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Part III

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Appendix C

Analysis of Trihalomethanes in Drinking Water

Analysis of Trihalomethanes

Part I: 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, dichlorobromomethane, 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 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 inteferences 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.

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 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 ¼-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 nonreproductible 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 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/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 180° 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—8 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 8°/minute to 170° C, then hold for 4 minutes or until all compounds have eluted. Trihalomethane retention times are listed in Table 1.

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.*

5.9.1 Bromoform—98%—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.

* 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° 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 of 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 or 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 silicone sepata 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 a area known to be free of organics.

Note.—Do not heat the TFE seals for extended period 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 trihalo-methanes after sample collection (3, 7). *Do not add the reducing agent to samples when data on maximum trihalomethane formation is desired.* 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 treatment 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 Sections 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±.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°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°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 variation 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. $CHBr_3$).

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

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

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	Column II n-octane Porasil-C
Chloroform	10.7	8.2	12.2
Bromodichloromethane	13.7	10.8	14.7
Chlorodibromomethane (Dibromochloromethane)	18.5	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 percent recovery
		Chloroform		
1.2	12	1.2	0.14	100
12.0	8	11	0.16	92
119.0	11	105	7.9	88
		Bromodichloromethane		
1.6	12	1.5	0.05	94
16.0	8	15	0.39	94
160.0	11	145.	10.2	91
		Chlorodibromomethane		
2.0	12	1.9	0.09	95
20.0	8	19	0.70	95
196.0	11	185.	10.6	94
		Bromoform		
2.3	12	2.3	0.16	100
23.0	8	23	1.38	100
231.0	11	223	16.3	97

BILLING CODE 6560-01-M

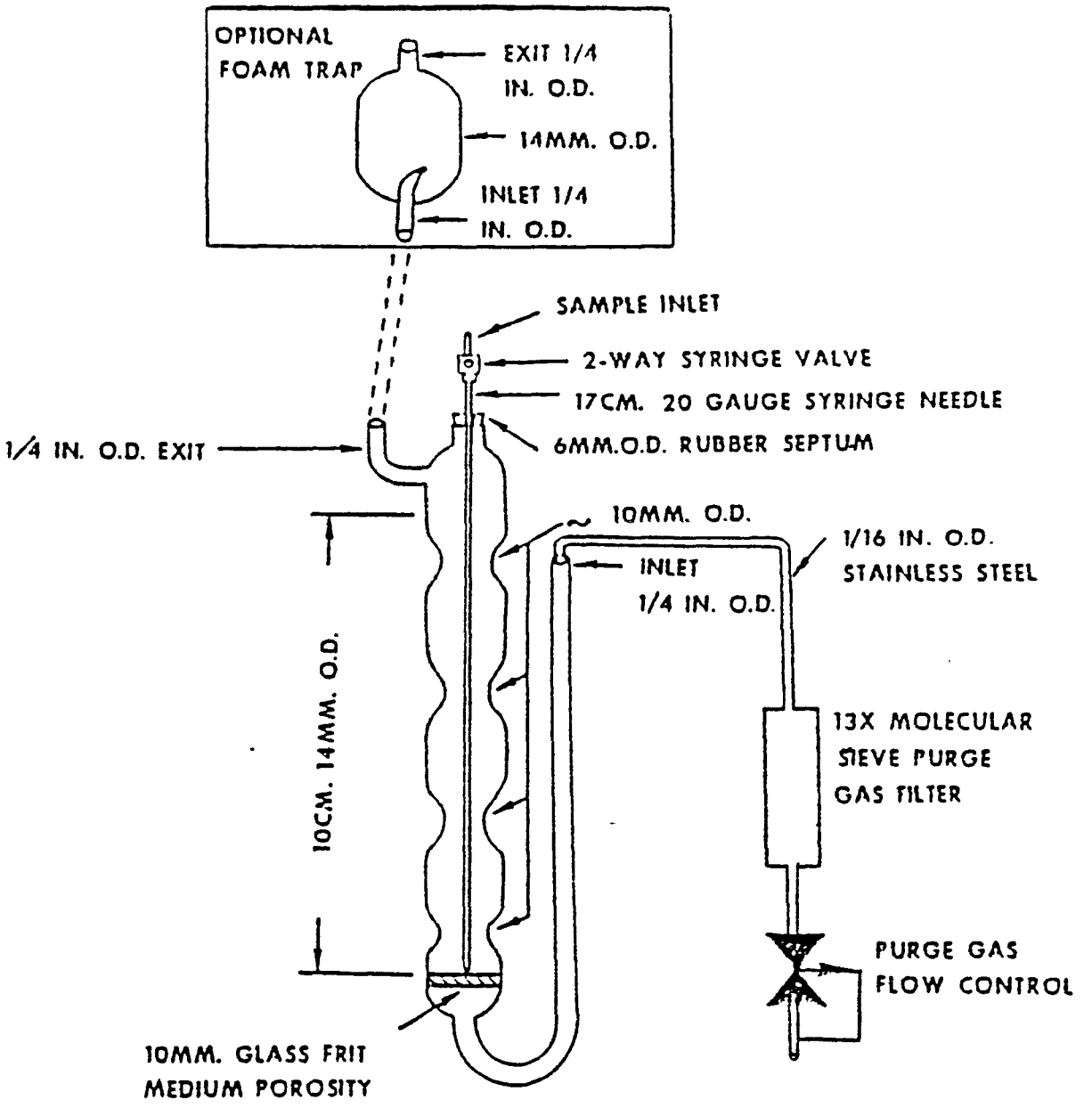
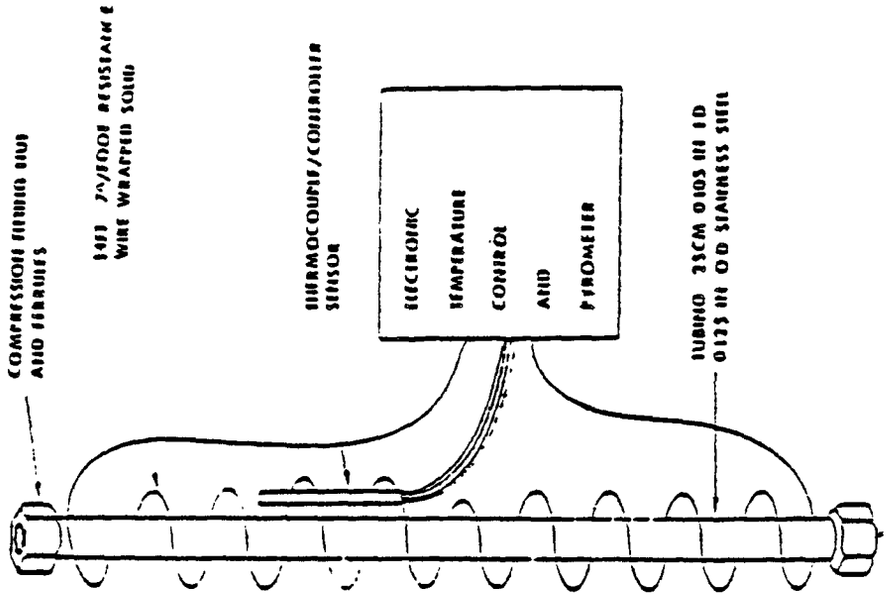


