THE ANALYSIS OF TRIHALOMETHANES IN FINISHED WATERS BY THE PURGE AND TRAP METHOD

Method 501.1

U. S. ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY

CINCINNATI, OHIO 45268

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Foreword

This method has been prepared by the staff of the Environmental Monitoring and Support Laboratory - Cincinnati, at the request of the Office of Drinking Water. Comments and suggestions offered by the Municipal Environmental Research Laboratory, the Technical Support Division, ODW, and the Health Effects Research Laboratory on the September 9, 1977, draft are gratefully acknowledged.

The procedure represents the current state-of-the-art, but as time progresses improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

The Analysis of Trihalomethanes in Drinking Water by the Purge and Trap Method

1. Scope

1.1 This method (1) is applicable in the determination of four trihalomethanes, i.e. chloroform, dichlorobromethane, dibromochloromethane, and bromoform in finished drinking water, raw source water, or drinking water in any stage of treatment. The concentration of these four compounds is totaled to determine total trihalomethanes (TTHM).

1.2 For compounds other than the above-mentioned trihalomethanes, or for other sample sources, the analyst must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples as described (2).

1.3 Although the actual detection limits are highly dependent upon the gas chromatographic column and detector employed, the method can be used over a concentration range of approximately 0.5 to 1500 micrograms per liter.

1.4 Well in excess of 100 different water supplies have been analyzed using this method. Supplementary analyses using gas chromatography mass spectrometry (GC/MS) have shown that there is no evidence of interference in the determination of trihalomethanes (3). For this reason, it is not necessary to analyze the raw source water as is required with the Liquid/Liquid Extraction Method (4).

2. Summary

2.2 Trihalomethanes are extracted by an inert gas which is bubbled through the aqueous sample. The trihalomethanes, along with other

If any trihalomethane is noted in the method blank in excess of 0.4 µg/l, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting the blank values is not recommended. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components should be avoided since such materials generally out-gas organic compounds which will be concentrated in the trap during the purge operation. Such out-gasing problems are common whenever new equipment is put into service; as time progresses, minor out-gasing problems generally cure themselves.

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

3.3 For compounds that are not efficiently purged, such as bromoform, small variations in sample volume, purge time, purge flow rate, or purge temperature can affect the analytical result. Therefore, samples and standards must be analyzed under identical conditions.

3.4 Cross-contamination can occur whenever high-level and low-level samples are sequentially analyzed. To reduce this likelihood, the purging device and sample syringe should be rinsed twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it is highly recommended that it be followed by a sample blank analysis to ensure that sample cross contamination does not occur. For samples containing large amounts of water soluble materials, it may be necessary to wash out the

organic constituents which exhibit low water solubility and a vapor pressure significantly greater than water, are efficiently transferred from the aqueous phase to the gaseous phase. These compounds are swept from the purging device and are trapped in a short column containing a suitable sorbent. After a predetermined period of time, the trapped components are thermally desorbed and backflushed onto the head of a gas chromatographic column and separated under programmed conditions. Measurement is accomplished with a halogen specific detector such as electrolytic conductivity or microcoulometric titration.

2.3 Confirmatory analyses are performed using dissimilar columns, or by mass spectrometry (5).

2.4 Aqueous standards and unknowns are extracted and analyzed under identical conditions in order to compensate for extraction losses.

2.5 The total analysis time, assuming the absence of other organohalides, is approximately 35 minutes per sample.

3. Interferences

3.1 Impurities contained in the purge gas and organic compounds outgasing from the plumbing ahead of the trap usually account for the majority of contamination problems. The presence of such interferences are easily monitored as a part of the quality control program. Sample blanks are normally run between each set of samples. When a positive trihalomethane response is noted in the sample blank, the analyst should analyze a method blank. Method blanks are run by charging the purging device with organic-free water and analyzing in the normal manner.

purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

3.5 Qualitative misidentifications are a problem in using gas chromatographic analysis. Whenever samples whose qualitative nature is unknown are analyzed, the following precautionary measures should be incorporated into the analysis.

3.5.1 Perform duplicate analyses using the two recommended columns (4.2.1 and 4.2.2) which provide different retention order and retention times for the trihalomethanes and other organohalides.

3.5.2 Whenever possible, use GC/MS techniques which provide unequivocal qualitative identifications (5).

4. Apparatus

4.1 The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. Construction details for a purging device and an easily automated trap-desorber hybrid which has proven to be exceptionally efficient and reproducible are shown in Figures 1 through 4 and described in 4.1.1 through 4.1.3. An earlier acceptable version of the above-mentioned equipment is described in (1).

4.1.1 Purging Device - Construction details are given in Figure 1 for an all-glass 5 ml purging device. The glass frit installed at the base of the sample chamber allows finely divided gas bubbles to pass through the sample while the

sample is restrained above the frit. Gaseous volumes above the sample are kept to a minimum to eliminate dead volume effects, yet allowing sufficient space for most foams to disperse. The inlet and exit ports are constructed from heavy-walled 1/4-inch glass tubing so that leak-free removable connections can be made using "finger-tight" compression fittings containing Teflon ferrules. The removable foam trap is used to control samples that foam.

4.1.2 Trapping Device - The trap (Figure 2) is a short gas chromatographic column which at <35°C retards the flow of the compounds of interest while venting the purge gas and, depending on which sorbent is used, much of the water vapor. The trap should be constructed with a low thermal mass so that it can be heated to 180°C in less than 1 minute for efficient desorption, then rapidly cooled to room temperature for recycling. Variations in the trap ID, wall thickness, sorbents, sorbent packing order, and sorbent mass could adversely affect the trapping and desorption efficiencies for compounds discussed in this text. For this reason, it is important to faithfully reproduce the trap configurations recommended in Figure 2. Traps containing Tenax only, or combinations of Tenax and other sorbents are acceptable for this analysis.

