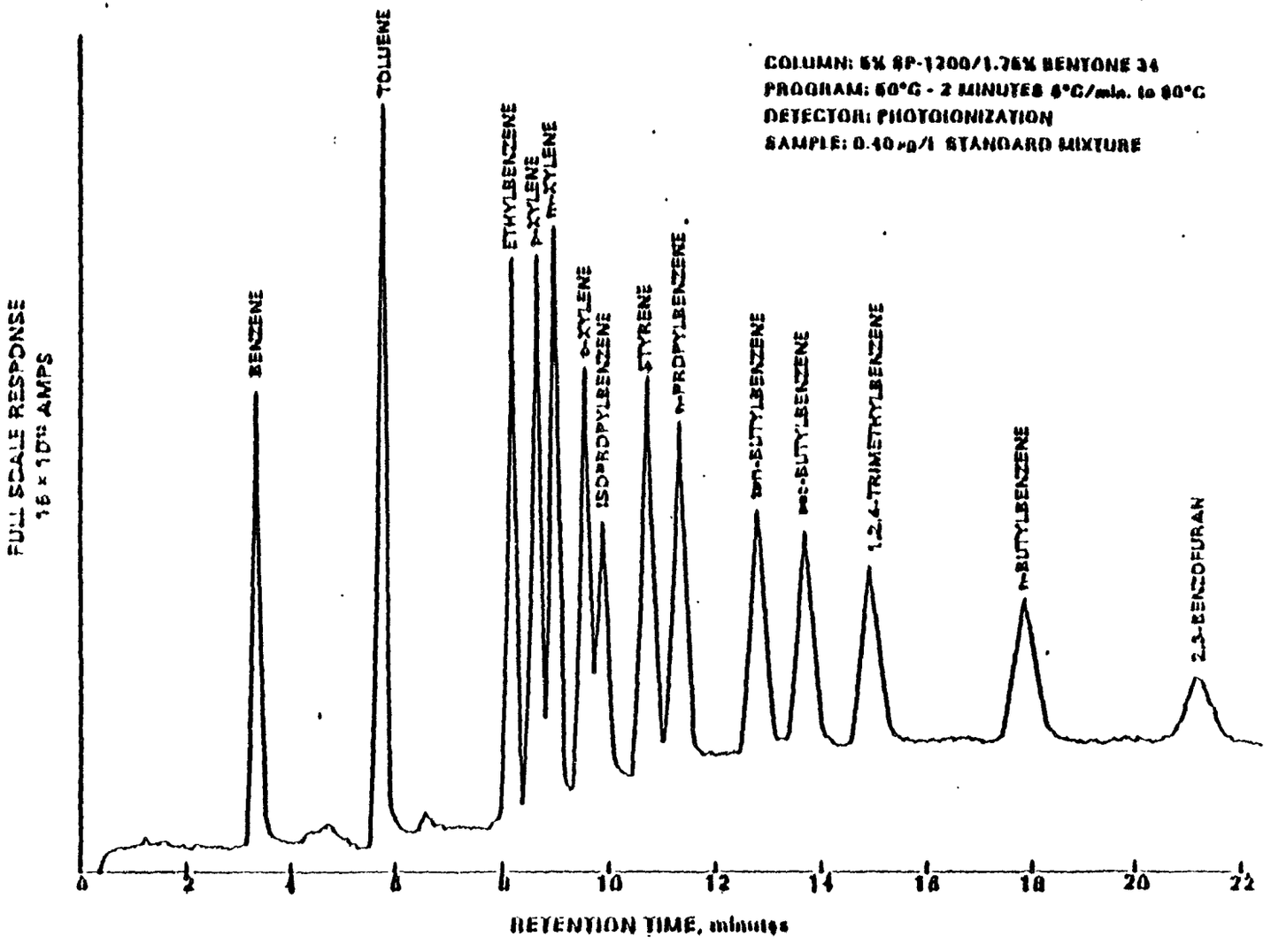

FIGURE 8. CHROMATOGRAM OF TEST MIXTURE.