FIGURE 1. PURGING DEVICE

CONSTRUCTION



PACKING PROCEDURE

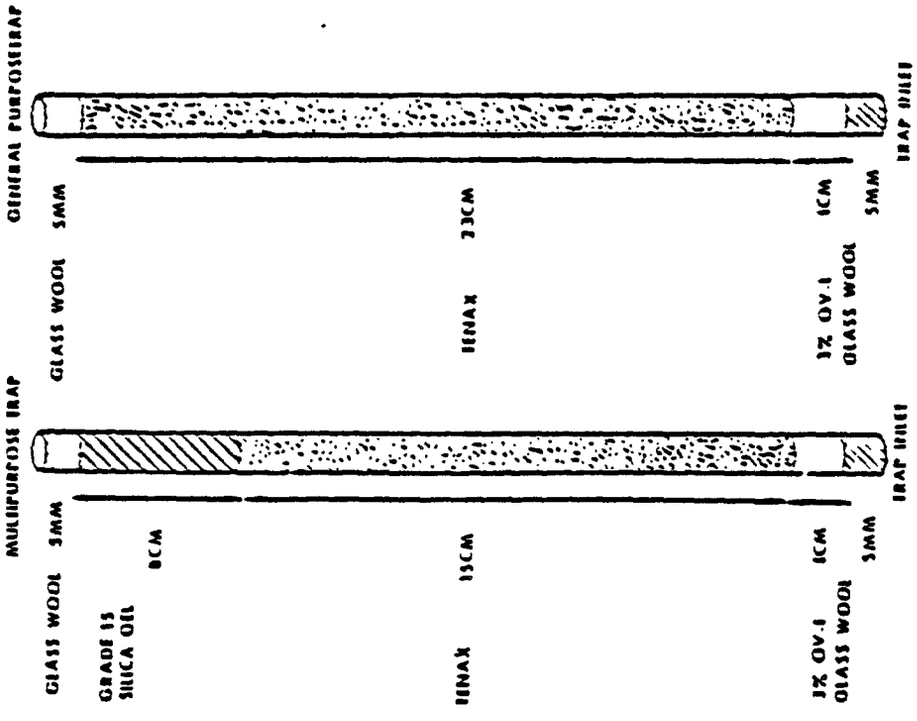


FIGURE 2 TRAP

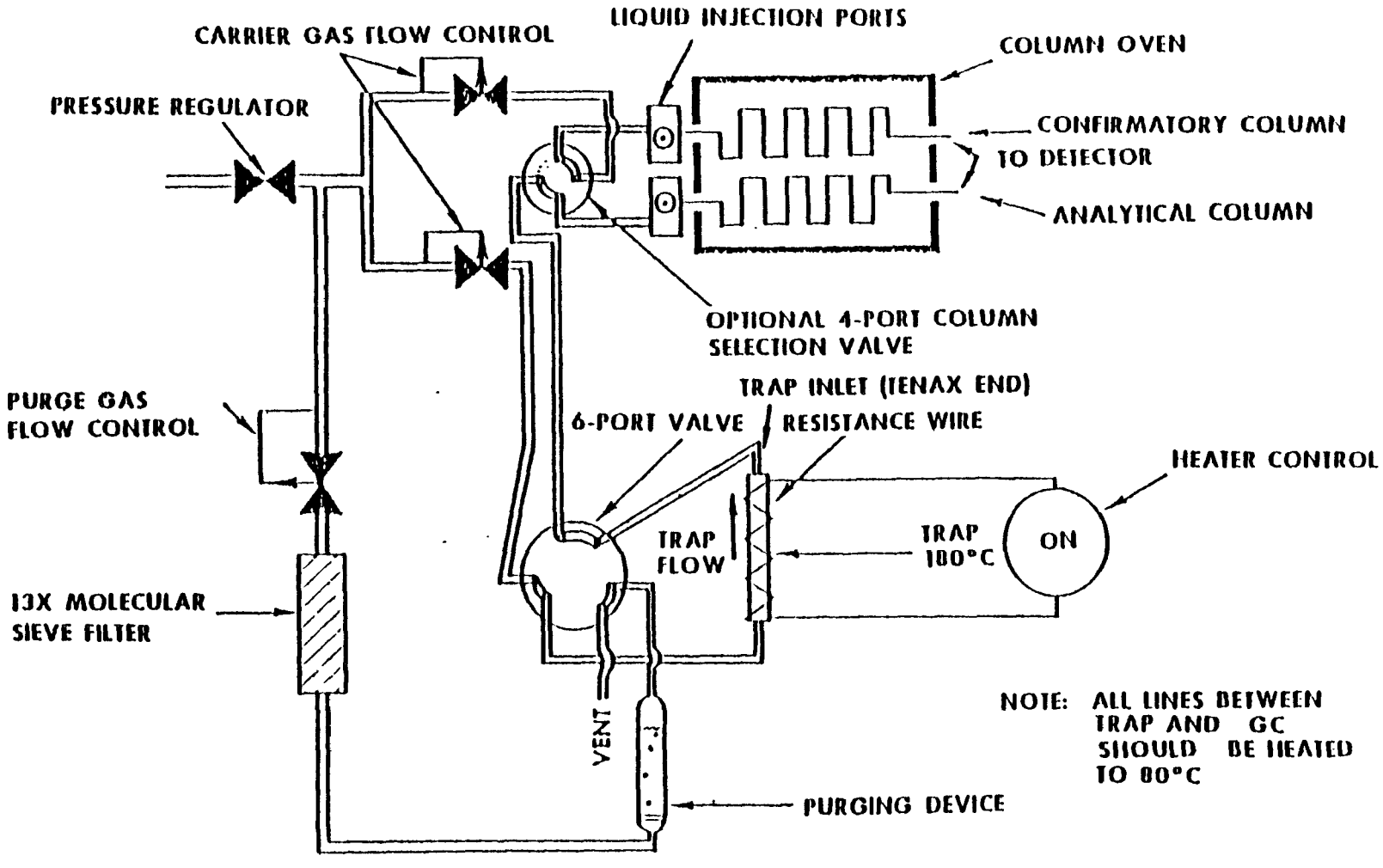


FIGURE 4 PURGE-TRAP SYSTEM (DESORB MODE)

