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Journal of Chromatography A, 810 (1998) 141–147

JOURNAL OF
CHROMATOGRAPHY A

Determination of very volatile organic compounds in environmental water by injection of a large amount of headspace gas into a gas chromatograph

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Received 19 January 1998; received in revised form 20 March 1998; accepted 23 March 1998

Abstract

An injection method for a large amount of headspace gas which enables determination of trace amounts of very volatile organic compounds (VVOCs), dichlorodifluoromethane, chloromethane, vinyl chloride, bromomethane, chloroethane and trichlorofluoromethane in all kinds of environmental water was developed. A gas phase equilibrated with the water phase in a vial was purged with helium for a short time. The VVOCs were then introduced into a trapping tube packed with Tenax TA, which had been cooled using carbon dioxide. After trapping, the VVOCs were thermally desorbed and put into a GC–MS system for subsequent analysis. This method is applicable to various types of samples. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Large-volume injection; Headspace analysis; Water analysis; Environmental analysis; Volatile organic compounds

1. Introduction

Static headspace (SHS) method and/or purge-and-trap (P&T) method are used as concentration methods for the sensitive analysis of volatile organic compounds (VOCs) in water. There are about 60 VOCs which need to be measured in water, the boiling points (b.p.) of which extend over a wide range of temperatures, e.g. from the lowest, -29.8°C (dichlorodifluoromethane) to the highest, 221°C (1,2,3-trichlorobenzene) [1]. To analyze these 60 compounds, P&T analytical conditions such as temperature of the sample, flow-rate of purge gas,

purging time, type of the trap adsorbent, temperature of the trapping tube at purging, and temperature of the trapping tube at heating must be strictly controlled. In addition, cryogenic focusing by liquid nitrogen is required for the P&T method. Moreover, samples which can be measured by the usual P&T method are limited to nonfoaming materials [2] and materials free of solid suspensions.

We designed a device which allows headspace gas to be sampled from a vial, and the 23 kinds of VOCs which it contains are introduced into a micro-trap, and then into a GC–MS system [3]. This measurement system enabled the analysis of 23 kinds of VOCs with short headspace purging time without cryogenic focusing. In the present paper, we attempt-

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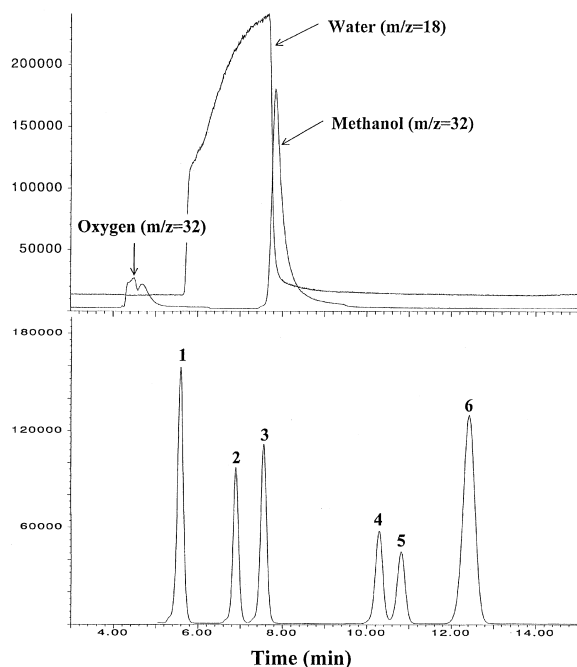


Fig. 1. SIM chromatograms of 10 $\mu\text{g}/\text{l}$ gaseous mixtures (lower); oxygen, water and methanol (upper). (1) Dichlorodifluoromethane, (2) chloromethane, (3) vinyl chloride, (4) bromomethane, (5) chloroethane and (6) trichlorofluoromethane.

ed the measurement of very volatile organic compounds (VVOCs); namely, dichlorodifluoromethane (b.p. -29.8°C), chloromethane (b.p. -23.7°C), vinyl chloride (b.p. -13.3°C), bromomethane (b.p. 3.6°C), chloroethane (b.p. 12.3°C) and trichlorofluoromethane (b.p. 23.7°C) in water using this method.