4.1.3 Desorber assembly - Details for the desorber are shown in Figures 3, and 4. With the 6-port valve in the Purge Sorb position (Figure 3), the effluent from the purging device

passes through the trap where the flow rate of the organics is retarded. The GC carrier gas also passes through the 6-port valve and is returned to the GC. With the 6-port valve in the Purge-Sorb position, the operation of the GC is in no way impaired; therefore, routine liquid injection analyses can be performed using the gas chromatograph. After the sample has been purged, the 6-port valve is turned to the desorb position (Figure 4). In this configuration, the trap is coupled in series with the gas chromatographic column allowing the carrier gas to backflush the trapped materials into the analytical column. Just as the valve is actuated, the power is turned on to the resistance wire wrapped around the trap. The power is supplied by an electronic temperature controller. Using this device, the trap is rapidly heated to 180°C and then maintained at 180°C with minimal temperature overshoot. The trapped compounds are released as a "plug" to the gas chromatograph. Normally, packed columns with theoretical efficiencies near 500 plates/foot under programmed temperature conditions can accept such desorb injections without altering peak geometry. Substituting a non-controlled power supply, such as a manually-operated variable transformer, will provide nonreproducible retention times and poor quantitative data unless Injection Procedure (8.9.2) is used.

4.1.4 Several Purge and Trap Devices are now commercially

available. It is recommended that the following be taken into consideration if a unit is to be purchased:

a. Be sure that the unit is completely compatible with the gas chromatograph to be used for the analysis.

b. Use a 5-ml purging device similar to that shown in Figure 1.

c. Be sure the Tenax portion of the trap meets or exceeds the dimensions shown in Figure 2.

d. With the exception of sample introduction, select a unit that has as many of the purge trap functions automated as possible.

4.2 Gas chromatograph - The chromatograph must be temperature programmable and equipped with a halide specific detector.

4.2.1 Column I is an unusually efficient column which provides outstanding separations for a wide variety of organic compounds. Because of its ability to resolve trihalomethanes from other organochlorine compounds, column I should be used as the primary analytical column (see Table 1 for retention data using this column).

4.2.1.1 Column I parameters: Dimensions - 8 feet long x 0.1 inch ID stainless steel or glass tubing. Packing - 1% SP-1000 on Carbopack-B (60/80) mesh. Carrier Gas - helium at 40 ml/minute. Temperature program sequence: 45°C isothermal for 3 minutes, program at 8°C/minute to 220°C then hold for 15 minutes or until all compounds have eluted.

NOTE: It has been found that during handling, packing, and programming, active sites are exposed on the Carbopack-B packing. This results in tailing peak geometry and poor resolution of many constituents. To correct this, pack the first 5 cm of the column with 3% SP-1000 on Chromosorb-W 60/80 followed by the Carbopack-B packing. Condition the pre-column 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/minute carrier flow, then the column should be repacked.

4.2.1.2 Acceptable column equivalent to Column I: Dimensions - 8 feet long x 0.1 inch ID stainless steel or glass tubing. Packing - 0.2% Carbowax 1500 on Carbopack-C (80/100) mesh. Carrier Gas - helium at 40 ml/minute. Temperature program sequence - 60°C isothermal for 3 minutes, program at 8°C/ minute to 160°C, then hold for 2 minutes or until all compounds have eluted.

NOTE: It has been found that during handling, packing, and programming, active sites are exposed on the Carbopack-C packing. This

results in poor resolution of constituents and poor peak geometry. To correct this, place a 1 ft. 0.125 in. OD x 0.1 in. ID stainless steel column packed with 3% Carbowax 1500 on Chromosorb-W 60/80 mesh in series before the Carbopack-C column. Condition the precolumn and the Carbopack columns with carrier gas flow at 190°C overnight. The two columns may be retained in series for routine analyses. Trihalomethane retention times are listed in Table 1.

4.2.2 Column II provides unique organohalide-trihalomethane separations when compared to those obtained from Column I (see Figures 5 and 6). However, since the resolution between various compounds is generally not as good as those with Column I, it is recommended that Column II be used as a qualitative confirmatory column for unknown samples when GC/MS confirmation is not possible.

4.2.2.1 Column II parameters: Dimensions - 6 feet long x 0.1 inch ID stainless steel or glass. Packing - n-octane on Porisil-C (100/120 mesh). Carrier Gas - helium at 40 cc/minute. Temperature program sequence - 50°C isothermal for 3 minutes, program at 6°/minute to 170°C, then hold for 4 minutes or until all compounds have eluted. Trihalomethane retention times are listed in Table 1.

4.3 Sampling containers - 40 ml screw cap vials sealed with Teflon faced silicone septa.

Vials and caps - Pierce #13075 or equivalent.

Septa - Pierce #12722 or equivalent.

4.4 Syringes - 5-ml glass hypodermic with luerlok tip (2 each).

4.5 Micro syringes - 10, 100 µl.

4.6 Micro syringe - 25 µl with a 2" x 0.006" ID needle-Hamilton #702N, or equivalent.

4.7 2-way syringe valve with luer ends (3 each) Hamilton #86570-1FM1, or equivalent.

4.8 Standard storage containers - 15 ml amber screw-cap septum bottles with Teflon faced silicone septa.

Bottles and Caps - Pierce #19830, or equivalent.

Septa - Pierce #12716, or equivalent.

5. <u>Reagents and Materials</u>

5.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2 Three percent OV-1 Chromosorb-W 60/80 mesh.

5.3 1.0% SP-1000 on Carbopack-B (60/80 mesh) available from Supelco.

5.4 n-Octane on Porasil-C (100/120 mesh) available from Waters Associates.

5.5 Three percent SP-1000 on Chromosorb-W (60/80 mesh).

5.6 Free and combined chlorine reducing agent - crystalline sodium thiosulfate, ACS Reagent Grade or sodium sulfite, ACS Reagent Grade.

5.7 Activated carbon - Filtrasorb-200, available from Calgon Corporation, Pittsburgh, PA, or equivalent.

5.8 Organic-free water is defined as water free of interference when employed in the purge and trap analysis.

5.8.1 Organic-free water is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. Change the activated carbon bed whenever the concentration of any trihalomethane exceeds 0.4 µg/l.

5.8.2 A Millipore Super-Q Water System or its equivalent may be used to generate organic-free water.

5.8.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle with a Teflon seal.

5.8.4 Test organic free water each day it is used by analyzing according to Section 8.

5.9 Standards[a]

5.9.1 Bromoform - 96% - available from Aldrich Chemical Company.

5.9.2 Bromodichloromethane 97% - available from Aldrich Chemical Company.

5.9.3 Chlorodibromomethane - available from Columbia Chemical Inc., Columbia, S.C.

5.9.4 Chloroform - 99% - available from Aldrich Chemical Company.

[a]As a precautionary measure, all standards must be checked for purity by boiling point determinations or GC/MS assays (5).