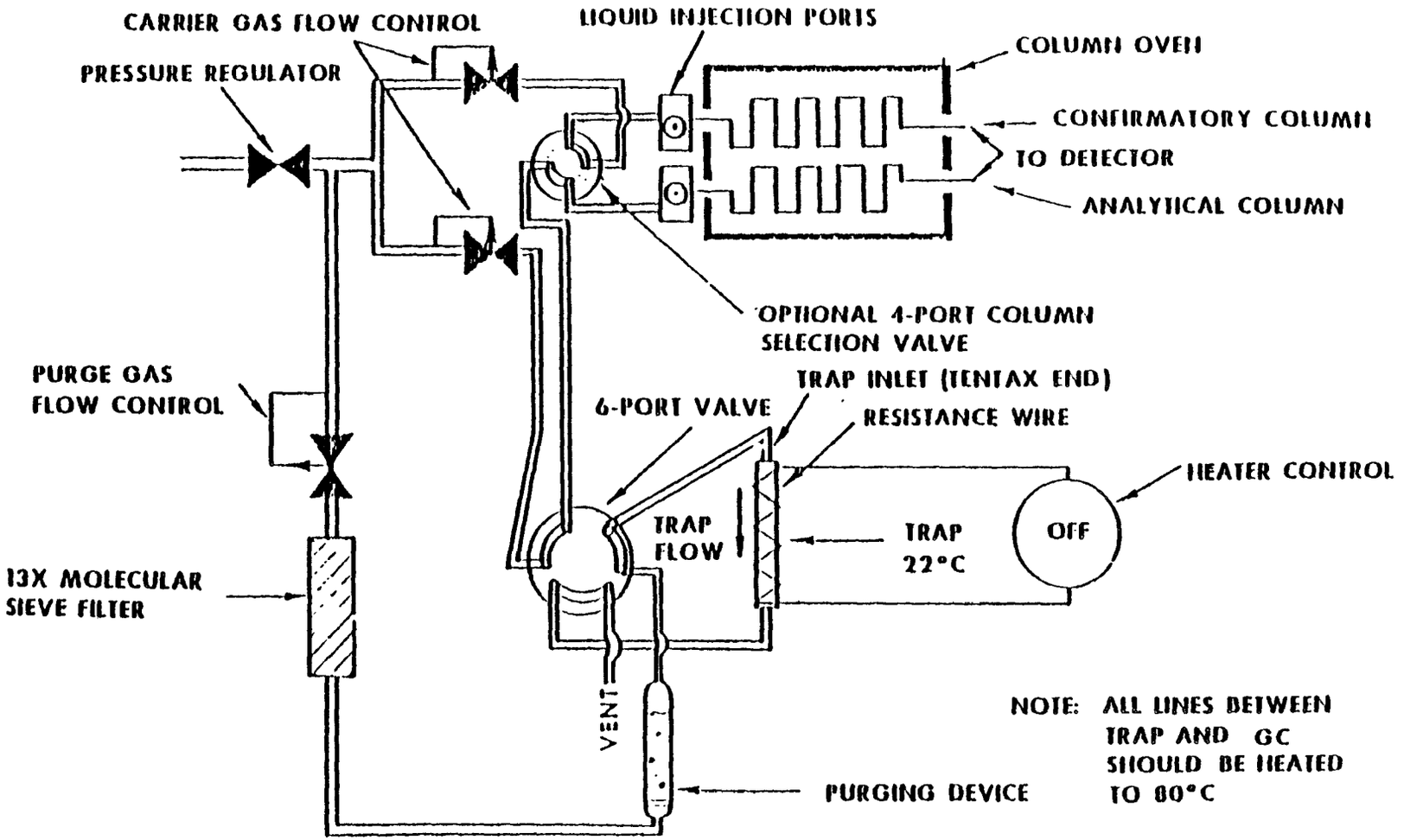


FIGURE 3 PURGE-TRAP SYSTEM (PURGE-SORB MODE)

