Simultaneous Determination of Volatile Organic Pollutants in Water by Headspace Gas Chromatographic Analysis with Dual Detection

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Headspace gas chromatographic analysis using a semi-wide bore capillary column and a dual detection system with a flame ionization detector (FID) and an electron capture detector (ECD) was carried out for the simple and rapid simultaneous determination of 13 kinds of volatile organic pollutants: benzene (1), toluene (2), ethyl benzene (3), *o*-, *m*- and *p*-xylenes (4–6), monochlorobenzene (7), *o*-, *m*- and *p*-dichlorobenzenes (8–10), 1,1,1-trichloroethane (11), trichloroethylene (12) and tetrachloroethylene (13) in drinking water at low ppb (10^{-9} g/ml) level. The effects of the headspace and syringe temperatures as well as the equilibration time and injection volume of headspace gas on the sensitivity and reproducibility of analysis were examined to find the optimal conditions. The capillary column permitted satisfactory separation of the target compounds except *m*- and *p*-xylenes (5 and 6) without interference by trihalomethanes in drinking water. FID was sensitive to all aromatic hydrocarbons (1–6) and monochlorobenzene (7) at 0.3–0.5 ppb, while ECD was poorly sensitive to them. By contrast, ECD was highly sensitive to chlorinated hydrocarbons (11–13) and aromatic chlorinated hydrocarbons except monochlorobenzene (8–10) with detection limits of 0.005–0.02 and 0.2–0.6 ppb, respectively, while FID was poorly sensitive to them. The coefficients of variation ($n=4$) in the simultaneous analysis using FID and ECD for sample water containing 0.1–20 ppb of the target compounds were 3.4–7.4% with good precision and reproducibility.

Keywords — volatile pollutants; drinking water; headspace analysis; semi-wide bore capillary column; dual detection; FID; ECD

Introduction

Volatile organic compounds such as benzene (1), toluene (2), ethyl benzene (3), *o*-, *m*- and *p*-xylenes (4–6), monochlorobenzene (7), *o*-, *m*- and *p*-dichlorobenzenes (8–10), 1,1,1-trichloroethane (11), trichloroethylene (12) and tetrachloroethylene (13) (in Table I) are widely used as industrial solvents and intermediate products of the chemical industry¹⁾ and they are known to be released into the environment as toxic pollutants. Compounds 11–13 have already been regulated for contaminant levels in drinking water

by tentative standards,²⁾ and these 3 chlorinated hydrocarbons have been the subjects of much research. Aromatic hydrocarbons (1–6) and aromatic chlorinated hydrocarbons (7–10) have also been suspected of being potential contaminants of drinking water, owing to the considerable quantity of their production and consumption.³⁾

In fact, compounds 1–3 and 8–10 have been detected in river water, soil, and groundwater^{4–6)} similar to compounds 11–13, and anxiety about the contamination of drinking water by aromatic compounds (1–10) has been expressed.⁷⁾ The Drinking Water Quality

Regulations of the US Environmental Protection Agency⁸⁾ mandate that these pollutants must be monitored at every water supply facility. Introduction of such regulations and monitoring is also anticipated in Japan, so simple and rapid methods for the simultaneous analysis of various volatile pollutants in drinking water are needed.

In gas chromatography (GC) of volatile pollutants, flame ionization detectors (FID) for aromatic hydrocarbons^{9,10)} and electron capture detectors (ECD) for chlorinated hydrocarbons and aromatic chlorinated hydrocarbons¹¹⁻¹⁴⁾ have been used because of their high sensitivities to the respective compounds. However, they were used separately, resulting in a complexity of the process. Recently, gas chromatographies with mass spectrometry¹⁵⁻¹⁸⁾ or with dual detection by photoionization and electrolytic conductivity detectors^{19,20)} have been reported for the simultaneous analysis of various volatile pollutants. These are not adopted for routine work, however because of the expense of the apparatuses and the difficulty of their operation.

As pretreatment of sample water, liquid-liquid extraction,²¹⁾ purge-and-trap,^{16,17,22)} Dean-Stark distillation,⁵⁾ and whole column cryotrapping¹⁸⁾ have been reported, but all these pretreatments are rather complex and none are easy to perform. For this reason, the headspace method²³⁾ is commonly used as a routine procedure for simple and rapid determination of volatile compounds.