The order of the retention times of these compounds with a nonpolar or intermediate polarity

separation column was the same as the ascending order of the boiling points of the compounds as shown in Fig. 1. The peaks of dichlorodifluoromethane, chloromethane, and vinyl chloride overlapped with that of water and methanol, which is the solvent for standard solutions. In order to improve the recovery of VVOCs in the P&T method, the temperature of the sample, the flow-rate of purge gas and the purging time are all raised. As a result, peaks of water and methanol deviate largely from the baseline, and poor vacuum makes the mass detector shut down during measurement.

The adsorbent resins Tenax TA or Tenax GC are widely used for P&T techniques. Tenax TA shows excellent trapping efficiency for many organic compounds, but low affinity for water as shown in Table 1. When good recovery rates are required from a sample, more moisture may be injected into the separation column. To remove moisture from the adsorbed analytes, dry helium was passed through the adsorbent tube for a few minutes after sample purging. This operation, however, causes the loss of dichlorodifluoromethane. Because the breakthrough volumes of Tenax TA for VVOCs are very small, adsorbing resins of different breakthrough volume are packed. Nevertheless, the two inverse requirements (improvement of recovery and removal of water from the adsorbent) exist as the major problems in using the P&T method.

A whole headspace gas injection method (WHSI) has enabled measurement of 23 VOCs without cryogenic focusing [3]. In this method, we put a whole headspace gas equilibrated in a vial into a GC system. If a small part of headspace gas equilibrated in a vial is introduced into a trap for a shorter time,

Table 1
Breakthrough volumes for relating compound on Tenax TA [4] (l/g of Tenax TA)

Compound	Temperature ($^\circ\text{C}$)			
	0	20	40	60
Dichlorodifluoromethane	0.34	0.12	0.05	0.021
Chloromethane	0.85	0.25	0.086	0.033
Vinyl chloride	1.70	0.55	0.180	0.063
Bromomethane	No data	No data	No data	No data
Chloroethane	18.0	4.0	1.00	0.300
Trichlorofluoromethane	11.0	2.20	0.750	0.230
Water	0.130	0.065	0.035	0.018
Methanol	1.30	0.362	0.140	0.055

WHSI can provide more sensitive measurement of VVOCs than SHS. This is because a short headspace sampling time prevents breakthrough of those compounds and reduces trap moisture.

2. Experimental

2.1. Reagents

Water for measuring VOCs was obtained from Wako (Osaka, Japan; manufactured by Sumitomo). Graded methanol for trihalomethane measurement and graded sodium chloride for water analysis were also obtained from Wako. Mixed VVOCs standard; dichlorodifluoromethane, chloromethane, vinyl chloride, bromomethane, chloroethane and trichlorofluoromethane each 2000 $\mu\text{g}/\text{ml}$ in methanol was obtained from Supelco (Tokyo, Japan). It was diluted with cooled methanol just before use. Fluorobenzene as internal standard 1000 $\mu\text{g}/\text{ml}$ in methanol was obtained from Kanto (Tokyo, Japan). It was diluted a hundred times with cooled reagent water just before use. The other compounds were used as described previously [3].

2.2. Apparatus

An adjustable electric 10- μl micropipette (Uniflex, Tokyo, Japan; manufactured by Biohit, Finland) was used for adding standard solutions to sample water. A V-10B vial (average capacity is 14.23 ml) obtained from Nichiden (Kobe, Japan) was used for the headspace sampling. A reciprocal shaker (SR-II) from Taitec (Tokyo, Japan) was used for complete dissolution of sodium chloride and faster equilibration of the analytes in the two phases in contact. The shaking frequency was adjusted to 200 times/min.

