

The analysis of trihalomethanes in drinking water by purge and trap and liquid-liquid extraction

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By Herbert J. Brass

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THE UNITED STATES Environmental Protection Agency (EPA)* has recently promulgated its final ruling controlling the concentration of total trihalomethanes (TTHM) in finished drinking waters.¹ The maximum contaminant level (MCL) established was 0.10 mg/L or 100 µg/L (ppb). The TTHM value is calculated by totaling the concentrations of four individually measured trihalomethanes: chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

The purge and trap and liquid-liquid extraction gas chromatographic methods have been approved for use in the analysis of THMs¹⁻³ and are being extended to the analysis of additional halocarbons. A number of investiga-

tions have described either or both of these techniques and in some cases comparative analytical data have been presented.⁴⁻¹⁴ In addition, videotapes demonstrating the two methods have been prepared¹⁵ and are available on loan from the EPA and the American Water Works Association.

There are four key elements to each of the two THM methods: sampling; the preparation of standards; analysis by either purge and trap or liquid-liquid extraction; and analytical quality assurance. This paper describes and compares the analytical techniques and provides some discussion of quality assurance.

Purge and trap

The steps in the analysis of THMs by purge and trap are shown in Table 1.² These steps follow a conventional analytical scheme. Trihalomethanes, as well as other organic compounds, are extracted from a water sample (Figure 1a) according to the experimental conditions shown in Table 2.² The purging vessel (sampler) is filled with care to prevent losses of compounds by volatilization. The purge gas is turned on and compounds are

transferred from the water into the vapor phase. They pass through the six-port valve and are collected on top of the trapping column which is maintained at ambient temperature (<35°C). After the purge gas passes through the trapping column, it flows through the valve and is vented to the atmosphere.

After the purge cycle is completed, the six-port valve is switched and the gas flow is redirected. The purge gas flow has stopped. The desorb gas (Figure 1b) now flows through the valve and into the bottom of the trap, backflushing it. At the same time, the trap is heated rapidly to

Table 1

Summary of the purge and trap method for THM analysis

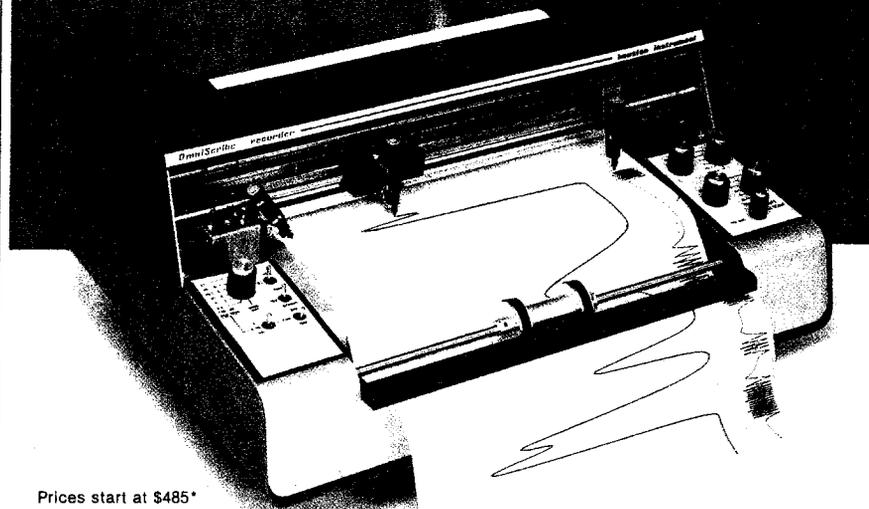
- Extract THMs from water by purging.
- Concentrate by adsorption onto a porous polymer trap.
- Desorb thermally from the trap onto a GC column.
- Separate by GC.
- Detect using a specific halide detector.
- Identify by comparing retention times of THMs in samples and standards.
- Quantify by measuring responses of THMs in samples and standards.

*Any mention of product names in this article is not intended to imply an endorsement by the EPA.

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Table 2

Purge and trap conditions for THM analysis

Purge volume: 5 mL

Purge gas — rate: Helium or nitrogen, 40 mL/min

Purge time: 11 min

Trap: 25-cm \times 0.105-in. i.d. stainless steel packed with Tenax or $\frac{2}{3}$ Tenax and $\frac{1}{3}$ silica gel

Desorb gas — rate: Generally helium, 20–60 mL/min

Desorb time: 4 min

Desorb temperature: 180°C

12-halocarbon standard in water, including the four THMs, also was analyzed. From the associated chromatogram shown in *Figure 3*, it is seen that these halocarbons are well-separated. Chromatographic retention times and detector responses of standards and samples are used both to identify and quantify the components that may be present.