5.10 Standard Stock Solutions

5.10.1 Place about 9.8 ml of methyl alcohol into a ground glass stoppered 10 ml volumetric flask.

5.10.2 Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces have dried.

5.10.3 Weigh the flask to the nearest 0.1 mg.

5.10.4 Using a 100 µl syringe, immediately add 2 drops of the reference standard to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5.10.5 Dilute to volume, stopper, then mix by inverting the flask several times.

5.10.6 Transfer the solution to a dated and labeled 15 ml screw cap bottle with a Teflon cap liner.

NOTE: Because of the toxicity of trihalomethanes, it is necessary to prepare primary dilutions in a hood. It is further recommended that a NIOSH/MESA approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

5.10.7 Calculate the concentration in micrograms per microliter from the net gain in weight.

5.10.8 Store the solution at $4^{o}C$.

NOTE: All standard solutions prepared in methyl alcohol are stable up to 4 weeks when stored under these conditions. They should be discarded after that time has elapsed.

5.11 Aqueous Calibration Standard Precautions

5.11.1 In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

a. Do not inject more than 20 µl of alcoholic standards into 100 ml of organic-free water.

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

c. Rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.

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

e. Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask as directed in Section 8.5.

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

g. Aqueous standards when stored with a headspace are not stable and should be discarded after one hour.

h. Aqueous standards can be stored according to Sections 6.4 and 8.6.

5.11.2 Prepare, from the standard stock solutions, secondary dilution mixtures in methyl alcohol so that a 20 µl

injection into 100 ml of organic-free water will generate a calibration standard which produces a response close (±10%) to that of the sample (See 9.1).

5.11.3 Purge and analyze the aqueous calibration standards in the same manner as the samples.

5.11.4 Other calibration procedures (3) which require the delivery of less than 20 µl of a methanolic standard into a 5.0 ml volume of water already contained in the sample syringe are acceptable only if the methanolic standard is delivered by the solvent flush technique (6).

5.12 Quality Check Standard (2.0 µg/l)

5.12.1 From the standard stock solutions, prepare a secondary dilution in methyl alcohol containing 10 ng/µl of each trihalomethane (See Section 5.10.8 Note).

5.12.2 Daily, inject 20.0 µl of this mixture into 100.0 ml of organic-free water and analyze according to Section 8.

6. Sample Collection and Handling

6.1 The sample containers should have a total volume of at least 25 ml.

6.1.1 Narrow mouth screw cap bottles with the TFE fluorocarbon face silicon septa cap liners are strongly recommended.

6.2 Sample Bottle Preparation

6.2.1 Wash all sample bottles and TFE seals in detergent. Rinse with tap water and finally with distilled water.

6.2.2 Allow the bottles and seals to air dry at room temperature, then place in a 105°C oven for one hour, then allow to cool in an area known to be free of organics.

NOTE: Do not heat the TFE seals for extended periods of time (>1 hour) because the silicone layer slowly degrades at 105°C.

6.2.3 When cool, seal the bottles using the TFE seals that will be used for sealing the samples.

6.3 Sample Stabilization - A chemical reducing agent (Section 5.6) is added to the sample in order to arrest the formation of trihalomethanes after sample collection (3, 7). <u>Do not add the reducing agent to samples when data on maximum trihalomethane formation is desired</u>. If chemical stabilization is employed, the reagent is also added to the blanks. The chemical agent (2.5 to 3 mg/40 ml) is added to the empty sample bottles just prior to shipping to the sampling site.

6.4 Sample Collection

6.4.1 Collect all samples in duplicate.

6.4.2 Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is filled.

6.4.3 Seal the bottles so that no air bubbles are entrapped in it.

6.4.4 Maintain the hermetic seal on the sample bottle until analysis.

6.4.5 Sampling from a water tap.

6.4.5.1 Turn on water and allow the system to flush until the temperature of the water has stabilized. Adjust the flow to about 500 ml/minute and collect duplicate samples from the flowing stream.

6.4.6 Sampling from an open body of water.

6.4.6.1 Fill a 1-quart wide-mouth bottle with sample from a representative area. Carefully fill duplicate sample bottles from the 1-quart bottle as noted in 6.4.2.

6.4.7 If a chemical reducing agent has been added to the sample bottles, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

6.4.8 Sealing practice for septum seal screw cap bottles.

6.4.8.1 Open the bottle and fill to overflowing, place on a level surface, position the TFE side of the septum seal upon the convex sample meniscus and seal the bottle by screwing the cap on tightly.

6.4.8.2 Invert the sample and lightly tap the cap on a solid surface. The absence of entrapped air indicates a successful seal. If bubbles are present, open the bottle, add a few additional drops of sample and reseal the bottle as above.

6.4.9 Blanks

6.4.9.1 Prepare blanks in duplicate at the laboratory by filling and sealing sample bottles with organic-free water just prior to shipping the sample bottles to the sampling site.

6.4.9.2 If the sample is to be stabilized, add an identical amount of stabilization reagent to the blanks.

6.4.9.3 Ship the blanks to and from the sampling site along with the sample bottles.

6.4.9.4 Store the blanks and the samples collected at a given site (sample set) together. A sample set is defined as all the samples collected at a given site (i.e., at a water tretment plant, the duplicate raw source waters, the duplicate finished waters and the duplicate blank samples comprise the sample set).

6.5 When samples have been collected according to Section 6, no measurable loss of trihalomethanes has been detected over extended periods of storage time (3). It is recommended that all samples be analyzed within 14 days of collection.

7. Conditioning Traps

7.1 Condition newly packed traps overnight at 180°C with an inert gas flow of at least 20 ml/min.

7.1.1 Vent the trap effluent to the room, not to the analytical column.

7.2 Prior to daily use, condition traps 10 minutes while backflushing at 180°C. It may be beneficial to routinely condition traps overnight while backflushing at 180°C.

7.2.1 The trap may be vented to the analytical column; however, after conditioning, the column must be programmed prior to use.

8. Extraction and Analysis

8.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min.

8.2 Attach the trap inlet to the purging device. Turn the valve to the purge-sorb position (Figure 3).

8.3 Open the syringe valve located on the purging device sample introduction needle.

8.4 Remove the plungers from two 5 ml syringes and attach a closed syringe valve to each.

8.5 Open the sample bottle and carefully pour the sample into one of the syringe barrels until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Close the valve.