The GC system used was a Hewlett-Packard Model 5890 Series gas chromatograph equipped with a Model 5971A mass-selective detector. The GC separation column used was Supelco Vocol, 60 m \times 0.32 mm I.D., with a 3.0- μm film.

The P&T GAS-20 with automatic sampler (DKK, Tokyo, Japan) was modified and assembled as the sampling and trap unit [3]. By decreasing the trap heat capacity, sharp peaks were obtained, and VVOCs adsorbed on Tenax TA were immediately

desorbed by rapid heating [5]. A smaller trapping tube (11 cm \times 2.17 mm I.D. \times 3.17 mm O.D.) compared to a US Environmental Protection Agency method tube (at least 25 cm long, at least 2.67 mm I.D. [1]) was used. The end of the tube was directly connected to the separation column. For the adsorbent cooling by carbon dioxide, the trap was surrounded by a PTFE tube (12 cm \times 12 mm I.D. \times 15 mm O.D.); the top of the tube was wrapped with an aluminum foil as shown in Fig. 2. Carbon dioxide, which was restricted by a filter union (pore size 2 μm ; Valco) from the primary pressure line and controlled by an electric valve, was released from a stainless steel pipe which passes through the PTFE tube. Released carbon dioxide could control the temperature of the trap to -40°C , within $\pm 2^\circ\text{C}$. About 10 l of carbon dioxide could cool the trap to -30°C from room temperature within 1 min.

2.3. Analytical procedure

Initially, 2 g of sodium chloride was added to the sample vial. Then, 5 ml of sample water and 5 μl of internal standard fluorobenzene solution were added. The vial was tightly closed with a silicone septum covered with a PTFE sheet and an aluminum perforated cap. It was shaken for more than 10 min. Before analysis, the vials were placed in an aluminum block in the automatic-sampler for 1 h at $20 \pm 0.2^\circ\text{C}$. Then, the septum was pierced with the

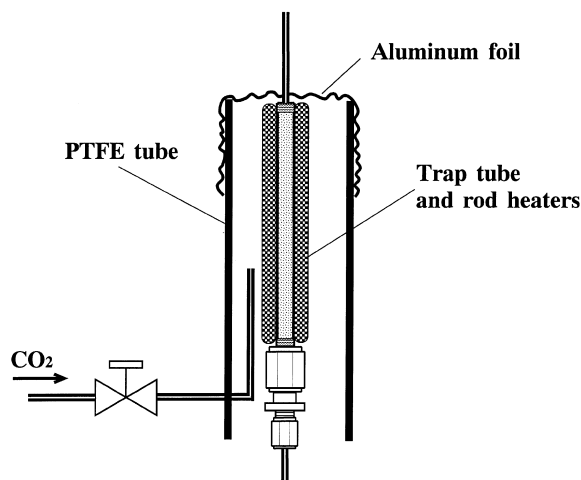


Fig. 2. Cooling the trap by a jet of carbon dioxide.

Table 2
Selected masses and retention times for VVOCs

Compound	Target ion (<i>m/z</i>)	Qualified ion (<i>m/z</i>)	Retention time (min)
Dichlorodifluoromethane	85	87	5.6
Chloromethane	50	52	6.9
Vinyl chloride	62	64	7.6
Bromomethane	94	96	10.3
Chloroethane	64	66	10.8
Trichlorofluoromethane	101	103	12.4
Fluorobenzene	96	70	29.4

sampling and helium inlet needles. VVOCs were carried with helium to the micro-trap, which had been cooled to $-30 \pm 2^\circ\text{C}$, for 15 s at a flow-rate of 20 ml/min. For the GC-MS analysis, the trap was heated rapidly to 230°C (holding 2 min) and VVOCs desorbed were introduced into the capillary column. The transfer lines and valves were maintained at about 70°C .