To ensure the validity of data obtained, a laboratory quality assurance program must be instituted. Specific elements of this program are detailed in the method² and include the analysis of standards, sample blanks, replicates, and quality control samples.

A potential problem with the purge and trap method concerns impurities contained in the purge and carrier gases and the plumbing ahead of the adsorbent trap. These impurities can have approximately the same retention times as the trihalomethanes and other halocarbons on the gas chromatographic column and can interfere with the analysis. When present in large amounts, impurities in the gases and the purge and trap system can overload both the trapping column and the gas chromatographic column. This leads to distorted gas chromatographic peaks, making identification and quantitation difficult. Impurities often present a problem when a purge and trap system is new. An extended effort is at times required to locate the sources of contamination and remove them.

Other potential problems can be traced to residual organic compounds that remain in the

180°C. The purgeable compounds, including THMs, are desorbed from the trap and pass onto the head of a cool gas chromatographic column for analysis. In the preferred mode, the purge and trap system is interfaced to the gas chromatograph so that the GC carrier gas also serves as the desorb gas.

Gas chromatographic analyses are performed using the primary columns and conditions shown in *Table 3*. A confirmatory column

using *n*-octane on Porasil-C also is specified.² The measurement of trihalomethanes and other purgeable organohalides is performed using electrolytic conductivity or microcoulometric detectors that are halogen specific. Individual organohalides can be determined over the concentration range of ~ 0.1 –1500 $\mu\text{g/L}$.

A chromatogram generated upon analysis of a THM standard in water at the indicated concentrations is shown in *Figure 2*. A

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Table 3

Gas chromatographic conditions for THM analysis by purge and trap

Column: 8-ft x 0.1-in. i.d. stainless steel or glass

Packing: a) 1% SP-1000 on carbo-pack B, 60/80 mesh; initial 2 in. with 3% SP-1000 on Chromosorb W, 60/80 mesh
b) 0.2% Carbowax 1500 on carbo-pack C, 80/100 mesh; 1-ft x 0.1 in. i.d. precolumn packed with 3% Carbowax 1500 on Chromosorb W, 60/80 mesh

Carrier gas: Helium at 40 mL/min

Injection port temperature: 150°-175°C

Temperature program:

a) 45°C-3 min, 8°C/min to 220°C, hold

b) 60°C-3 min, 8°C/min to 160°C, hold

purging vessel and on the trap and associated plumbing from analysis of the previous sample. Rinsing the vessel with organic-free water should resolve the former problem, while baking the trap for 10 min at 225°C should rectify the latter situation.

Liquid-liquid extraction

A summary of the procedures used in the analysis of THMs by the liquid-liquid extraction (LLE) method is shown in *Table 4*. Four hydrocarbon solvents can be used for extraction purposes. They are pentane, hexane, methylcyclohexane, and isooctane. A summary of the steps used in performing the extraction is given in *Table 5*. These manipulations are relatively straightforward and simple. Again, extreme caution must be exercised in transferring

Table 4

Summary of the liquid-liquid extraction method for THM analysis

Extract THMs from water and concentrate into an organic solvent.

Separate by GC.

Detect by electron capture.

Identify by comparing retention times of THMs in samples and standards.

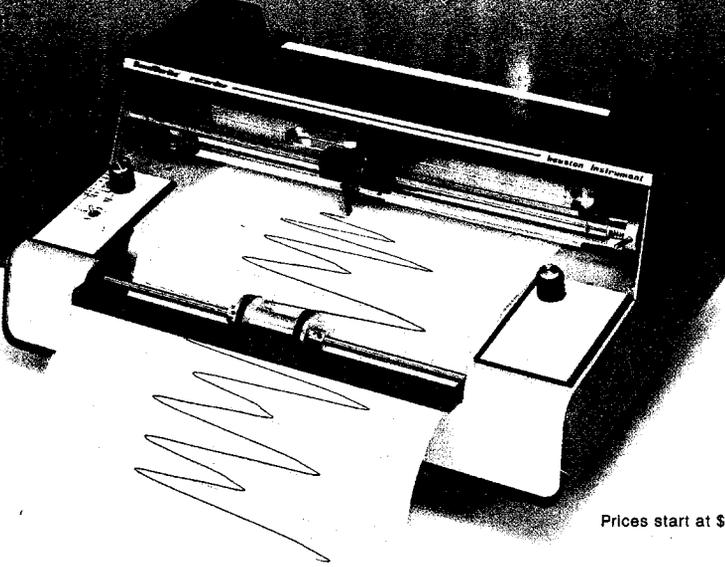
Quantify by measuring responses of THMs in samples and standards.