8.6 Fill the second syringe in an identical manner from the same sample bottle. This second syringe is reserved for a duplicate analysis, if necessary (See Section 9.3 and 9.4).

8.7 Attach the syringe-valve assembly to the syringe valve on the purging device.

8.8 Open the syringe valve and inject the sample into the purging chamber. Close both valves. Purge the sample for 11.0 $\pm$ .05 minutes.

8.9 After the 11-minute purge time, attach the trap to the chromatograph (turn the valve to the desorb position) and 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 minutes.

8.9.1 If the trap can be rapidly heated to 180°C and maintained at this temperature, the GC analysis can begin as the

sample is desorbed, i.e., the column is at the initial $45^{o}C$ operating temperature. The equipment described in Figure 4 will perform accordingly.

8.9.2 With other types of equipment (see Section 4.1.4 and Reference 1) where the trap is not rapidly heated or is not heated in a reproducible manner, it may be necessary to transfer the contents of the trap into the analytical column at $<30^{o}C$ where it is once again trapped. Once the transfer is complete (4 minutes), the column is rapidly heated to the initial operating temperature for analysis.

8.9.3 If injection procedure 8.9.1 is used and the early eluting peaks in the resulting chromatogram have poor geometry or variable retention times, then Section 8.9.2 should be used.

8.10 After the extracted sample is introduced into the gas chromatograph, empty the gas purging device using the sample introduction syringe, followed by two 5-ml flushes of organic-free water. When the purging device is emptied, leave the syringe valve open allowing the purge gas to vent through the sample introduction needle.

8.11 Analyze each sample and sample blank from the sample set in an identical manner (see Section 6.4.9.4) on the same day.

8.12 Prepare calibration standards from the standard stock solutions (Section 5.10) in organic-free water that are close to the unknown in trihalomethane composition and concentration (Section 9.1). The concentrations should be such that only 20 µl or less of the secondary dilution need be added to 100 ml of organic-free water to

produce a standard at the same level as the unknown.

8.13 As an alternative to Section 8.12, prepare a calibration curve for each trihalomethane containing at least 3 points, two of which must bracket the unknown.

9. Analytical Quality Control

9.1 Analyze the 2 µg/l check sample daily before any samples are analyzed. Instrument status checks and lower limit of detection estimations based upon response factor calculations at five times the noise level are obtained from these data. In addition, response factor data obtained from the 2 µg/l check standard can be used to estimate the concentration of the unknowns. From this information, the appropriate standard dilutions can be determined.

9.2 Analyze the sample blank to monitor for potential interferences as described in Sections 3.1, 3.2, and 3.4.

9.3 Spiked Samples

9.3.1 For laboratories analyzing more than 10 samples a day, each 10th sample should be a laboratory generated spike which closely duplicates the average finished drinking water in trihalomethane composition and concentration. Prepare the spiked sample in organic-free water as described in Section 5.11.

9.3.2 For laboratories analyzing less than 10 samples daily, each time the analysis is performed, analyze at least 1 laboratory generated spike sample which closely duplicates the average finished drinking water in trihalomethane composition and concentration. Prepare the spiked sample

in organic-free water as described in Section 5.11.

9.4 Randomly select and analyze 10% of all samples in duplicate.

9.4.1 Analyze all samples in duplicate which appear to deviate more than 30% from any established norm.

9.5 Maintain an up-to-date log on the accuracy and precision data collected in Sections 9.3 and 9.4. If results are significantly different than those cited in Section 11.1, the analyst should check out the entire analyses scheme to determine why the laboratory's precision and accuracy limits are greater.

9.6 Quarterly, spike an EMSL-Cincinnati trihalomethane quality control sample into organic-free water and analyze.

9.6.1 The results of the EMSL trihalomethane quality control sample should agree within 20% of the true value for each trihalomethane. If they do not then the analyst must check each step in the standard generation procedure to solve the problem (Section 5.9, 5.10, and 5.11).

9.7 Maintain a record of the retention times for each trihalomethane using data gathered from spiked samples and standards.

9.7.1 Daily calculate the average retention time for each trihalomethane and the variance encountered for the analyses.

9.7.2 If individual trihalomethane retention time varies by more than 10% over an eight hour period or does not fall with 10% of an established norm, the system is "out of control." The source of retention data variantion must be corrected before acceptable data can be generated.

10. Calculations

10.1 Locate each trihalomethane in the sample chromatogram by comparing the retention time of the suspect peak to the data gathered in 9.7.1. The retention time of the suspect peak must fall within the limits established in 9.7.1 for single column identification.

10.2 Calculate the concentration of the samples by comparing the peak height or peak areas of the samples to the standard peak height (8.12). Round off the data to the nearest µg/l or two significant figures.

$$\mu g/l = \left(\frac{\text{peak height sample}}{\text{peak height standard}}\right) \times (\text{conc. std. } \mu g/l)$$

10.3 Report the results obtained from the lower limit of detection estimates along with the data for the samples.

10.4 Calculate the total trihalomethane concentration (TTHM) by summing the 4 individual trihalomethane concentrations in µg/l.

TTHM (µg/l) = (Conc. $CHCl_3$)+(Conc. $CHBrCl_2$)+(Conc. $CHBr_2Cl$)+ Conc. CHBr).

10.5 Calculate the limit of detection (LOD) for each trihalomethane not detected using the following criteria:

$$\text{LOD } (\mu g/l) = \frac{(A \times ATT)}{(B \times ATT)} \quad (2\ \mu g/l)$$

where B = peak height (mm) of 2 µg/l quality check standard

A = 5 times the noise level in (mm) at the exact retention time of the trihalomethane or the baseline displacement in (mm) from the theoretical zero at the exact retention time of the trihalomethane.

ATT = Attenuation factor

11. Accuracy and Precision

11.1 One liter of organic-free water was spiked with the trihalomethanes and used to fill septum seal vials which were stored under ambient conditions. The spiked samples were randomly analyzed over a 2-week period of time. The single laboratory data listed in Table II reflect the errors due to the analytical procedure and storage.

