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## Determination of Halocarbons in Drinking Water by Direct Aqueous Injection Gas Chromatography

Hou Dingyuan\* and Tang Jianfei

Suzhou Environmental Monitoring Central Station, Suzhou, 215004 People's Republic of China

### INTRODUCTION

Recently, the determination of halocarbons in drinking water has become an important item in environmental monitoring. For the analysis of halocarbons, a common method requires the use of a gas chromatograph equipped with an electron capture detector (ECD). Other techniques that have been in use are purge and trap (P&T) (1), liquid-liquid extraction (LLE) (2, 3), headspace (4-6), and direct aqueous injection (7, 8). These methods have different advantages and shortcomings. For example, purge and trap is sensitive and accurate enough to detect organic compounds, but the device is complicated and analysis time is longer. Liquid-liquid extraction is simpler, but the extract is easily contaminated and background may affect accuracy. Headspace has avoided some shortcomings in the two aforementioned methods, but in water samples of different chemical composition and salt content, the distribution coefficients are varied and will affect the accuracy (9).

This paper describes the characteristics of direct aqueous injection (DAI) and its actual application. This method is easy to perform. On the one hand, it has sufficient accuracy, good precision, and high sensitivity for 0.4-1- $\mu$ L injections. On the other hand, its operation does not affect the ECD. With direct aqueous injection on column, the separation of water from halocarbons requires a special column. By using a porous polymer (GDX-103) as the support, 1% SE-30 is coated on the GDX-103 polymer beads. The column is much better than an OV-101 column (Chromosorb W HP DMCS as support) and provides satisfactory results.

### EXPERIMENTAL SECTION

**Chemicals and Apparatus.** The following compounds were analyzed: (1) methanol, (2) chloroform, (3) tetrachloromethanol, and (4)  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . Bromodichloromethane, chlorodibromomethane, and bromoform were of chromatography grade. The pure water used in this study did not contain halocarbons.

The gas chromatograph was a Hewlett-Packard 5890A fitted with an electron capture detector. Chromatograms were recorded with a Hewlett-Packard 3392A reporting integrator. High-purity nitrogen was used as the carrier gas, and the gas line was equipped with moisture and oxygen traps.

**Procedures.** A standard mixture containing five halocarbons (see Table I) was prepared: Methanol was used as the solvent for the stock solution, while pure water was used to prepare the dilute test solution.

**Sampling and Analysis.** First, about 10 mg of sodium thiosulfate was added to the sample to remove residual chlorine in the tap water. Second, the tap was opened and run until a steady stream was achieved, and the sample container was then filled to a point short of overflowing. The tube was capped and shaken until the thiosulfate was dissolved. The water sample was then analyzed by the indicated GC conditions. Injection volume

Table I. Standard Mixture of Halocarbons in Water<sup>a</sup>

amount, $\mu\text{g/L}$				
$\text{CHCl}_3$	$\text{CCl}_4$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$
12	2	16	4	20

<sup>a</sup> Each component concentration in the standard mixture of five carbons was close to that in the drinking water samples.

Table II. Accuracy of the Method (% Recovery)

method	% recovery				
	$\text{CHCl}_3$	$\text{CCl}_4$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$
DAI	105	99	102	110	99
LLE (EPA)	110		125	94	114
P&T (EPA)	102	81	101	98	89

Table III. Precision of the Method (Relative Standard Deviation (%))

method	rel std dev, %				
	$\text{CHCl}_3$	$\text{CCl}_4$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$
DAI (0.4 $\mu\text{L}$ )	5.3	6.2	4.1	10.8	2.1
DAI (1.0 $\mu\text{L}$ )	2.4	7.4	2.7	3.1	9.9
LLE (EPA)	11		1.4	9.9	1.2
P&T (EPA)	0.6	25.6	5	6.5	9

Table IV. Detection Limits<sup>a</sup>

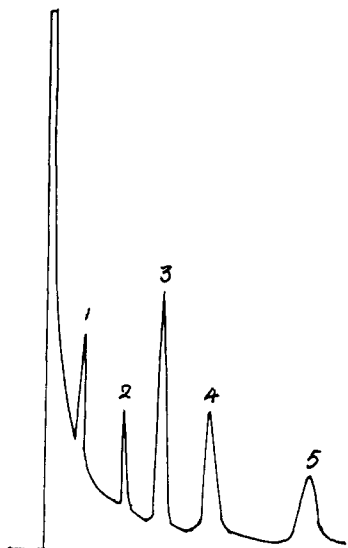
limit, $\mu\text{g/L}$				
$\text{CHCl}_3$	$\text{CCl}_4$	$\text{CHBrCl}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$
1.2	0.4	1.0	0.9	2.6

<sup>a</sup> Range 16.

was 0.4-1  $\mu\text{L}$ . Quantitative computation was based on peak areas. Samples were compared with standards run under the same conditions by using the HP 3392A integrator.

### RESULTS AND DISCUSSION

**Selection of the Column.** In DAI, a key problem was rapid elution of water. This problem would affect the separation of water from trihalomethanes and the analytical accuracy. In headspace and other methods, the stationary phases that have been used in separation of halocarbons are SE-30, OV-101, squalane, SP-1000, SP-2100, OV-11, etc., and the support is either Chromosorb or Carbowax. A column of OV-101 on Chromosorb W HP DMCS can separate water from trihalomethanes, but the effect is not ideal (see Figure 1). The column packing used for this work was SE-30 on



**Figure 1.** Gas chromatogram of halocarbons. Column: 10% OV-101 on Chromosorb W HP DMCS, 80–100 mesh, 1.8 m × 4-mm i.d. glass. Temperature: oven 65 °C, injector 200 °C, detector 300 °C. Carrier gas flow: 40 mL/min (N<sub>2</sub>). Retention time: 1-CHCl<sub>3</sub> (1.98 min), 2-CCl<sub>4</sub> (2.68 min), 3-CHBrCl<sub>2</sub> (3.19 min), 4-CHBr<sub>2</sub>Cl (5.56 min), 5-CHBr<sub>3</sub> (10.10 min).