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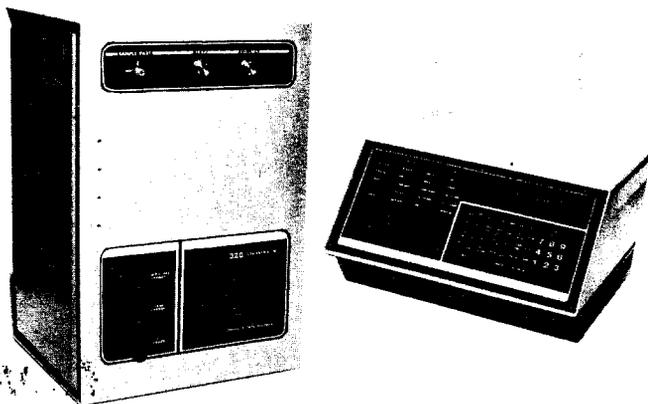
the aqueous sample containing volatile organic constituents.³ To inject the sample accurately into the gas chromatograph, a solvent-flush technique must be used.¹⁶

Gas chromatographic determination using a semi-specific electron capture detector is performed using one of three analytical columns.³ Conditions for the suggested primary column are given in *Table 6*. Alternative chromatographic columns are

packed with 3% SP-1000 on Supelcoport 100/120 mesh or 6% OV-11/4% SP-2100 on Supelcoport 100/120 mesh. Individual THMs can be determined over the concentration range of ~ 0.5 -200 $\mu\text{g/L}$. Method validation for the analysis of additional halocarbons is not as far advanced using LLE as compared to purge and trap, though procedures do exist for their measurement.^{2,3,10,13,14}

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Table 5

Liquid-liquid extraction steps

Pipet 2 mL of solvent into an extraction flask.

Add 10 mL of aqueous sample to an extraction flask.

Shake vigorously for 1 min.

Allow the solvent (top) and aqueous (bottom) phases to separate.

Withdraw 3 μ L of extract.

Inject into a gas chromatograph.

upon analysis of an aqueous THM standard is shown in *Figure 4*. This standard is identical to that analyzed by purge and trap and shown in *Figure 2*. The chromatographic analysis time clearly is less for the LLE measurement. A nine-component halocarbon standard in water also was analyzed under temperature programmed conditions. The resultant chromatogram is shown in *Figure 5*. In general, lower limits of detection for halocarbons are five-fold higher (poorer) than via the purge and trap method. However, for 1,2-dichloroethane it is approximately twenty-fold poorer. Higher retention times and detector responses are used to both identify and quantify components of interests. Again, ensuring the validity of data through a laboratory quality assurance program is essential.

While separation of THMs under isothermal GC conditions appears good, potential interferences can be a major problem. For example, bromodichloromethane and trichloroethylene coelute under the conditions given in Table 6 (*Figure 4*). Temperature programming is required to effect a separation. However, this option is not always available with an ECD system. Method validation of an LLE procedure using capillary columns¹¹ would, of course, be desirable.

Table 6

**Gas chromatographic conditions
for THM analysis
by liquid-liquid extraction**

Column: 6-ft \times 2-mm i.d. glass
Packing: 10% Squalane on Chromo-
sorb WAW, 80/100 mesh
Carrier gas: Argon/methane at
25 mL/min
Injection port temperature: 90°-110°C
Column temperature: 67°C
Detector temperature: 300°C