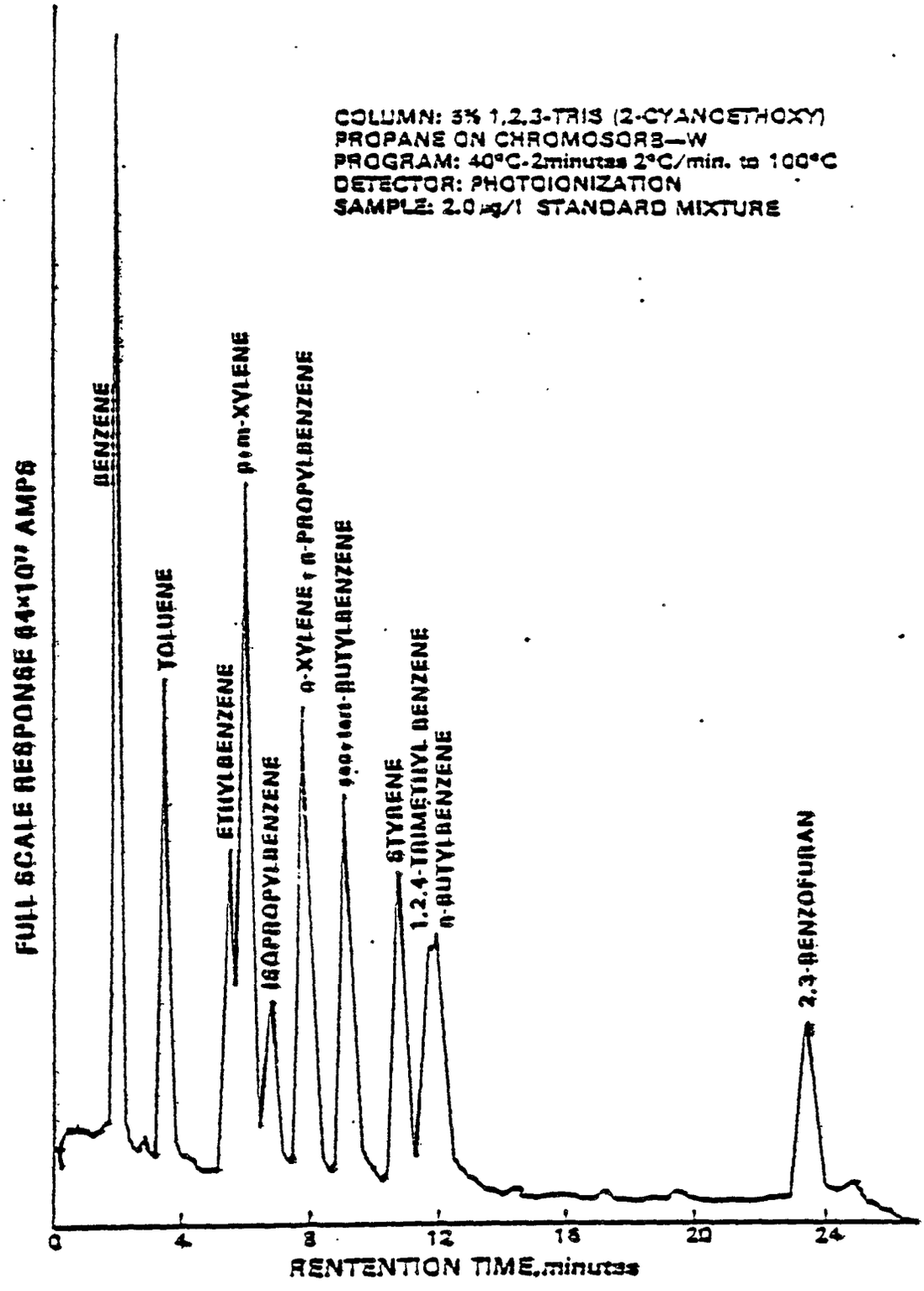

FIGURE 9. CHROMATOGRAM OF TEST MIXTURE.

METHOD 504. MEASUREMENT OF 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) IN DRINKING WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

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 µg/L. The method has been shown to be useful for these analytes over a concentration range from approximately 0.03 to 200 µg/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 µL 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 µg/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 µg/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 samoler, screw cap with 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.

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 at 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 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 an analyte varies from the predicted response by more than ±15%, 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 standard solutions. The single point calibration standard 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 solution to produce a single point calibration standard in reagent water.

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 MONITORING FOR INTERFERENCES

9.1.1 Field Blanks - A field blank is a sealed bottle of reagent water that accompanies a set of sample bottles from the

laboratory to a sampling site and back. Analyze a field blank along with each sample set (Sect. 7.1.1). If the field blank contains a reportable level of EDB or DBCP, analyze a laboratory reagent blank as described in Sect. 9.1.2. If the contamination is not detected in the laboratory reagent blank, the sampling or transportation practices have caused the contamination. In this case, discard all samples in the set and resample the site.

9.1.2 Laboratory Reagent Blanks - A laboratory reagent blank is a 35-mL aliquot of reagent water analyzed as if it were a sample. Analyze a laboratory reagent blank each time fresh reagent water is prepared and as necessary to identify sources of contamination. The laboratory reagent blank should contain less than 0.01 µg/L response of each analyte.

9.2 ASSESSING ACCURACY

9.2.1 Each quarter, it is essential that the laboratory analyze quality control check standards for each contaminant. If the criteria established by USEPA and provided with the QC standards are not met, corrective action needs to be taken and documented.

9.2.2 After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments and the laboratory control standard may not be used for calibration of the analytical system.

9.2.2.1 Laboratory Control Standard Concentrate - If internally prepared laboratory control standards are used to provide the routine assessment of accuracy, they should be prepared from a separate set of stock standards. From stock standards prepared as described in Sect. 6.4, add a sufficient volume of each stock standard to methanol in a 10-mL volumetric flask to yield a concentration of 2.5 µg/mL and adjust to volume.

9.2.2.2 Laboratory Control Standard (0.5 µg/L) - Add 20 µL of the control standard concentrate to 100 mL of reagent water in a 100-mL volumetric flask.

9.2.2.3 Analyze a 35-mL aliquot of the laboratory control standard as described in Sect. 10. For each analyte in the laboratory control standard, calculate the percent recovery (P_i) with the equation:

$$P_i = \frac{100\ S_i}{T_i}$$

where S_i = the analytical result from the laboratory control standard, in µg/L; and

T_i = the known concentration of the spike, in µg/L.

9.2.3 It is essential that the laboratory analyze an unknown performance evaluation sample (when available) once per year for all regulated contaminants measured. Results need to be within acceptance limits established by USEPA for each analyte.

9.3 ASSESSING PRECISION

9.3.1 Precision assessments for this method are based upon the analysis of field duplicates (Sect. 7.1.2). Analyze both sample bottles for at least 10% of all samples. To the extent practical, the samples for duplication should contain reportable levels of the analytes.

9.3.2 For each analyte in each duplicate pair, calculate the relative range (RR_i) with the equation:

$$RR_i = \frac{100\ R_i}{X_i}$$

where R_i = the absolute difference between the duplicate measurements X_1 and X_2, in µg/L

X_i = the average concentration found ($[X_1 + X_2]/2$), in µg/L.

9.3.3 Individual relative range measurements are pooled to determine the average relative range or to develop an expression of relative range as a function of concentration.

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, (see Sect. 10.3 for continuation of weighing and calculation of true volume).

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 0.1 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

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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, µg/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 (µg/L)	Average Accuracy (%)	Relative Standard Deviation (%)
1,2-Dibromoethane	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
1,2-Dibromo-3-chloropropane	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 µg/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.