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TABLE I

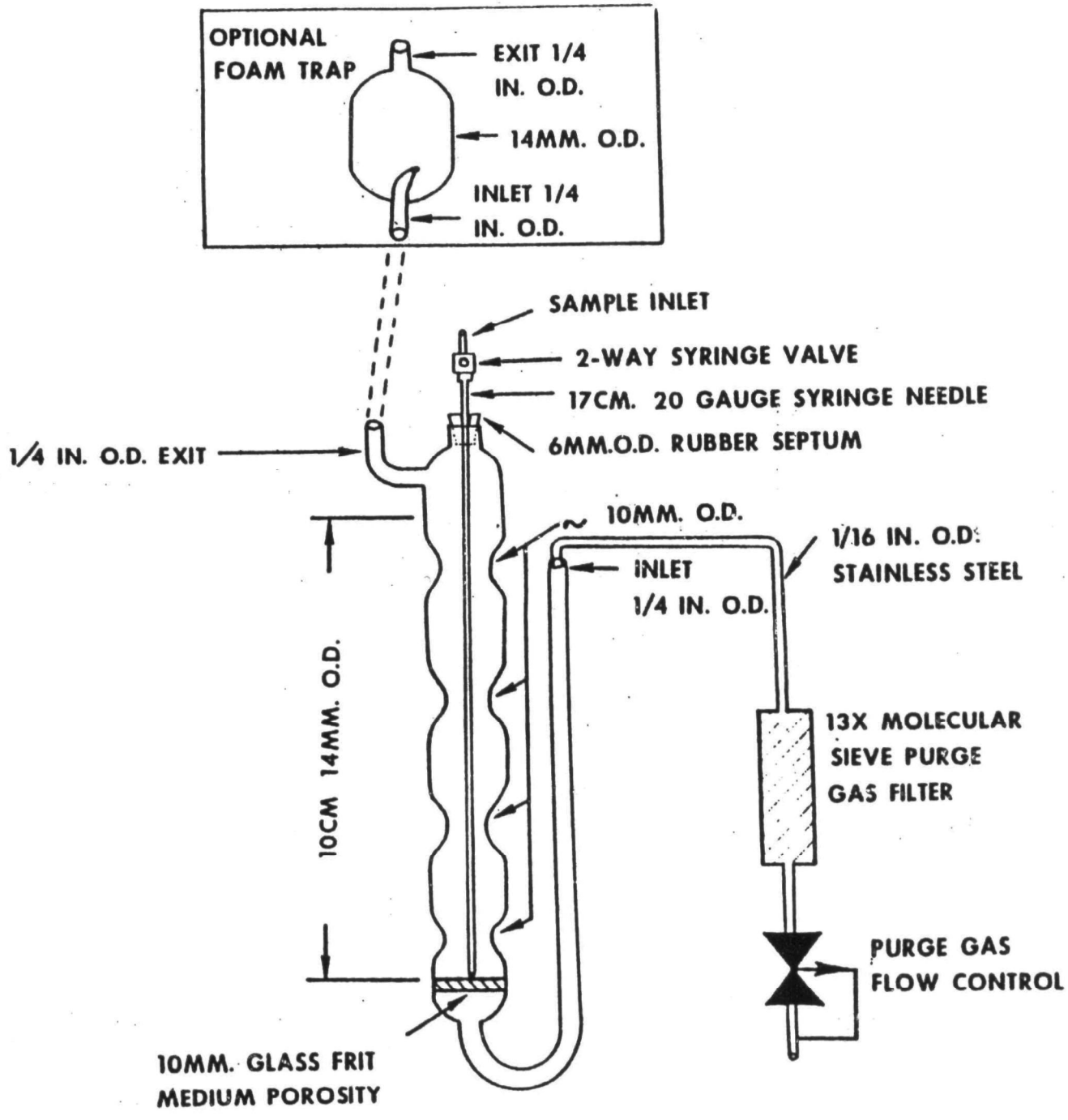
Retention Data for Trihalomethanes

Trihalomethane	Retention Time Minutes		
	Column I 1% SP1000 Carbopack B	Acceptable Alternative to Column I 0.4% Carbowax Carbopack C	Column II n-Octane Porasil-C
Chloroform	10.7	8.2	12.2
Bromodichloromethane	13.7	10.8	14.7
Chlorodibromomethane (Dibromochloromethane)	16.5	13.2	16.6
Bromoform	19.2	15.7	19.2

TABLE II

Single Laboratory
Accuracy and Precision for Trihalomethanes

Spike µg/l	Number Samples	Mean µg/l	Precision Standard Deviation	Accuracy % Recovery
		Chloroform		
1.2	12	1.2	0.14	100
12.	8	11.	0.16	92
119	11	105	7.9	88
		Bromodichloromethane		
1.6	12	1.5	0.05	94
16.	8	15.	0.39	94
160	11	145.	10.2	91
		Chlorodibromomethane		
2.0	12	1.9	0.09	95
20.	8	19.	0.70	95
196.	11	185.	10.6	94
		Bromoform		
2.3	12	2.3	0.16	100
23.	8	23.	1.38	100
231.	11	223	16.3	97


OPTIONAL
FOAM TRAP
EXIT 1/4
IN. O.D.
14MM. O.D.
INLET 1/4
IN. O.D.
SAMPLE INLET
2-WAY SYRINGE VALVE
17CM. 20 GAUGE SYRINGE NEEDLE
6MM.O.D. RUBBER SEPTUM
1/4 IN. O.D. EXIT
10MM. O.D.
1/16 IN. O.D.
STAINLESS STEEL
INLET
1/4 IN. O.D.
10CM 14MM. O.D.
13X MOLECULAR
SIEVE PURGE
GAS FILTER
PURGE GAS
FLOW CONTROL
10MM. GLASS FRIT
MEDIUM POROSITY