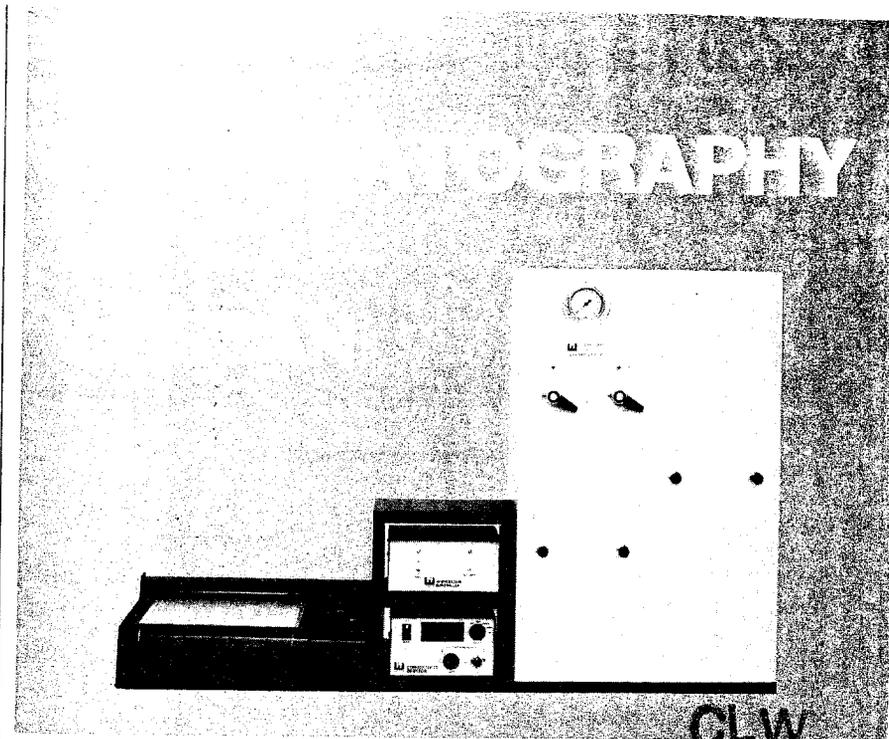
Due to the high probability of interferences in the sample coeluting with the THMs, the analysis of a raw water sample is mandatory to characterize a given water system.³ Since THMs are products of chlorination, they are generally not found at appreciable levels in raw waters. Compounds most likely to interfere, such as trichloroethylene, will generally also be found in source waters.

The most serious problem in the LLE method is the presence of contaminants in the extracting solvent which coelute and interfere with THM analysis.^{3,10,14} Solvent clean-up required for low-level analysis is often tedious and difficult.

Method comparisons

Experimental values

Available data have shown that the purge and trap and liquid-liquid extraction methods are comparable for the analysis of THMs.^{10,13,14} Chromatograms generated upon analysis of a finished water sample by both methods are shown in *Figures 6* and *7*. The THM concentrations compare favorably. It should be noted that there are unidentified compounds observed on analyses by both methods. The GC column was operated at slightly lower



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temperature (Figure 7) than for the analysis shown in Figure 4, accounting for the differences in retention times.

In addition, 35 water samples were analyzed for THMs by both methods.¹⁴ Samples were selected from 24 water utilities, representing varying water source types and having a wide range of concentrations of each of the THMs. The average difference between the values determined for each

THM varied from -6.7% to +4.6%. Statistical treatment showed the methods to be equivalent.¹⁴

Another way of comparing the two methods is by the analysis of samples of known concentration. Data for such measurements are given in *Table 7*. Comparative purge and trap and LLE data agree to within $\pm 20\%$. Expected values also agree to within $\pm 20\%$ of values determined by each

Table 7

Analysis of quality control samples by purge and trap and liquid-liquid extraction

Sample	No. of analyses	Concentrations ^a			
		CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃
QC 1276-2					
Expected	—	68	12	17	14
LLE	5	71 ± 5.1	14 ± 1.7	15 ± 1.7	14 ± 1.3
P and T	5	68 ± 2.6	17 ± 0.5	17 ± 1.9	16 ± 1.2

^aExpressed in µg/L with standard deviation

method, except in this example, for the value for bromodichloromethane as determined by purge and trap.

Table 8

THM method comparison

Purge and trap	
Advantages	Disadvantages
Method well-characterized	Less familiar
Chromatography more versatile; analyze for broad range of compounds	Lengthy learning curve
Specific detector	Longer analysis time
Selective extraction	Precision can be poor
Minimum sample preparation	More difficult to automate

Liquid-liquid extraction	
Advantages	Disadvantages
More familiar	Method less well characterized: THMs validated
Easier to learn	Chromatography less versatile
Shorter analysis time	Detector semi-specific
Generally better precision	Extraction not selective
Amenable to automation	Longer sample preparation time
	More susceptible to interferences from solvent contamination and contaminants in sample