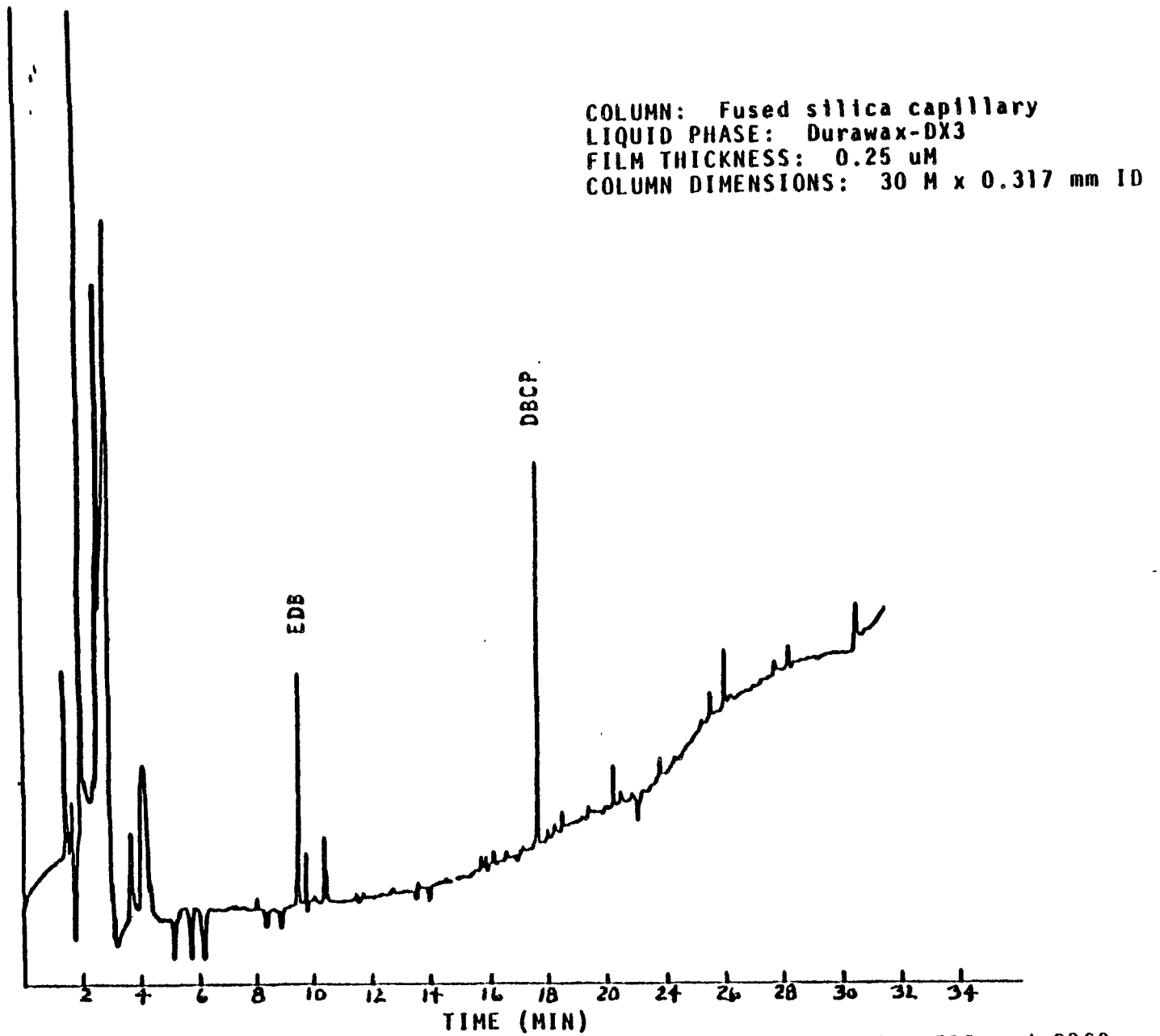

Figure 1. Extract of Reagent Water Spiked at 0.114 ug/L with EDB and DBCP

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

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 method may be used to calculate total trihalomethane (TTHM) concentrations as defined and required in 40 CFR Part 141.30 if a reducing agent is added as described in Sect. 7.1.2. 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
bis-2-Chloroisopropyl ether	108-60-1
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
Pentachloroethane	76-01-7
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

*The measurement of this analyte can only be achieved using chromatographic techniques that are less than optimum. The preferred method of analysis is Method 503.1. See discussion in Sect. 10.4.

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 Based upon data obtained using Methods 502.1 or 503.1 or on

chemical similarity to other analytes, certain compounds were included in the November 13, 1985 proposed monitoring regulation without supporting accuracy and precision data using 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.

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 Samples may be contaminated during shipment or storage by diffusion of volatile organics through the sample bottle septum seal. Field reagent blanks (Sect. 9.2.1) must be analyzed to determine if contamination has occurred.

3.2 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 field reagent blanks (Sect. 9.2.1) and laboratory reagent blanks (Sect. 9.2.2) 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.

3.3 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, bis-2-chloroisopropyl ether, 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 1 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-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 (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 - water meeting specifications in Sect. 9.2.2. 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.

6.3.5 Reducing agent - Crystalline sodium thiosulfate, ACS Reagent Grade or sodium sulfite, ACS Reagent Grade.

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 1,4-dichlorobutane-d_8, 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 CONTROL STANDARD CONCENTRATE - Using standard stock solutions, prepare a solution containing each analyte of interest of a concentration of 10 µg/mL in methanol.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Replicate field reagent 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 empty sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by field reagent blanks.

7.1.2 For samples collected to determine compliance with trihalomethane regulations (40CFR, Part 141.30), add 2.5 to 3.0 mg reducing agent (Sect. 6.3.5) per 40 mL to the empty sample bottles and blanks just prior to shipping to the sampling site.

7.1.3 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.

7.1.4 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.