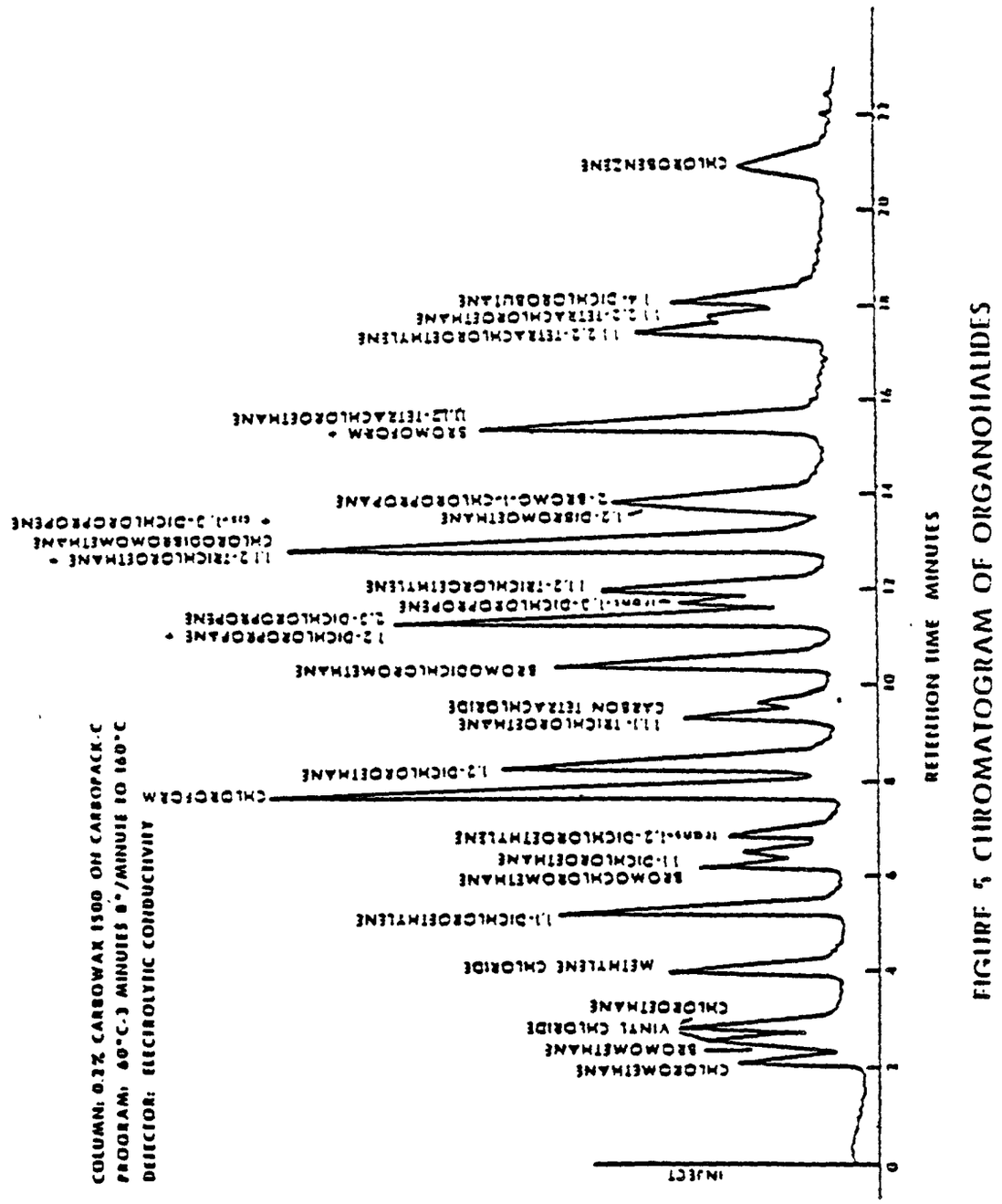


FIGURE 5. CHROMATOGRAM OF ORGANOHALIDES

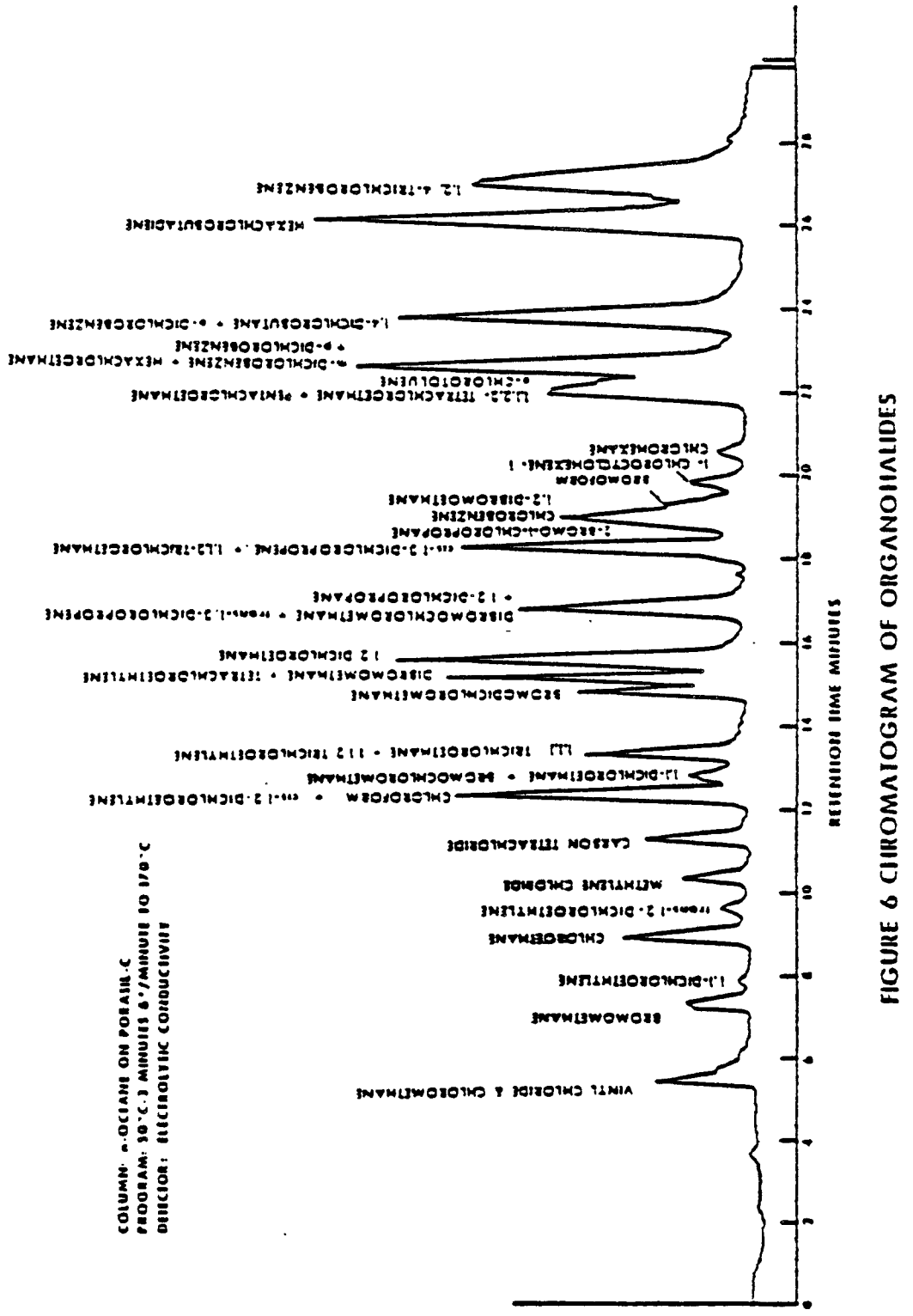


FIGURE 6 CHROMATOGRAM OF ORGANOHALIDES

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Part II: Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction

1. *Scope.*

1.1 This method (1,2) is applicable only to the determination of four trihalomethanes, i.e., chloroform, bromodichloromethane, chlorodibromomethane, and bromoform in finished drinking water, drinking water during intermediate stages of treatment, and the raw source water.

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 in (3) and provide qualitative confirmation of results by Gas Chromatography/Mass Spectrometry (GC/MS) (4).

1.3 Qualitative analyses using GC/MS or the purge and trap method (5) must be performed to characterize each raw source water if peaks appear as interferences in the raw source analysis.

1.4 The method has been shown to be useful for the trihalomethanes over a concentration range from approximately 0.5 to 200 μg/l. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2. *Summary*

2.1 Ten milliliters of sample are extracted one time with 2 ml of solvent. Three μl of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis.

2.2 The extraction and analysis time is 10 to 50 minutes per sample depending upon the analytical conditions chosen. (See Table 1 and Figures 1, 2, and 3.)

2.3 Confirmatory evidence is obtained using dissimilar columns and temperature programming. When component concentrations are sufficiently high (>50 μg/l), halogen specific detectors may be employed for improved specificity.

2.4 Unequivocal confirmatory analyses at high levels (>50 μg/l) can be performed using GC/MS in place of the electron capture detector. At levels below 50 μg/l, unequivocal confirmation can only be performed by the purge and trap technique using GC/MS (4, 5).

2.5 Standards dosed into organic free water and the samples are extracted and analyzed in an identical manner in order to compensate for possible extraction losses.