GC was operated as follows: isothermal operation at 30°C for 14 min, then heated in a linear temperature mode to 160°C ($20^\circ\text{C}/\text{min}$), and then held for 15 min. After desorption, the trap was baked at 230°C for 12 min to prepare for the next analysis. The carrier gas was helium and its flow-rate was constant at 1 ml/min.

GC-MS in the selected-ion monitoring (SIM) mode was chosen to obtain the highest analytical sensitivity. Two ions for each compound were chosen as shown in Table 2. Concentration of each compound was calculated from an internal standardization technique.

3. Result and discussion

3.1. Relationship between temperature of trap and breakthrough volume

Table 1 shows the breakthrough volumes of Tenax TA for VVOCs at different temperatures. The headspace purging time was limited by compounds with the smallest breakthrough volume, i.e. dichlorodifluoromethane. For 70–72 mg of Tenax TA in the trapping tube, if the purge gas flow-rate was 20

ml/min at the trap temperature 0°C , a purging time of 1 min, which does not cause the loss of dichlorodifluoromethane, could be predicted from its breakthrough volume data in Table 1.

Changing the temperature of the trapping tube between 22° and -40°C , the breakthrough volume of each VVOC was measured as follows:

A 5-ml volume of reagent water and 50 ng of VVOCs were added to every vial. The vial was tightly closed and shaken for 10 min at 20°C . Then, the septum was pierced by the sampling and helium inlet needles. VVOCs were carried with helium at a constant flow-rate of 20 ml/min for 15 or 60 s to the micro-trap, which had previously been cooled at a fixed temperature. The trap was heated up rapidly to 230°C and the VVOCs desorbed were measured by GC-MS.

During headspace purging for 60 s at a trap temperature of 22°C , vinyl chloride was not desorbed from the adsorbent. However, for the same purging time, chloromethane was desorbed at temperatures above -10°C as shown in Fig. 3; dichlorodifluoromethane was desorbed even at -40°C as shown in Fig. 4. Consequently, the headspace purge time was set at 15 s to prevent the breakthrough of these compounds. The results showed that, to prevent breakthrough of dichlorodifluoromethane, the micro-trap temperature must be below -20°C (Fig. 4). In our injection system, about 39.8% of the whole headspace gas was taken by purging of the headspace for 15 s, which was calculated from the previous result [3]. The difference between our breakthrough data and those of Table 1 could be explained by the presence of frozen water on the adsorbent surface, i.e. the amount was evaluated to

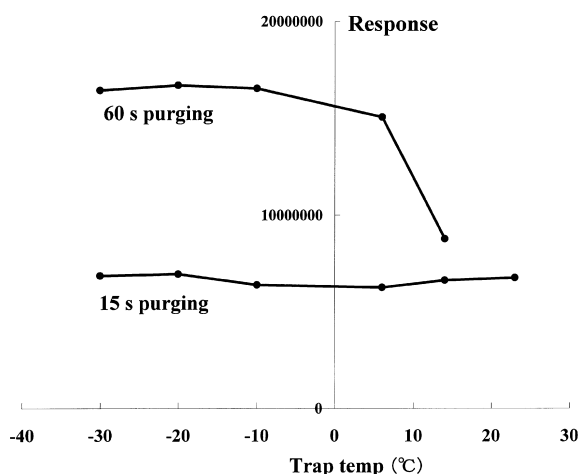


Fig. 3. Breakthrough of chloromethane.

be ca. 63 μg from vapor pressure of water at 20°C; decreasing the effective adsorption area.