7.1.5 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 and the field reagent blanks 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 and field reagent 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 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. Do not add less than 20 µL of an alcoholic standard to the reagent water or poor precision will result. Use a 25-µL 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. 9.5, 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 = Volume of standard injected in milliliters.

9. QUALITY CONTROL

9.1 PRECISION TEST

9.1.1 The analyst must make an initial one-time, demonstration of the ability to generate acceptable precision with this method. The purpose of this test is to demonstrate that the equipment configuration and the technique of the analyst are adequate to produce data of acceptable quality.

9.1.2 Prepare a laboratory control standard to contain 20 µg/L of each analyte by adding 200 µL of laboratory control standard concentrate (Sect. 6.8) to 100 mL of reagent water.

9.1.3 Analyze four 25-mL aliquots of the well-mixed laboratory control standard according to the procedure in Sect. 10.

9.1.4 For each analyte, calculate the standard deviation in µg/L, of the measured concentration. For each analyte, the standard deviation must be less than 4.0 µg/L.

9.1.5 If the standard deviation for any analyte exceeds the listed criterion in Sect. 9.1.4, locate and correct the source of the problem and repeat the test for all analytes.

9.2 MONITORING FOR INTERFERENCES

9.2.1 Field Reagent Blanks - A field reagent blank (Sect. 7.1.1) is a sealed bottle of reagent water that accompanies a set of sample bottles from the laboratory to a sampling site and back. Analyze a field reagent blank along with each sample set. If the field reagent blank contains a reportable level of any analyte, analyze a laboratory reagent blank as described in Sect. 9.1.2. If the contamination is not detected in the laboratory reagent blank, the sampling or

transportation practices have caused the contamination. In this case, discard all samples in the set and resample the site.

9.2.2 Laboratory Reagent Blanks - A laboratory reagent blank is a 25-mL aliquot of reagent water analyzed as if it were a sample. Analyze a laboratory reagent blank each time fresh reagent water is prepared and as necessary to identify sources of contamination. The laboratory reagent blank should represent less than 0.1 µg/L response (see Sect. 3).

9.3 ASSESSING ACCURACY

9.3.1 At least quarterly, analyze a quality control check sample obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (EMSL), Quality Assurance Branch, Cincinnati. If measured analyte concentrations are not within acceptance limits provided with the sample, check the entire analytical procedure to locate and correct the problem source.

9.3.2 After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments and the laboratory control standard may not be used for calibration of the analytical system.

9.3.2.1 Analyze a 25-mL aliquot of a laboratory control standard (Sect. 9.1.2) as described in Sect. 10. For each analyte in the laboratory control standard, calculate the percent recovery (P_i) with the equation:

$$P_i = \frac{100\ S_i}{T_i}$$

where S_i = the analytical result from the laboratory control standard, in µg/L; and
T_i = the known concentration of the spike, in µg/L.

9.3.2.2 Recovery data can be pooled to develop an expression of method accuracy for each analyte. These accuracy statements should be updated regularly for on-going quality assurance.

9.3.3 At least annually, the laboratory should participate in formal performance evaluation studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared.

9.4 ASSESSING PRECISION

9.4.1 Precision assessments for this method are based upon the analysis of field duplicates (Sect. 7.1). Analyze both sample bottles for at least 10% of all samples. To the extent practical, the samples selected for duplication should contain reportable levels of many analytes.

9.4.2 For each analyte in each duplicate pair, calculate the relative range (RR_i) with the equation:

$$RR_i = \frac{100\ R_i}{X_i}$$

where R_i = the absolute difference between the duplicate measurements X_1 and X_2, in µg/L

X_i = the average concentration found ($[X_1 + X_2]/2$), in µg/L.

9.4.3 Individual relative range measurements can be pooled to determine average relative range or to develop an expression of relative range as a function of concentration.

9.5 DAILY GC/MS PERFORMANCE TESTS

9.5.1 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.

9.5.2 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. PROCEDURE

10.1 INITIAL CONDITIONS

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

Electron Energy:	70 V (nominal)
Mass Range:	20 to 270 amu
Scan Time:	To give at least 5 scans per peak but not to exceed 7 s per scan.

10.1.2 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 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 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 (Fig. 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 (Fig. 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 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 GAS CHROMATOGRAPHY - The column described in this method is less than optimum for the analytes footnoted in Sect. 1.1. Method 503.1 is the method of choice for these analytes. However, in an effort to offer the maximum number of analytical options to the regulated community, this method permits two options for gas chromatography to meet the proposed monitoring requirements through a single analysis. These options are described below.

10.4.1 Hold the column temperature at 40°C for 3 min, then program at 8°C/min to 220°C and hold until all analytes elute. This

procedure results in excessively long (70+ minutes) determinations, broad peaks for a number of late eluting analytes and a relatively poor detection limit for tnese compounds.

10.4.2 Hold the column temperature at 40°C for 3 min, then program at 8°C/min to 245°C and hold until all analytes elute. This procedure exceeds the recommended maximum temperature for the column and may reduce the column life and affect separations. The trichlorobenzenes will have broad peaks and poor detection limits.

10.4.3 Chromatograph the analytes footnoted in Sect. 1.1 by substituting the SP-1200/Bentone 34 column from Method 503.1 and selecting one of the temperature programs described in that method for incorporation into this method.

10.5 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.