2.6 The concentration of each trihalomethane is summed and reported as total trihalomethanes in μg/l.

3. *Interferences*

3.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be analyzed before a new bottle of solvent is used to extract samples. Indirect daily checks on the extracting solvent are obtained by monitoring the sample blanks (6.4.10). Whenever an interference is noted in the sample blank, the analyst should reanalyze the extracting solvent. The extraction solvent should be discarded whenever a high level (>10 μg/l) of interfering compounds are traced to it. Low level interferences generally can be removed by distillation or column chromatography (6); however, it is generally more economical to obtain a new source of solvent or select one of the approved alternative solvents listed in Section 5.1. Interference free solvent is defined as a solvent containing less than 0.4 μg/l individual trihalomethane interference. Protect interference-free solvents by storing in a non-laboratory area known to be free of organochlorine solvents. *Subtracting blank values is not recommended.*

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal on the sample bottle during shipment and storage. The sample blank (6.4.10) 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 the polar organic components of the sample with varying efficiencies. In order to perform the trihalomethane analysis as rapidly as possible with sensitivities in the low μg/l range, it is necessary to use the semi-specific electron capture detector and chromatographic columns which have relatively poor resolving power. Because of these concessions, the probability of experiencing chromatographic interferences is high. Trihalomethanes are primarily products of the chlorination process and generally do not appear in the raw source water. The absence of peaks in the raw source water analysis with retention times similar to the trihalomethanes is generally adequate evidence of an interference-free finished drinking water analysis. Because of these possible interferences, in addition to each finished drinking water analysis, a representative raw source water (6.4.5) must be analyzed. When potential interferences are noted in the raw source water analysis, the alternate chromatographic columns must be used to reanalyze the sample set. If interferences are still noted, qualitative identifications should be performed according to Sections 2.3 and 2.4. If the peaks are confirmed to be other than trihalomethanes and add significantly to the total trihalomethane value in the finished drinking water analysis, then the sample set must be analyzed by the purge and trap method (5).

4. *Apparatus*

4.1 Extraction vessel—A 15 ml total volume glass vessel with a Teflon lined screw-cap is required to efficiently extract the samples.

4.1.1 For samples that do not form emulsions 10 ml screw-cap flasks with a Teflon faced septum (total volume is ml) are recommended. Flasks and caps—Pierce—#13310 or equivalent. Septa—Teflon silicone—Pierce #12718 or equivalent.

4.1.2 For samples that form emulsions (turbid source water) 15 ml screw cap centrifuge tubes with a Teflon cap liner are recommended. Centrifuge tube—Corning 8062-15 or equivalent.

4.2 Sampling containers—40 ml screw cap sealed with Teflon faced silicone septa. Vials and caps—Pierce #13075 or equivalent. Septa—Pierce #12722 or equivalent.

4.3 Micro syringes—10, 100 μl.

4.4 Micro syringe—25 μl with a 2-inch by 0.006-inch needle—Hamilton 702N or equivalent.

4.5 Syringes—10 ml glass hypodermic with luerlok tip (2 each).

4.6 Syringe valve—2-way with luer ends (2 each)—Hamilton #86570—1FM1 or equivalent.

4.7 Pipette—2.0 ml transfer.

4.8 Glass stoppered volumetric flasks—10 and 100 ml.

4.9 Gas chromatograph with linearized electron capture detector. (Recommended option—temperature programmable. See Section 4.12.)

4.10 Column A—4 mm ID x 2m long glass packed with 3% SP-1000 on Supelcoport (100/120 mesh) operated at 50°C with 60 ml/min flow. (See Figure 1 for a sample chromatogram and Table 1 for retention data.)

4.11 Column B—2 mm ID x 2m long glass packed with 10% squalane on Chromosorb WAW (80/100 mesh) operated at 67°C with 25 ml/min flow. This column is recommended as the primary analytical column. Trichloroethylene, a common raw source water contaminate, coelutes with bromodichloromethane. (See Figure 2 for a sample chromatogram and Table 1 for retention data.)

4.12 Column C—2 mm ID x 3m long glass packed with 6% OV-11/4% SP-2100 on Supelcoport (100/120 mesh) temperature program 45°C for 12

minutes, then program at 1°/minute to 70°C with a 25 ml/min flow. (See Figure 3 for a sample chromatogram and Table I for retention data.)

4.13 Standard storage conteiners—15 ml amber screw-cap septum bottles with Teflon faced silicone septa. Bottles and caps—Pierce #13830 or equivalent. Septa—Pierce #12716 or equivalent.

5. Reagents

5.1 Extraction solvent—(See 3.1). Recommended—Pentane[a]. Alternative—hexane, methylcyclohexane or 2,2,4-trimethylpentane.

5.2 Methyl alcohol—ACS Reagent Grade.

5.3 Free and combined chlorine reducing agents—Sodium thiosulfate ACS Reagent Grade—sodium sulfite ACS Reagent Grade.

5.4 Activated carbon—Filtrasorb—200, available from Calgon Corporation, Pittsburgh, PA, or equivalent.

5.5 Standards.[b]

5.5.1 Bromoform 96%—available from Aldrich Chemical Company.

5.5.2 Bromodichloromethane 97%—available from Aldrich Chemical Company.

5.5.3 Chlorodibromomethane—available from Columbia Chemical, Incorporated, Columbia, S.C.

5.5.4 Chloroform 99%—available from Aldrich Chemical Company.

5.6 Organic-free water—Organic-free water is defined as water free of interference when employed in the procedure described herein.

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

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

5.6.3 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 at 100 ml/minute for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle with a Teflon seal.

5.6.4 Test organic free water each day it is used by analyzing it according to Section 7.

5.7 Standard stock solutions.

5.7.1 Fill a 10.0 ml ground glass stoppered volumetric flask with approximately 9.8 ml of methyl alcohol.

5.7.2 Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces dry.

5.7.3 Weigh the unstoppered flask to the nearest 0.1 mg.

5.7.4 Using a 100 μl syringe, immediately add 2 to 3 drops of the reference standard to the flask, then reweigh. *Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask.*

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

5.7.6 Transfer the standard 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.

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

5.7.8 Store the solution at 4° 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.

5.8 Aqueous calibration standard precautions.

5.8.1 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 alcholic 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 7.

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

g. Aqueous standards, when stored with a headspace, are not stable and should be discarded after one hour. Aqueous standards can be stored according to Sections 6.4.9 and 7.2.

5.9 Calibration standards.

5.9.1 Prepare, from the standard stock solutions, a multicomponent secondary dilution mixture 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 (± 25%) to that of the unknown. (See 8.1.)

5.9.2 Alternative calibration procedure.

5.9.2.1 Construct a calibration curve for each trihalomethane containing a minimum of 3 different concentrations. Two of the concentrations must bracket each unknown.

5.9.3 Extract and analyze the aqueous calibration standards in the same manner as the unknowns.

5.9.4 Other calibration procedures (7) which require the delivery of less than 20 μl of methanolic standards to 10.0 ml volumes of water contained in the sample syringe are acceptable only if the methanolic standard is delivered by the solvent flush technique (8).

5.10 Quality Check Standard Mixture.

5.10.1 Prepare, from the standard stock solutions, a secondary dilution mixture in methyl alcohol that contains 10.0 ng/μl of each compound. (See 5.7.6 and 5.7.8.)