3.2. Trace analysis

In surface water and groundwater, amounts of dichlorodifluoromethane, chloromethane, vinyl chloride, bromomethane and trichlorofluoromethane have been reported in the nanograms per litre or micrograms per litre range [6]. Therefore, analytical precision within those levels is required for the

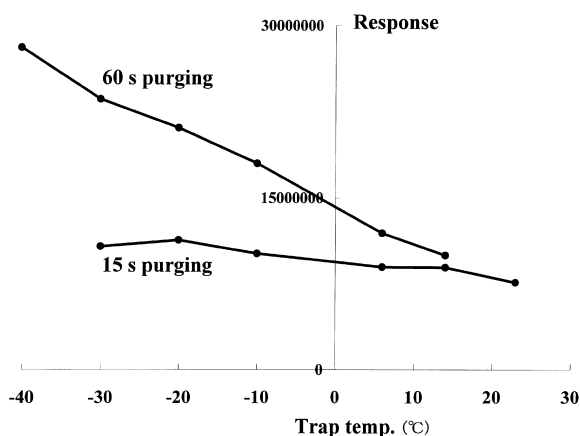


Fig. 4. Breakthrough of dichlorodifluoromethane.

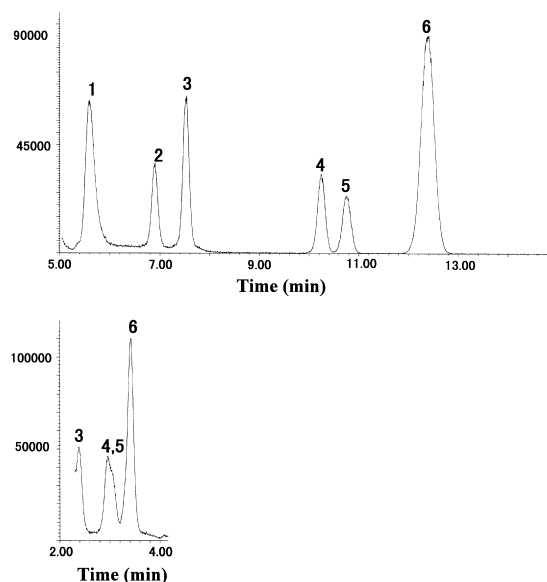


Fig. 5. Total ion chromatograms of 20 $\mu\text{g}/\text{l}$ mixture using a 60 $\text{m} \times 0.32$ mm I.D. with 3.0- μm film thickness (upper) and a 30 $\text{m} \times 0.25$ mm I.D. with 1.5- μm film thickness column (lower). (1) dichlorodifluoromethane, (2) chloromethane, (3) vinyl chloride, (4) bromomethane, (5) chloroethane, (6) trichlorofluoromethane.

determination of these compounds in water. Fig. 5 presents data obtained using two different columns on a 20 $\mu\text{g}/\text{l}$ mixture of six VVOCs. For the separation of these compounds, the column flow-rate was constant at 1 ml/min and the column oven temperature was 30°C (isothermal). The top chromatogram shows the results using a separation column of 60 $\text{m} \times 0.32$ mm I.D. with 3.0- μm film thickness, and the lower one was obtained using a 30 $\text{m} \times 0.25$ mm I.D. column with 1.5- μm film thickness. The narrow bore column was expected to give better separation and *S/N* ratio than the middle bore column, but it could not separate these compounds at 30°C (isothermal) and caused frequent shut down of the mass detector.

If a separation column which is longer than 30 m and with a larger phase ratio is used, it might give a good performance, but it is not commercially available. The 0.32 mm I.D. column, however, could separate the six compounds completely at 30°C (isothermal), and the peak areas of VVOCs measured in the range of 0–20 $\mu\text{g}/\text{l}$ increased linearly

Table 3

R.S.D.s at the concentration of 0.1 $\mu\text{g}/\text{l}$ and MDLs by the proposed method

Compound	R.S.D. ^a (%)	MDL ^a ($\mu\text{g}/\text{l}$)
Dichlorodifluoromethane	11.6	0.04
Chloromethane	8.0	0.03
Vinyl chloride	12.4	0.04
Bromomethane	8.0	0.03
Chloroethane	12.5	0.04
Trichlorofluoromethane	12.9	0.04

^a Spiked with 0.5 ng VVOCs in 5 ml pure water. R.S.D.s and MDLs were calculated from the peak area of target ion of seven replicate runs.

with the sample mass. The correlation coefficients ranged from 0.9988 to 0.9997.