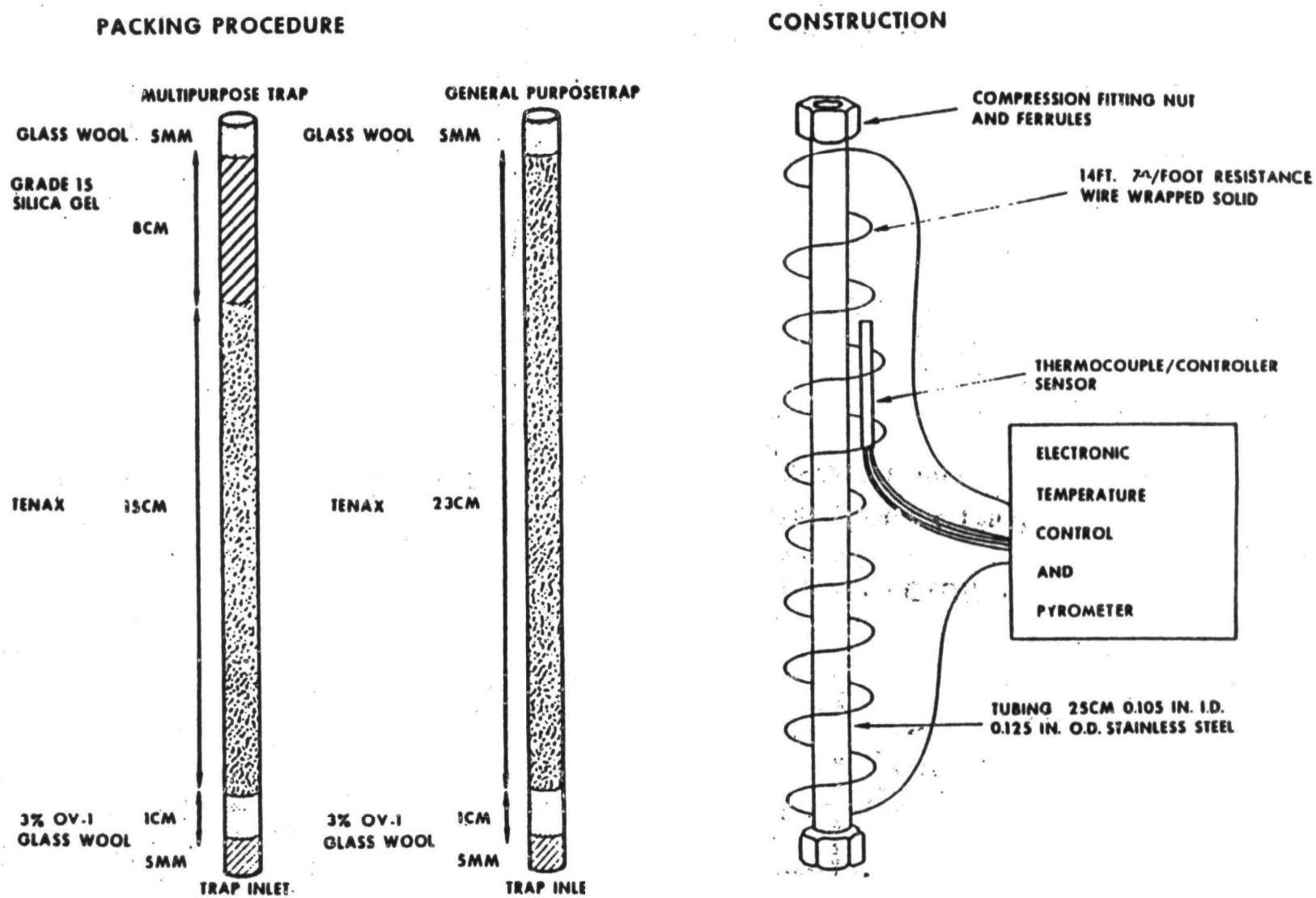


FIGURE 2 TRAP

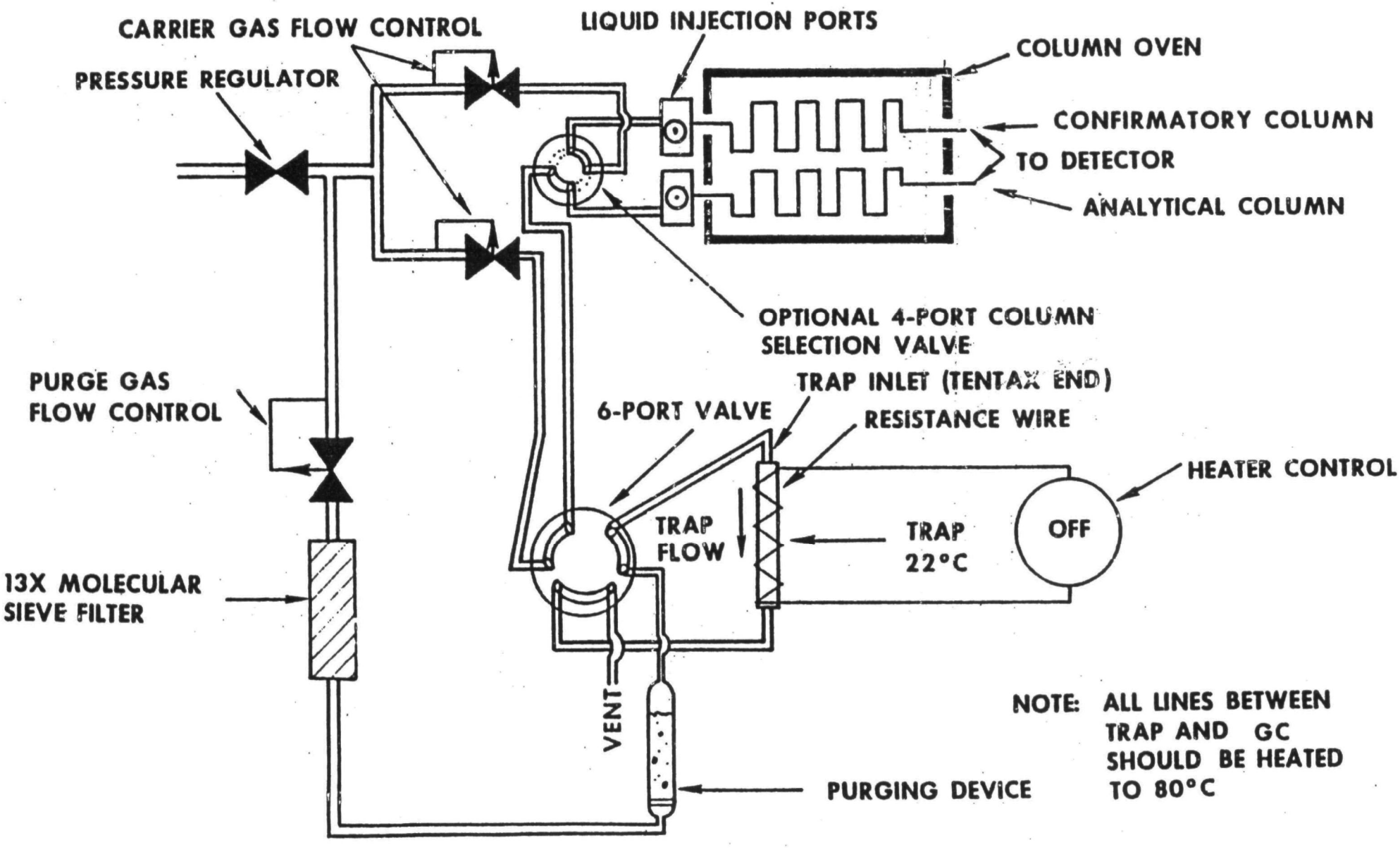


FIGURE 3 PURGE-TRAP SYSTEM (PURGE-SORB MODE)