10.6 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 Obtain EICPs for the primary m/z (Table 4) and the secondary masses listed for each analyte. The following criteria must be met to make a qualitative identification:

11.1.1 The characteristic masses of each analyte of interest must maximize in the same or within one scan of each other.

11.1.2 The retention time must fall within ± 30 s of the retention time of the authentic compound.

11.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ± 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

11.2 Structural isomers that have very similar mass spectra (e.g. dichlorobenzenes and xylenes) and less than 30 s difference in

retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers 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

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

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
Pentachloroethane	24.6	—	—	—
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 (28.2)[3]	—	—	—
m-Xylene	29.5 (29.0)	—	—	—
Styrene	29.7 (29.2)	1.3	0.20	—
n-Propylbenzene	30.7 (30.4)	—	—	—
o-Xylene	30.9 (30.4)	—	0.20	—
p-Xylene	30.9 (30.4)	0.18	0.13	—
bis-(2-Chloroisopropyl)ether	31.1 (30.8	—	—	—
t-Butylbenzene	31.5 (30.5)	—	—	—

Table 1. (Continued)

Analyte	Retention Time[1] (min)	Method Detection Limits (µg/L) Ref. 1	Ref. 8	Ref. 9
2-Chlorotoluene	31.5 (30.5)	—	—	—
Hexachlorobutadiene	32.0 (30.9)	—	—	—
4-Chlorotoluene	32.5 (31.6)	—	—	—
sec-Butylbenzene	32.5 (31.5)	—	—	—
1,2-Dichlorobenzene	35.0 (33.8)	—	1.0	—
1,4-Dichlorobenzene	35.3 (34.0)	0.3	2.0	0.1
p-Isopropyltoluene	40.9 (35.7)	—	—	—
n-Butylbenzene	45.5 (38.0)	—	—	—
1,3,5-Trimethylbenzene	46.5 (38.6)	—	—	—
1,2,4-Trimethylbenzene	51.0 (40.5)	—	—	—
1,2,4-Trichlorobenzene	71.0 (51.5)	—	—	—
1,2,3-Trichlorobenzene	77.5 (53.9)	—	—	—

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

3 Values in parentheses refer to retention times when the final hold temperature is raised to 245°C. See Sect. 10.4 for discussion.

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	< 1% of mass 95
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 µg/L	Number of Samples	Average Conc. Measured µg/L	Standard Deviation µg/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 4. CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANICS

Analyte	Primary Ion	Secondary Ions
Benzene	78	—
Bromobenzene	77	156, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	127	83, 85, 129
Bromoform	173	171, 175, 250
Bromomethane	94	96
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
bis-2-Chloroisopropyl ether	45	77, 79
Carbon tetrachloride	117	119, 121
Chlorobenzene	112	114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
Dibromochloromethane	127	129, 208
1,2-Dibromo-3-chloropropane	75	155, 157
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174, 176
1,2-Dichlorobenzene	146	148, 113
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 113
Dichlorodifluoromethane	85	87, 111
1,1-Dichloroethane	63	65, 83, 85
1,2-Dichloroethane	98	62, 64, 100
1,1-Dichloroethene	96	61, 98
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,1-Dichloropropane	63	41, 77
1,2-Dichloropropane	112	63, 114
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97, 41, 99
1,1-Dichloropropene	110	112, 77
Ethyl benzene	106	91
Hexachlorobutadiene	225	223, 227
Isopropylbenzene	91	120
p-Isopropyltoluene	119	134, 91
Methylene chloride	84	49, 51, 86
Pentachloroethane	117	119, 95, 167
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133, 117, 119

Table 4. (Continued)

Analyte	Primary Ion	Secondary Ions
1,1,2,2-Tetrachloroethane	168	83, 85
Tetrachloroethene	164	129, 131
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,2-Trichloroethane	97	83, 99
1,2,3-Trichloropropane	75	77, 110, 112
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Toluene	92	91
1,1,1-Trichloroethane	97	99, 117
Trichloroethene	130	95, 97
Trichlorofluoromethane	101	103
Vinyl chloride	62	64
m-Xylene	91	106
o-Xylene	91	106
p-Xylene	91	106