5.10.2 Daily, prepare and analyze a 2.0 μg/l aqueous dilution from this mixture by dosing 20.0 μl into 100 ml of organic-free water (See Section 8.1).

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 faced silicone septa cap liners are strongly recommended.

6.2 Glassware Preparation.

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

6.2.2 Allow the bottles and seals to air dry, then place in an 105° C oven for 1 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 5.3) is added to all samples in order to arrest the formation of additional

[a] Pentane has been selected as the best solvent for this analysis because it elutes on all of the columns, well before any of the trihalomethanes. High altitudes or laboratory temperatures in excess of 75°F may make the use of this solvent impractical. For these reasons, alternative solvents are acceptable; however, the analyst may experience baseline variances in the elution areas of the trihalomethanes due to coelution of these solvents. The degree of difficulty appears to be dependent upon the design and condition of the electron capture detector. Such problems should be insignificant when concentrations of the coeluting trihalomethane are in excess of 5 μg/l.

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

trihalomethanes after sample collection (7,9) and to eliminate the possibility of free chlorine reacting with impurities in the extraction solvent to form interfering organohalides. *DO NOT ADD THE REDUCING AGENT TO SAMPLES AT COLLECTION TIME WHEN DATA FOR MAXIMUM TRIHALOMETHANE FORMATION IS DESIRED.* If chemical stabilization is employed, then the reagent is also added to the blanks. The chemical agent (2.5 to 3 mg/40 ml) is added in crystalline form to the empty sample bottle just prior to shipping to the sampling site. If chemical stabilization is not employed at sampling time then the reducing agent is added just before extraction.

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 bottle 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 The raw source water sample history should resemble the finished drinking water. The average retention time of the finished drinking water within the water plant should be taken into account when sampling the raw source water.

6.4.6 Sampling from a water tap.

6.4.6.1 Turn on the 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.

6.4.7 Sampling from an open body of water.

6.4.7.1 Fill a 1-quart wide-mouth bottle with sample from a representative area. Carefully fill duplicate sample bottles from the 1-quart bottle as in 6.4.

6.4.8 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.

6.4.9 Sealing practice for septum seal screw cap bottles.

6.4.9.1 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.

6.4.9.2 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, then reseal bottle as above.

6.4.10 Sample blanks.

6.4.10.1 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.

6.4.10.2 If the sample is to be stabilized, add an identical amount of reducing agent to the blanks.

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

6.4.10.4 Store the blanks and the samples, collected at a given site (sample set), together in a protected area known to be free from contamination. A sample set is defined as all the samples collected at a given site (i.e., at a water treatment plant, duplicate raw source water, duplicate finished water and the duplicate sample blanks comprise the sample set).

6.5 When samples are collected and stored under these conditions, no measurable loss of trihalomethanes has been detected over extended periods of time (7). It is recommended that the samples be analyzed within 14 days of collection.

7. *Extraction and Analysis.*

7.1 Remove the plungers from two 10-ml syringes and attach a closed syringe valve to each.

7.2 Open the sample bottle [*] (or standard) and carefully pour the sample into one of the syringe barrels until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residue air while adjusting the sample volume to 10.0 ml. Close the valve.

7.3 Fill the second syringe in an identical manner from the same sample bottle. This syringe is reserved for a replicate analysis (see 8.3 and 8.4).

7.4 Pipette 2.0 ml of extraction solvent into a clean extraction flask.

7.5 Carefully inject the contents of the syringe into the extraction flask.

7.6 Seal with a Teflon faced septum.

7.7 Shake vigorously for 1 minute.

7.8 Let stand until the phases separate ($\int$ 60 seconds).

7.8.1 If the phases do not separate on standing then centrifugation can be used to facilitate separation.

7.9 Analyze the sample by injecting 3.0 µl (solvent flush technique, (8)) of the upper (organic) phase into the gas chromatograph.

8. *Analytical Quality Control.*

8.1 A 2 µg/l quality check standard (See 5.10) should be extracted and analyzed each day before any samples are analyzed. Instrument status checks and lower limit of detection estimations based upon response factor calculations at 5 times the noise level are obtained from these data. In addition, the data obtained from the quality check standard can be used to estimate the concentration of the unknowns. From this information the appropriate standards can be determined.

8.2 Analyze the sample blank and the raw source water to monitor for potential interferences as described in Sections 3.1, 3.2, and 3.3.

8.3 Spiked samples.

8.3.1 For those laboratories analyzing more than 10 samples a day, each 10th sample analyzed 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 5.9.

8.3.2 In those laboratories analyzing less than 10 samples daily, each time the analysis is performed, analyze at least one 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 5.9.

8.3.3 Maintain an up-to-date log on the accuracy and precision data collected in Sections 8.3 and 8.4. If results are significantly different than those cited in Section 10.1, the analyst should check out the entire analysis scheme to determine why the laboratory's precision and accuracy limits are greater.

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

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

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

8.6.1 The results of the EMSL trihalomethane quality control sample should agree within 20% of the true value for each trihalomethane. If they do not, the analyst must check each step in the standard generation procedure to solve the problem.

8.7 It is important that the analyst be aware of the linear response characteristics of the electron capture system that is utilized. Calibration curves should be generated and rechecked quarterly for each trihalomethane over the concentration range encountered in the samples in order to confirm the linear response range of the system. Quantitative data cannot be calculated from non-linear

[*] If for any reason the chemical reducing agent has not been added to the sample, then it must be added just prior to analyses at the rate of 2.5 to 3 mg/40 ml or by adding 1 mg directly to the sample in the extraction flask.

responses. Whenever non-linear responses are noted, the analyst must dilute the sample for reanalysis.

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

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

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

9. *Calculations.*

9.1 Locate each trihalomethane in the sample chromatogram by comparing the retention time of the suspect peak to the data gathered in 8.8.1. The retention time of the suspect peak must fall within the limits established in 8.8.1 for a single column identification.

9.2 Calculate the concentration of each trihalomethane by comparing the peak heights or peak areas of the samples to those of the standards. Round off the data to the nearest μg/l or two significant Figures.

Concentration, μg/l = sample peak height/standard peak height × standard concentration, μg/L

9.3 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. $CHBr_3$)

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

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

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 base line displacement in mm from theoretical zero at the exact retention time for the trihalomethane.

ATT = attenuation factor.

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

10. *Precision and Accuracy*

10.1 Single lab precision and accuracy. The data in Table II were generated by spiking organic-free water with trihalomethanes as described in 5.9. The mixtures were analyzed by the analyst as true unknowns.

Table I.—*Retention Times for Trihalomethanes*

Trihalomethane	Retention time minutes		
	Column A	Column B	Column C
Chloroform	1.0	1.3	4.9
Bromodichloromethane	1.5	*2.5	11.0
Chlorodibromomethane	2.6	5.6	23.1
(Dibromochloromethane) bromoform	5.5	10.9	39.4

*On this column, trichloroethylene, a common raw source water contaminate, coelutes with bromodichloromethane.