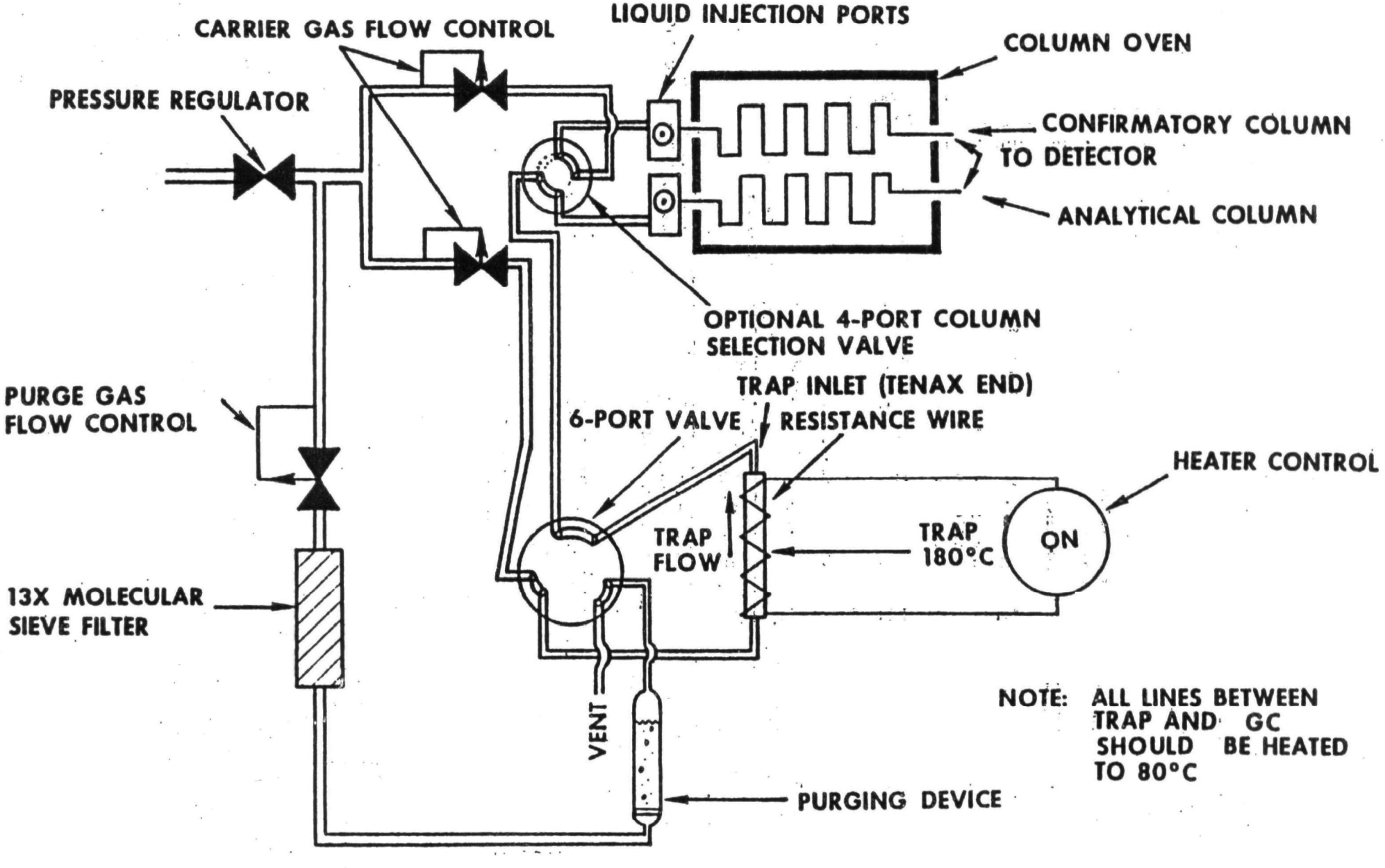


FIGURE 4 PURGE-TRAP SYSTEM (DESORB MODE)