General features

The THM methods also can be compared in a more general way (Table 8). It is seen that advantages and disadvantages of each method are interrelated. Thus, in choosing a method to use, laboratory needs must be determined carefully. For example, if samples are to be analyzed solely for THMs and the source water is free of industrial contamination and thus potential interferences, LLE may be the method of choice. On the other hand, if a polluted source water is to be analyzed, purge and trap should be selected. For a broad range of halocarbons to be determined in addition to THMs, the purge and trap method offers greater flexibility and selectivity. Another consideration is the training and experience of the laboratory's

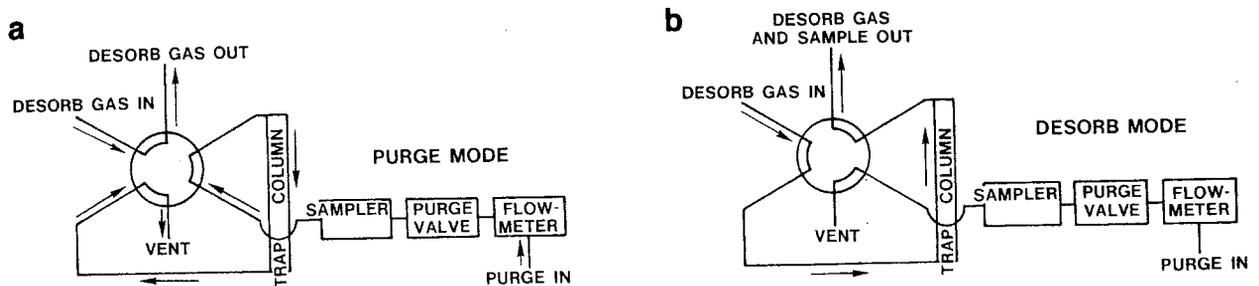


Figure 1 Sequence schematics, a) purge and b) desorb.

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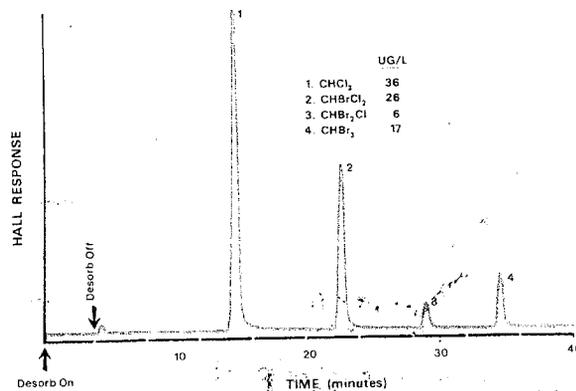


Figure 2 Chromatogram of a THM standard in water and analyzed by purge and trap using primary column b.

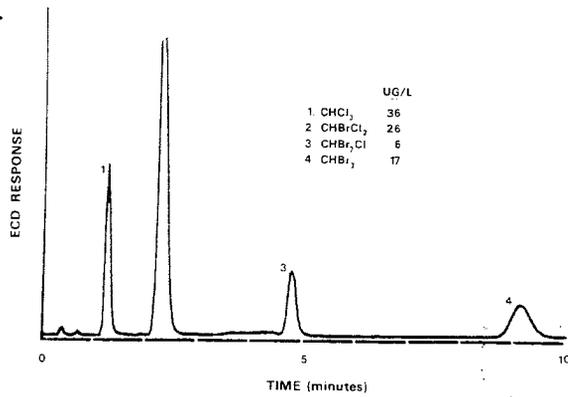


Figure 4 Chromatogram of a THM standard in water analyzed by LLE using a 10% squalane column.

analytical staff. A laboratory having inexperienced personnel may opt for LLE, while one with experienced personnel may choose purge and trap. In certain cases, laboratories may choose to develop capabilities for both methods and permit the probable complexity of samples and required analyses to dictate the method to be used.