Table II.—*Single Laboratory Accuracy and Precision*

	Dose level μg/l	Number of samples	Mean μg/l	Precision relative standard deviation, percent	Accuracy percent recovery
Compound:					
$CHCl_3$	9.1	5	10	11	110
$CHCl_3$	69	3	73	5.3	106
$CHBrCl_2$	1.2	5	1.3	9.8	108
$CHBrCl_2$	12	2	15	1.4	125
$CHBr_2Cl$	2.7	5	2.0	17	74
$CHBr_2Cl$	17	3	16	9.9	94
$CHBr_3$	2.9	5	2.2	10	76
$CHBr_3$	14	3	16	12	114

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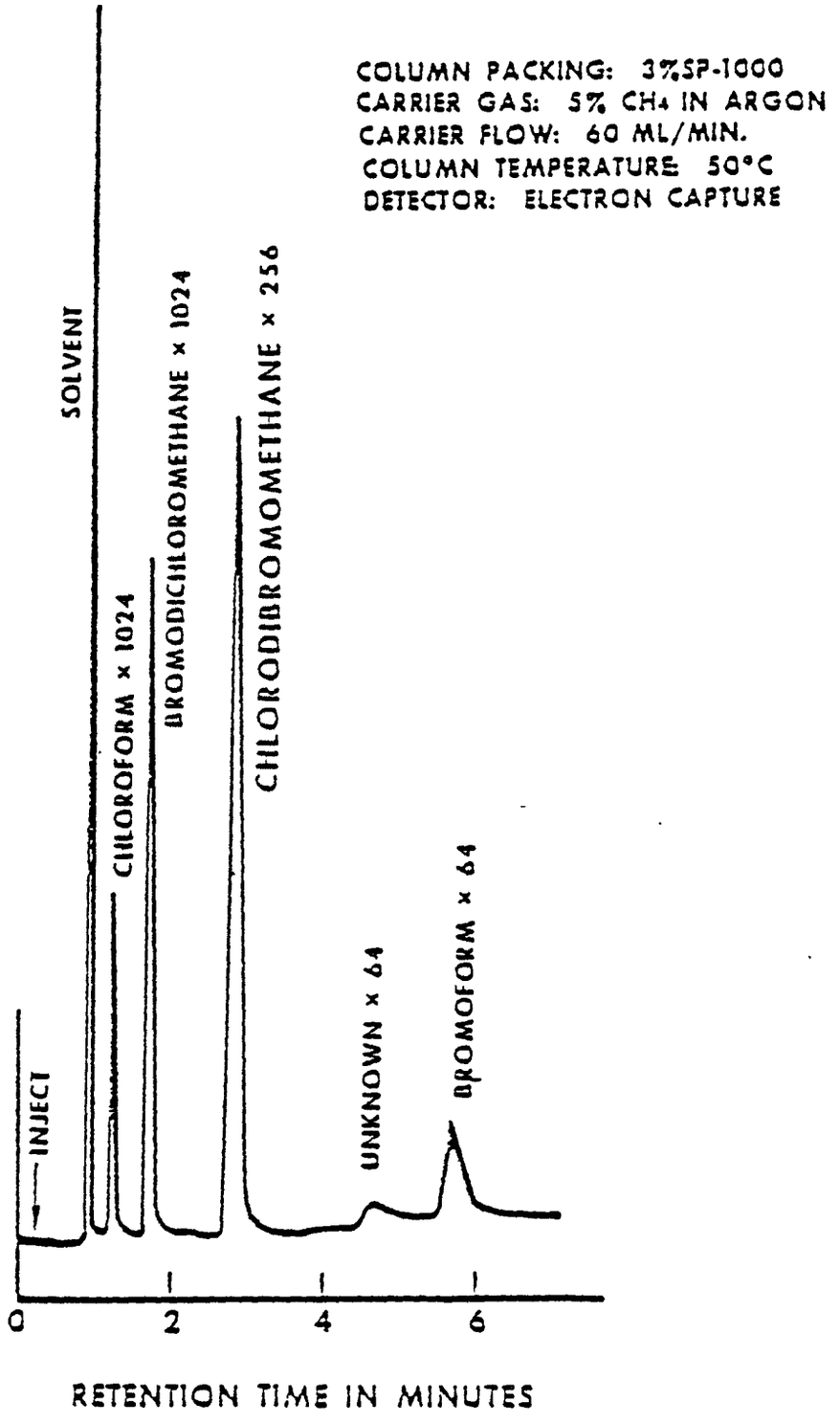