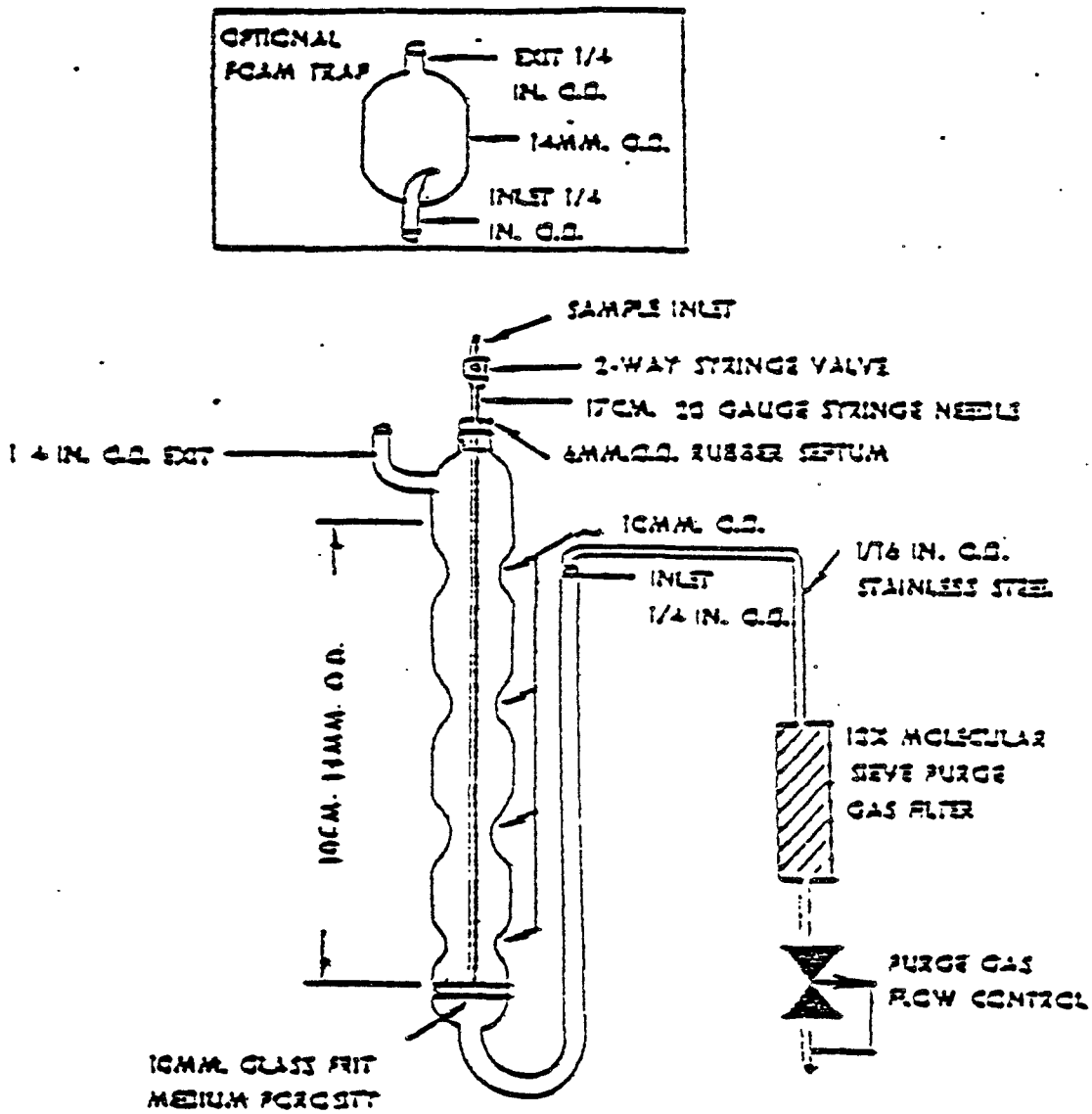

FIGURE 1. PURGING DEVICE.

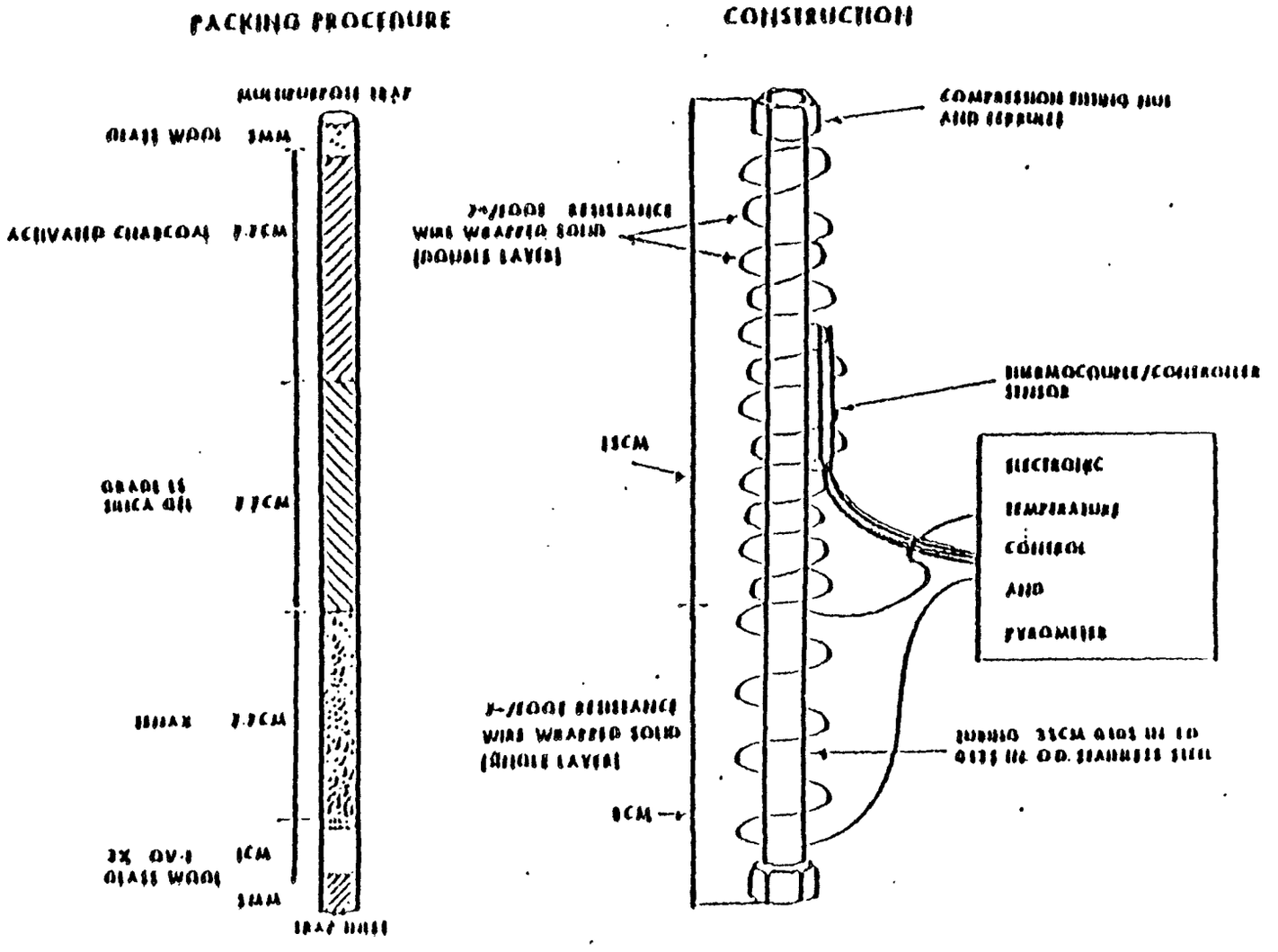

FIGURE 2. TRAP.