**Table V. Detected Results in the Tap Water Sample and Recovery**

compd	amount, µg/L			recovery, %
	tap water	added std	measd	
CHCl <sub>3</sub>	9.4	20	29.5	100.3
CCl <sub>4</sub>	0.0	10	10.1	101
CHBrCl <sub>2</sub>	8.0	16	24.1	100.4
CHBr <sub>2</sub> Cl	3.2	16	18.4	96
CHBr <sub>3</sub>	0.0	30	31	103

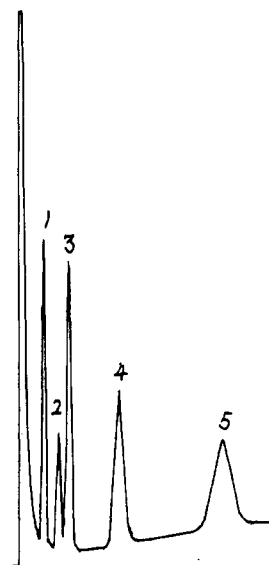
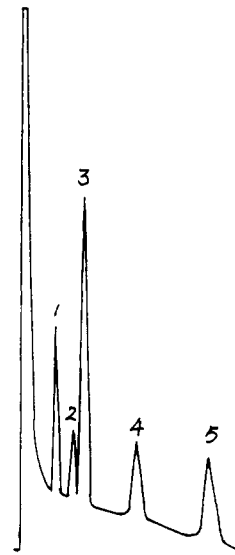
GDX-103. This selection provided for adequate separation of the halocarbons and rapid elution of water.

**Accuracy, Precision, and Detection Limits.** By using the DAI method, 10 repetitive analyses were made of a standard solution of the halocarbons (concentrations as indicated in Table I) in pure water. Five of these analyses were made with 1.0-µL injections and five with 0.4-µL injections. Table II summarizes the average recovery of each component including both sets of measurements. Table III indicates the relative standard deviation for the two sets of measures computed separately, while Table IV indicates the estimated lower limits of detection. In addition, Tables II and III include results published by the U.S. EPA (2), indicating accuracy and precision of the LLE and P&T methods.

Finally, five replicate analyses of a tap water sample were made. The sample was then fortified by addition of the five components of concern. The fortified sample was again analyzed 5 times. The results of these analyses (averages) are summarized in Table V.

**Discussion.** In comparison with other methods, DAI did not need any processing from sampling to detection; thus, interferences and losses were avoided. The method was simpler, faster, and more accurate. Compared with LLE, the DAI method gave a measure of chloroform of 21.7 µg/L, while LLE gave 16.5 µg/L in the same sample.

ECD characteristics were not affected by DAI. Some analysts have suggested (8) that a large-volume aqueous injection would decrease the ECD sensitivity and that injection should not exceed 1 µL. Early ECD, though, with good sensitivity required an injection of 20–100 µL of sample to detect 0.5 µg/L of chloroform (7). Hence, a sizable quantity of water needed to be removed with a precolumn and the wide application of



**Figure 2.** Standard sample of halocarbons in water. Column: 1% SE-30 on GDX-103, 40–60 mesh, 1.2 m × 4-mm i.d. glass. Injection volume: 1 µL. (A, left) Temperature program 160–190 °C, rate 3 °C/min, injector temperature 200 °C, detector temperature 300 °C. Carrier gas flow rate: 70 mL/min (N<sub>2</sub>). Retention times: 1-CHCl<sub>3</sub> (2.16 min), 2-CCl<sub>4</sub> (3.20 min), 3-CHBrCl<sub>2</sub> (3.80 min), 4-CHBr<sub>2</sub>Cl (6.40 min), 5-CHBr<sub>3</sub> (10.10 min). (B, right) Isothermal oven temperature 160 °C, injector temperature 200 °C, detector temperature 300 °C. Carrier gas flow rate: 70 mL/min (N<sub>2</sub>). Retention times: 1-CHCl<sub>3</sub> (1.92 min), 2-CCl<sub>4</sub> (2.96 min), 3-CHBrCl<sub>2</sub> (3.65 min), 4-CHBr<sub>2</sub>Cl (7.15 min), 5-CHBr<sub>3</sub> (14.18 min).

DAI was thus restricted. However, in this method, a new type <sup>63</sup>Ni ECD was used with a 1% SE-30 on GDX-103 column with greater sensitivity and better separation (Figure 2). The detector is sensitive enough to detect routinely the microgram/liter levels permissible in drinking water in a sample as small as 0.4 µL.

In this method, GDX-103 was used as the support for separation of halocarbons (10), considering its characteristics similar to the Porapak series (GDX-103 specific surface area 670 m<sup>2</sup>/g, low pole, maximum allowable operating temperature 270 °C; Tianjin Chemical Reagent Factory of China), but in DAI, the injection of a large amount of water as the solvent affected the separation from chloroform. With 1% SE-30 on GDX-103, the separation between water and chloroform was more complete.

By selecting large particle size GDX-103 (40–60 mesh) and using a high carrier gas flow rate (70 mL/min) in order to elute

water rapidly, the results showed that water retention time was clearly affected by flow rate but not by increasing temperature.

This method can be applied to detect halocarbons in natural waters, including surface water, groundwater, and tap water.

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