FIGURE 1. FINISHED WATER EXTRACT

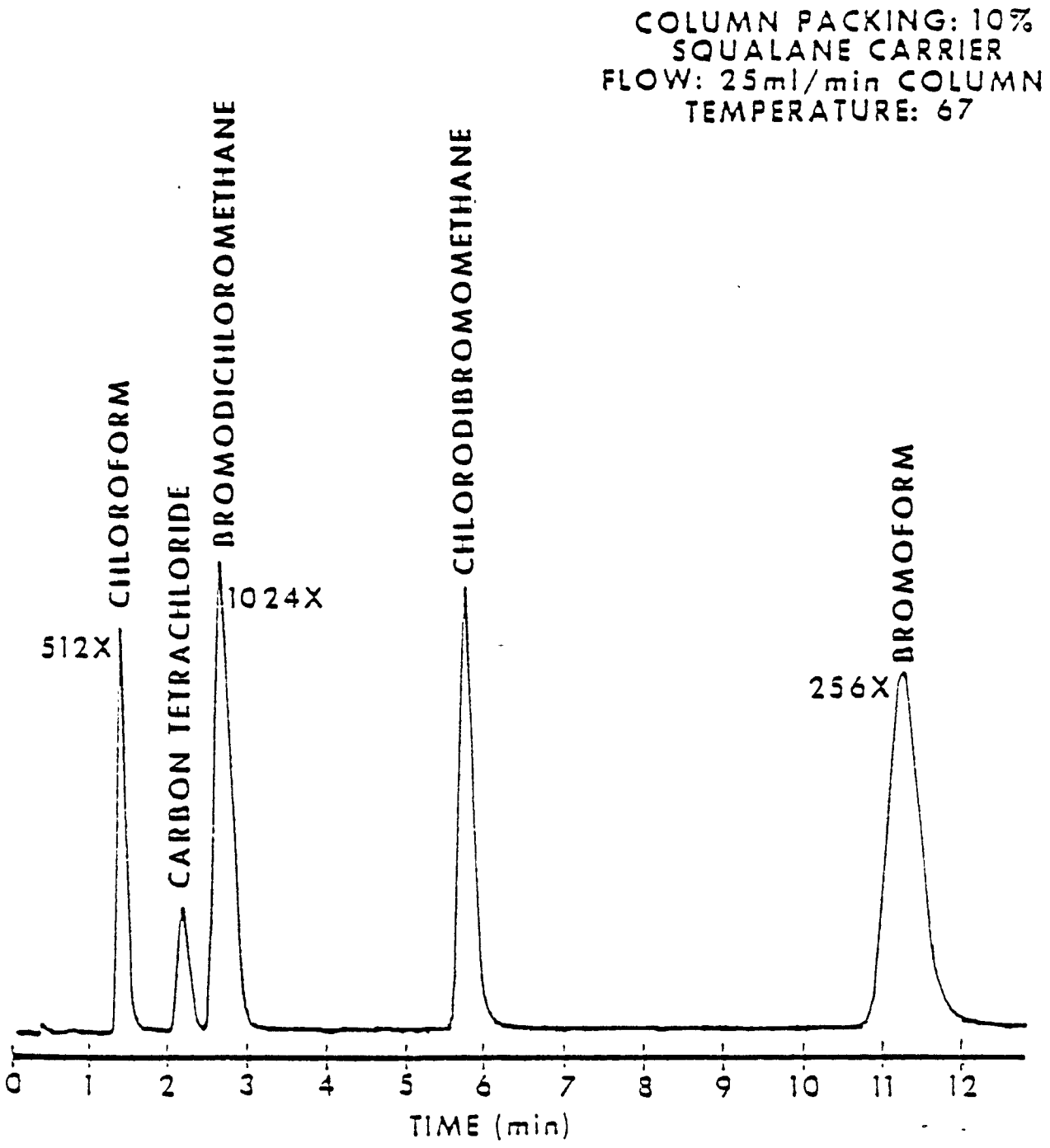

FIGURE 2. EXTRACT OF STANDARD

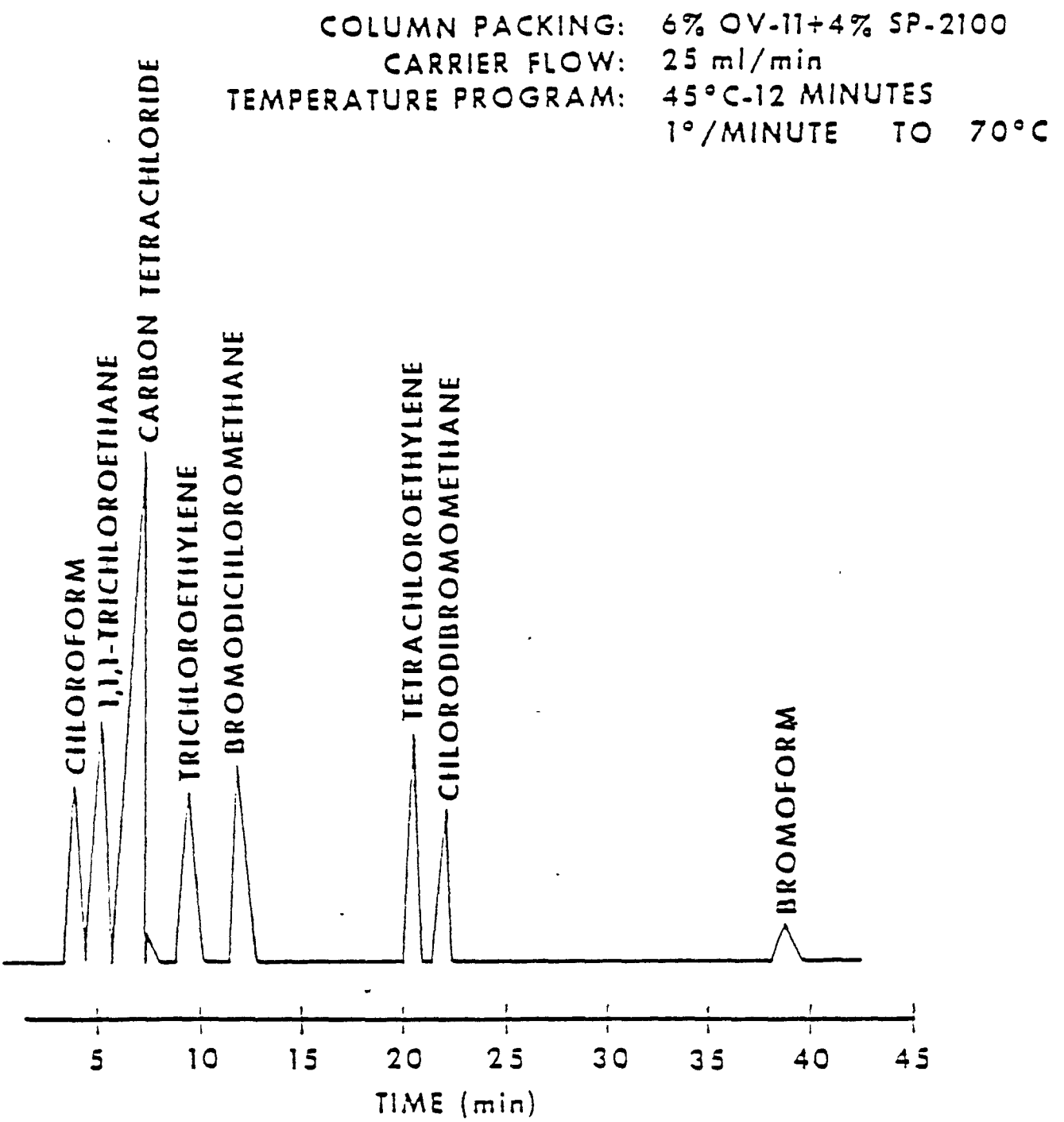

FIGURE 3. EXTRACT OF STANDARD

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Part III—Determination of Maximum Total Trihalomethane Potential (MTP)

The water sample used for this determination is taken from a point in the distribution system that reflects maximum residence time. Procedures for sample collection and handling are given in EMSL Methods 501.1 and 501.2. No reducing agent is added to "quench" the chemical reaction producing THMs at the time of sample collection. The intent is to permit the level of THM precursors to be depleted and the concentration of the THMs to be maximized for the supply being tested.

Four experimental parameters affecting maximum THM production are pH. temperature. reaction time and the presence of a disinfectant residual. These parameters are dealt with as follows:

Measure the disinfectant residual at the selected sampling point. Proceed only if a measurable disinfectant residual is present. Collect triplicate 40 ml water samples at the pH prevailing at the time of sampling. and prepare a method blank according to the EMSL methods. Seal and store these samples together for 7 days at 25°C or above. After this time period. open one of the sample containers and check for disinfectant residual. Absence of a disinfectant residual invalidates the sample for further analyses. Once a disinfectant residual has been demonstrated. open another of the sealed samples and determine total THM concentration using either of the EMSL analytical methods.

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