A final consideration may be equipment cost. If the choice is made to add equipment to perform liquid-liquid extraction and purge and trap determinations to an existing laboratory operation, costs will range from approximately \$8,000-15,000. Equipment required for LLE will tend to be on the low end of this range, while equipment for purge

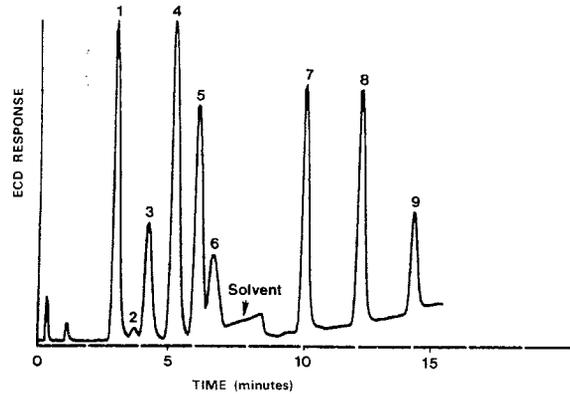


Figure 5 Chromatogram of a nine component halocarbon standard in water analyzed by LLE using a 10% squalane column under temperature programmed conditions. Halocarbons and their concentrations in $\mu\text{g/L}$ are: 1) chloroform 34; 2) 1,2-dichloroethane 14; 3) 1,1,1-trichloroethane 5.6; 4) carbon tetrachloride 6.3; 5) bromodichloromethane 6.0; 6) trichloroethylene 9.5; 7) dibromochloromethane 8.6; 8) tetrachloroethylene 4.4; and 9) bromoform 7.1.

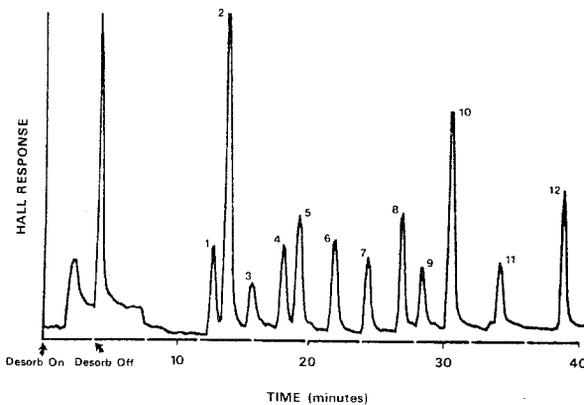


Figure 3 Chromatogram of a 12-component halocarbon standard in water analyzed by purge and trap using primary column b. Halocarbons and their concentrations in $\mu\text{g/L}$ are: 1) 1,1,2-dichloroethylene 0.72; 2) chloroform 1.4; 3) 1,2-dichloroethane 0.43; 4) 1,1,1-trichloroethane 0.60; 5) carbon tetrachloride 0.62; 6) bromodichloromethane 0.75; 7) 1,2-dichloropropane 0.58; 8) trichloroethylene 0.56; 9) dibromochloromethane 0.78; 10) 2-bromo-1-chloropropane 2.7; 11) bromoform 1.2; and 12) tetrachloroethylene 0.54.

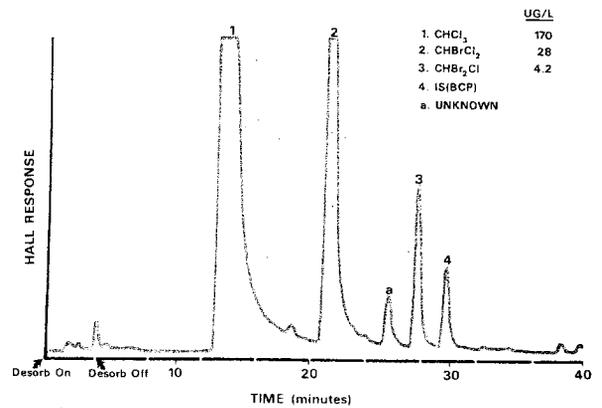


Figure 6 Chromatogram of a finished water sample analyzed by purge and trap using primary column b. The internal standard was 2-bromo-1-chloropropane (BCP).

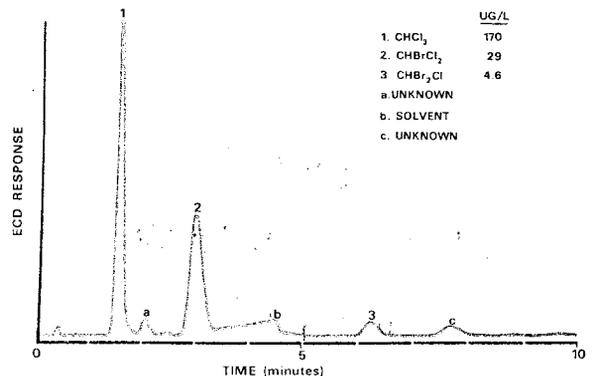


Figure 7 Chromatogram of a finished water sample analyzed by LLE (isooctane) using a 10% squalane column.

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