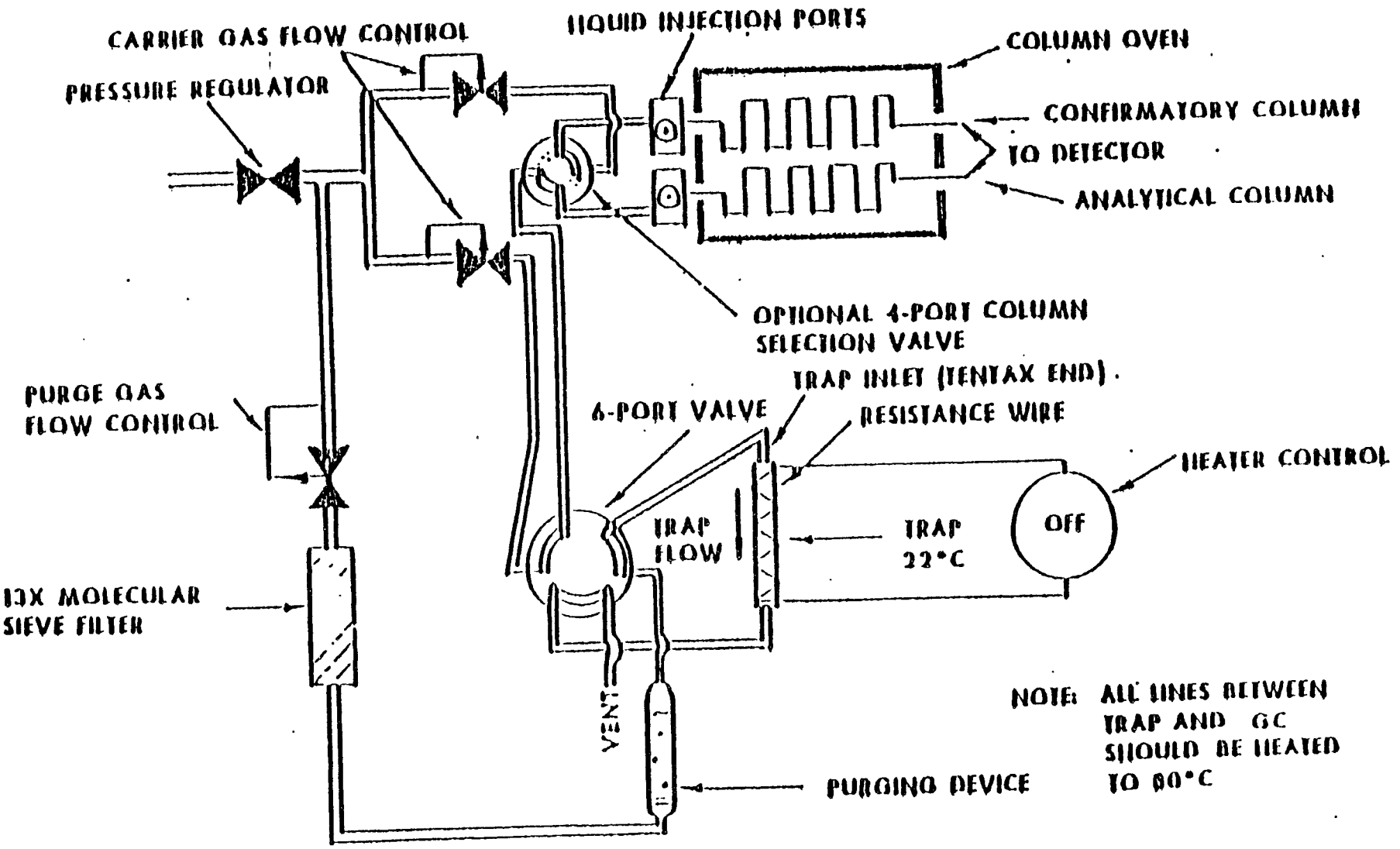

FIGURE 3. PURGE AND TRAP SYSTEM (PURGE-SORB MODE).