The method detection limits (MDLs [1]) were calculated from peak areas for 0.1 μg VVOC/l of seven replicate runs as shown in Table 3. When these data were obtained, the laboratory reagent blanks were less than the detection limits ($S/N=2$). The actual limits of determinations, however, were occasionally strongly influenced by the degree of contamination in the laboratory air and reagent water. Therefore, a few laboratory reagent blanks had to be included for each set of measurements.

Twenty-two samples of drinking water in Japan were measured by the proposed method, i.e. injection of a large headspace gas. Dichlorodifluoromethane, vinyl chloride, bromomethane and chloroethane were not detected in any of the samples. Chloromethane was detected in nine samples and the concentration range was 0.03–0.12 $\mu\text{g}/\text{l}$. Trichlorofluoromethane was detected in 11 samples and its concentration range was 0.04–2.2 $\mu\text{g}/\text{l}$.

Table 4

Recoveries of VVOCs spiked to artificial seawater and tap water

Compound	Artificial seawater		Tap water	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Dichlorodifluoromethane	93.8	6.2	95.8	3.9
Chloromethane	100.0	5.6	103.6	1.9
Vinyl chloride	95.6	5.5	94.9	4.5
Bromomethane	88.7	6.5	87.7	8.1
Chloroethane	96.4	5.3	96.4	4.0
Trichlorofluoromethane	94.6	5.4	97.2	3.9

Spiked 50 ng VVOCs in 5 ml artificial seawater and tap water separately. All values are calculated from the peak area of six replicate runs.

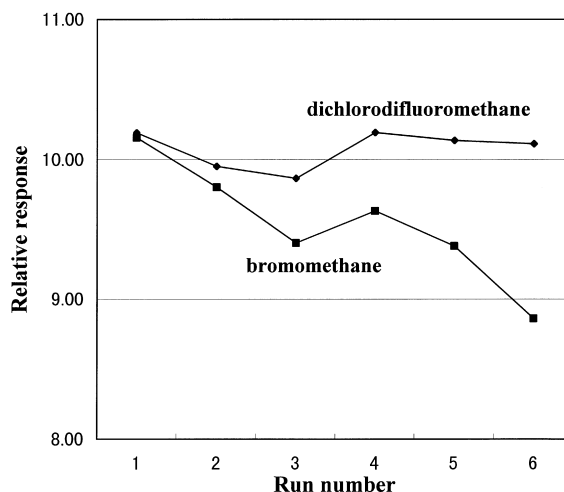


Fig. 6. Variation of relative response on repeated runs.

The proposed method is applicable to environmental water samples which are difficult to measure with P&T method. Five milliliters of tap water and the same amount of separate artificial seawater, which is one of the undesirable samples for P&T method, were added with 50 ng of each VVOC, and measured six times repeatedly by the proposed method. Table 4 shows the results including the reproducibility of the recoveries. Recoveries were determined using working curves. The reproducibility on artificial seawater for each VVOC was excellent as in the case of tap water except for bromomethane. The peak areas of bromomethane decreased with an increase in measuring times as shown in Fig. 6. Since this phenomenon could not be seen in other compounds, it is thought that bromomethane may be decomposed in water or adsorbed on the wall of the vials. We are

planning to study the decomposition of VOCs in water in the near future.

4. Conclusion

We proposed a concentration method in a previous paper in which an equilibrated whole headspace gas is sampled from a vial, and VOCs are brought into a micro-trap. In this paper, we proposed a short headspace purge time (15 s) and a cooling trap (-30°C) to prevent breakthrough. As a result, a highly sensitive measurement of VVOCs with small breakthrough volumes for all kinds of water sample was achieved.

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