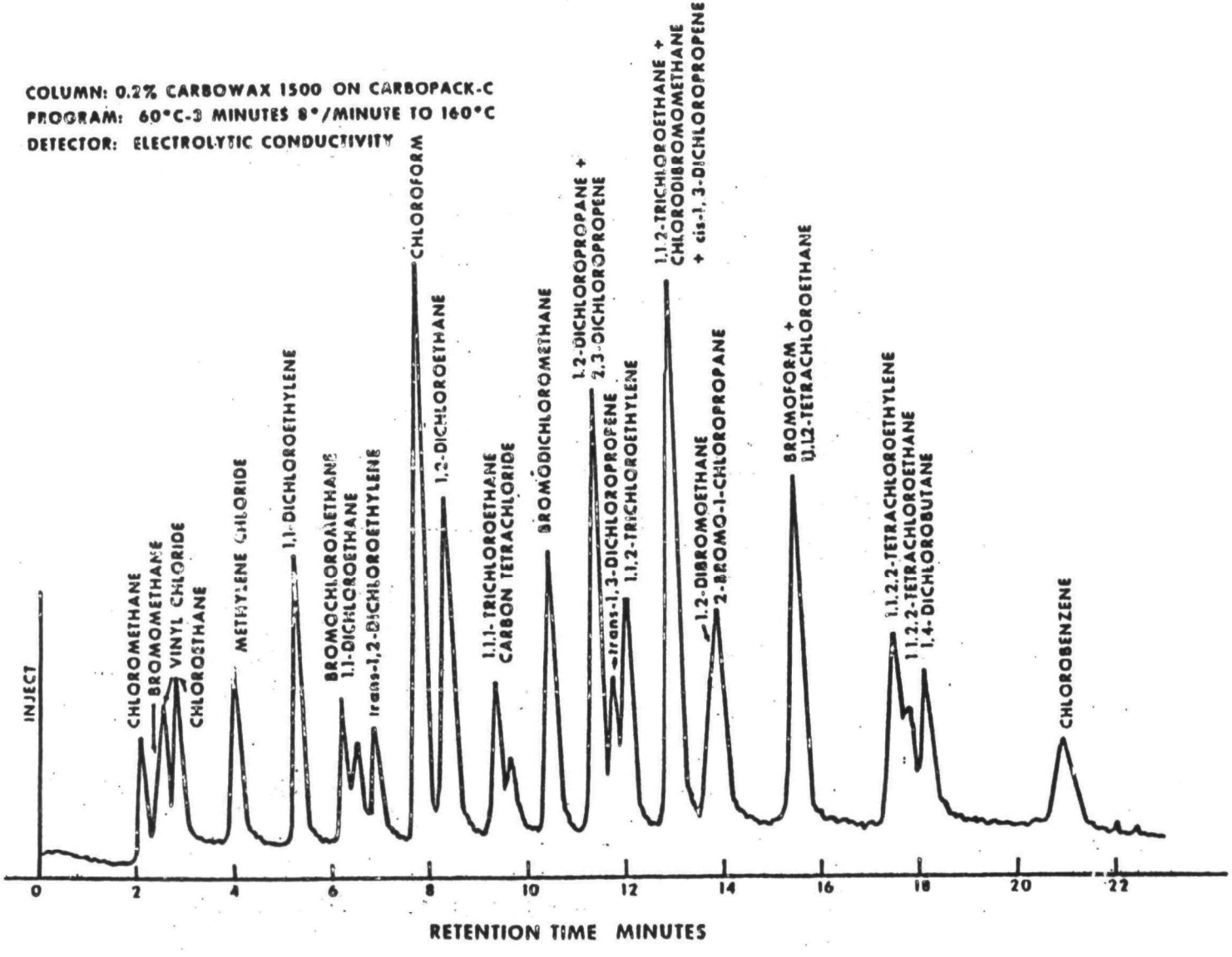


FIGURE 5 CHROMATOGRAM OF ORGANOHALIDES

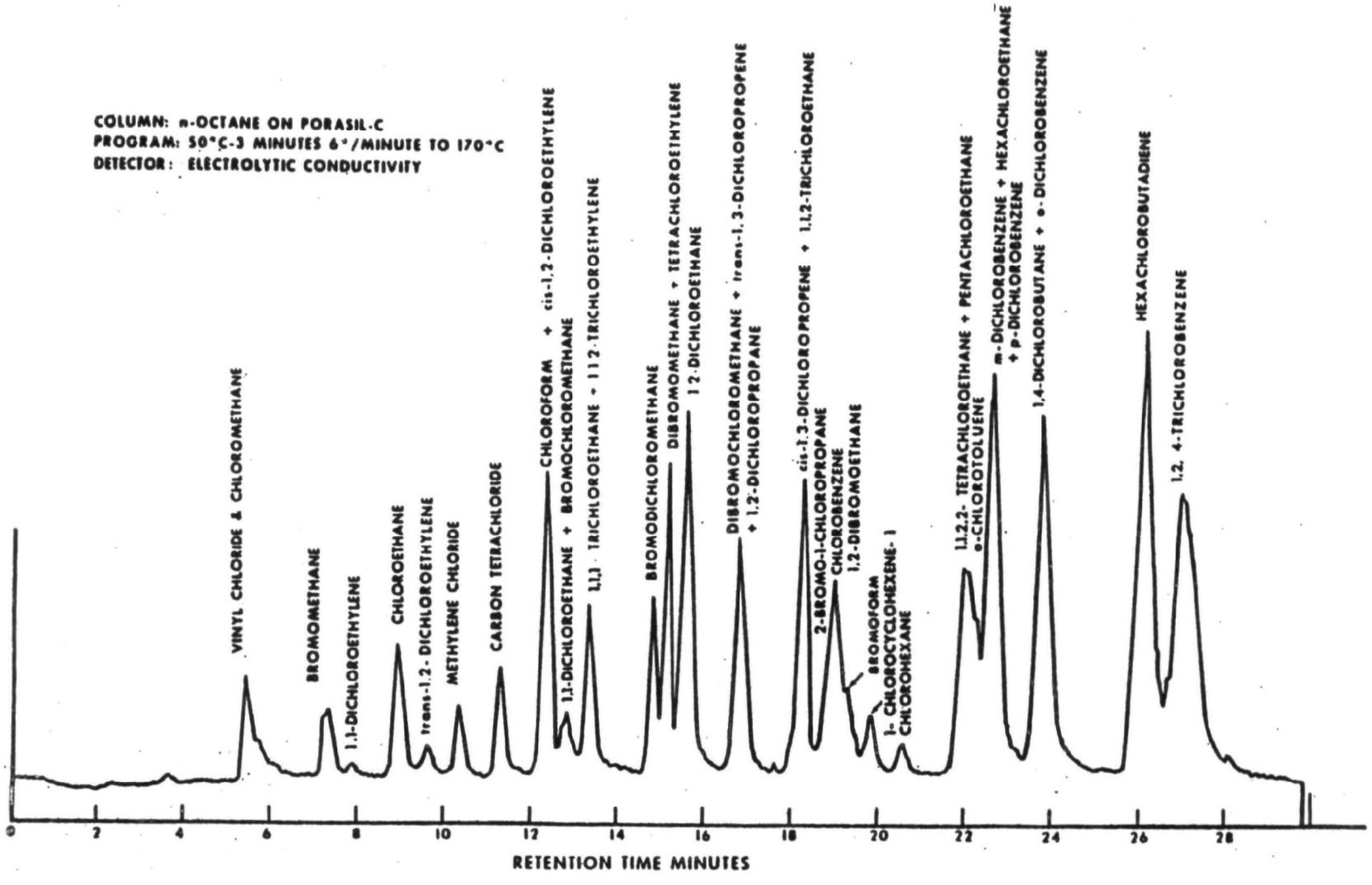


FIGURE 6 CHROMATOGRAM OF ORGANOHALIDES