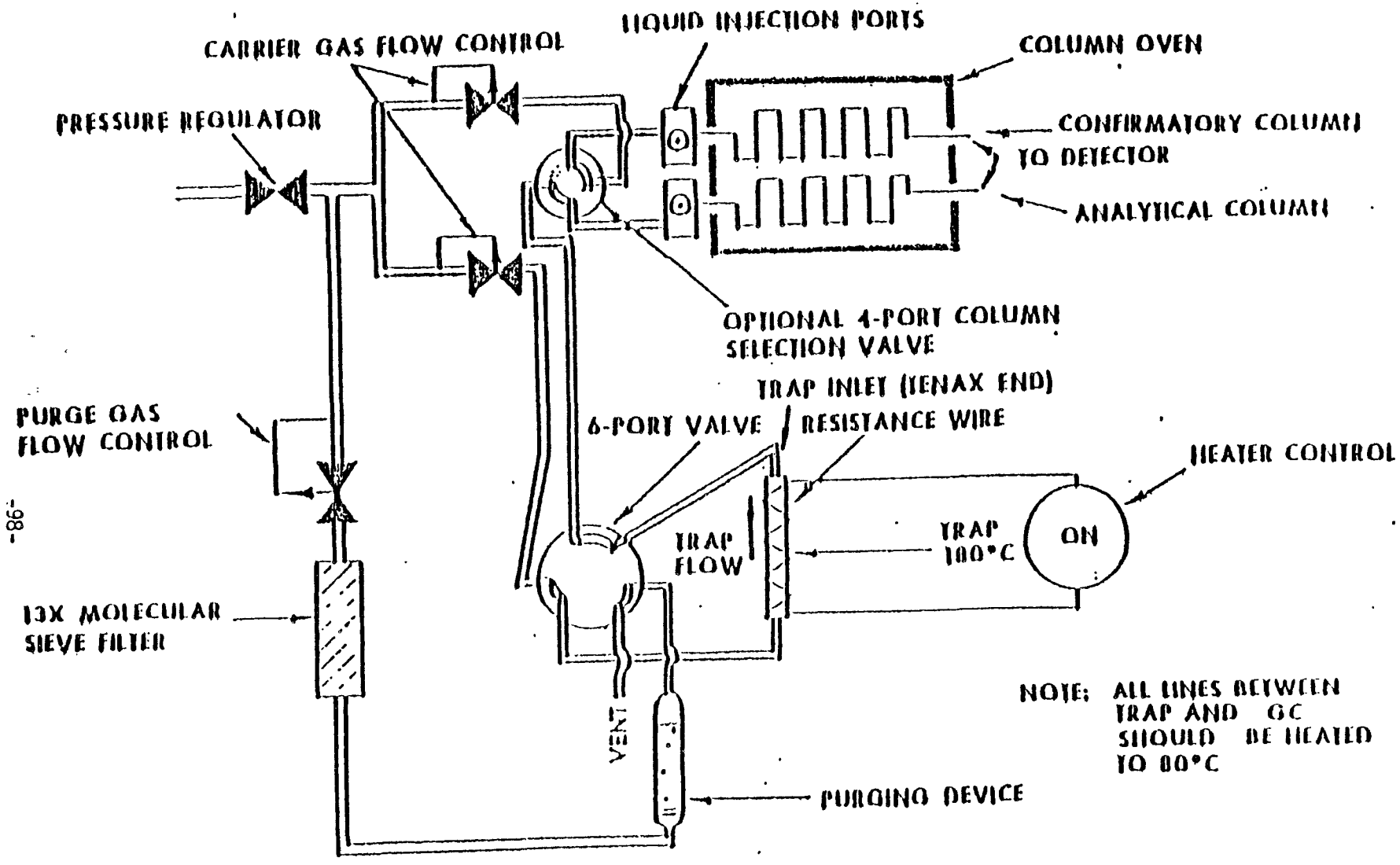

FIGURE 4. PURGE AND TRAP SYSTEM (DESORB MODE).

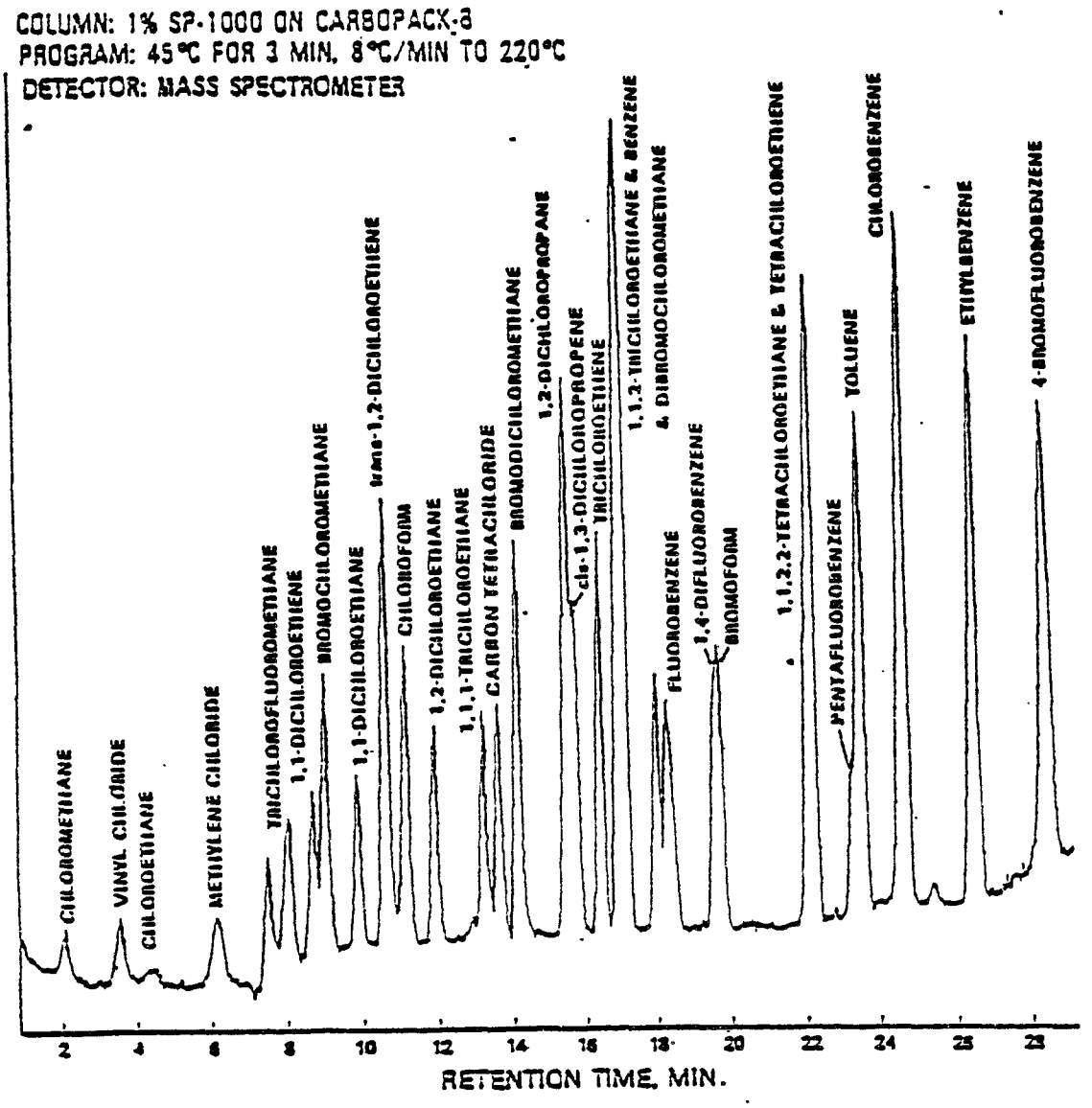

Figure 5. Gas chromatogram of volatile organics.