In this study, headspace GC was carried out with a splitless injection to attain simultaneous determination at low ppb (10^{-9} g/ml) level of 13 kinds of volatile pollutants (1-13) in drinking water. These target compounds were separated using a semi-wide bore capillary column (0.32 mm i.d.), and determined with dual detection by a combination of FID and ECD. This procedure was not interfered with by trihalomethanes (A-D in Table I), which were generated by chlorination in

TABLE I. Target Compounds and Their Retention Times

No.	Target compounds	t_R (min)
Aromatic hydrocarbons		
1	Benzene	18.56
2	Toluene	26.81
3	Ethyl benzene	34.10
4	<i>o</i> -Xylene	36.67
5	<i>m</i> -Xylene	34.68
6	<i>p</i> -Xylene	34.67
Aromatic chlorinated hydrocarbons		
7	Monochlorobenzene	33.49
8	<i>o</i> -Dichlorobenzene	48.27
9	<i>m</i> -Dichlorobenzene	45.38
10	<i>p</i> -Dichlorobenzene	45.91
Chlorinated hydrocarbons		
11	1,1,1-Trichloroethane	17.10
12	Trichloroethylene	21.26
13	Tetrachloroethylene	29.71
Trihalomethanes		
A	Chloroform	15.90
B	Bromodichloromethane	22.90
C	Dibromochloromethane	30.21
D	Bromoform	37.48

drinking water.

The reason for using the semi-wide bore capillary column is as follows: Narrow-bore capillary columns (0.20-0.25 mm i.d.) have high separation ability and are effective for the separation of many components, but the volume of injection is limited because of their small loading capacity. Wide-bore capillary columns (0.53-0.70 mm i.d.), on the other hand, have the merit that the samples can be introduced directly to them, similar to packed columns, and were used in some cases,²⁴⁾ but they are inappropriate for multi-component analysis due to their low separation ability. Then, we made a compromise that target compounds were separated using a semi-wide bore capillary column by splitless injection.

Experimental

Materials — Standard solutions used for this study were obtained from Kanto Chemicals at the concentration of 1 mg per ml methanol. Sec-

dary standards were prepared using methanol (pesticide residue analysis grade from Katayama Chemical). Organic-free water was prepared by distilled water boiled for more than 15 min, followed by continued purging with nitrogen while cooling to 30°C. Glass vials (vol. 125 ml) were washed and rinsed with distilled water and methanol, heated at 150°C and kept in a desiccator. Sodium chloride (NaCl), to be added to the vials, was heated at 500°C for 1 d. Residual chlorine in sample drinking water, obtained from the tap in our laboratory, was removed by addition of sodium thiosulfate. The decomposition of chlorinated hydrocarbons was prevented by addition of phosphoric acid.

Apparatus and Conditions of Analysis —

The analyses were carried out on a Shimadzu 14A gas chromatograph equipped with both an FID and an ECD. A 30 m × 0.32 mm i.d. fused silica capillary column (Halo-matics 624) with a 3.0 μm film thickness obtained from Quadrex and helium (1.4 ml/min) as the carrier gas were used to separate target compounds in the splitless injection mode (0.5 min) at 35°C. The end of the

capillary column was combined with the FID and ECD, respectively, using a Chromfit Y Splitter (Gasukuro Kogyo), consisting of a low-dead-volume union, and two deactivated fused silica capillary tubings (0.5 m × 0.25 mm i.d.). Each detector was supplied with half the carrier gas (0.7 ml/min), and 40 ml/min of nitrogen as the make-up gas.

The column was maintained at 35°C for 5 min, followed by heating to 150°C at 3°C/min, and held for 8 min at 150°C. The detector temperature was 210°C and injection temperature was 180°C. The flow-rates of hydrogen and air to the FID were 40 and 500 ml/min, respectively. Peak areas were obtained by integration using Shimadzu Chromatopac CR-3A and CR-5A instruments.

A gas syringe equipped with a side port needle was kept at a constant temperature in an incubator for the succeeding GC analysis. Until otherwise stated, the temperature was 60°C.

Analytical Procedure — Sample water (80 ml) was placed in a glass vial to which 30 g of NaCl was added to decrease the solubility of dissolved compounds, and immediately closed

Fig. 1. Typical Gas Chromatograms Obtained by Dual Detection for Target Compounds

The peak numbers correspond to those in Table I.

with a silicone septum and seat. The vial was shaken gently for 1 min and equilibrated at 60°C for 2–3 h in a water bath. Five-tenths of a milliliter of the headspace gas in the vial was injected into the GC in the splitless injection mode (0.5 min).

Results and Discussion

1. Separation Using a Semi-wide Bore Capillary Column

Table I shows the retention time (t_R) of target compounds (1–13) and trihalomethanes (A–D) in the semi-wide bore capillary column, and Fig. 1 shows the corresponding chromatograms obtained by dual detection. The use of this column permitted satisfactory separation of the target compounds except *m*- and *p*-xylenes without interference by trihalomethanes. The range of variation in t_R for these compounds in 4 determinations by this headspace analysis was 0.02–0.04 min, indicating a satisfactory reproducibility. The values of t_R of *m*- and *p*-xylenes were very close to each other, *i.e.* 34.67 and 34.68 min, respectively, resulting in their poor separation. This situation could not be improved, despite repeated trials in which changing the rate of increase of the column temperature and the carrier flow-rate were changed.

2. Conditions of the Headspace Analysis

2-1. Headspace and Syringe Temperatures — The equilibration temperature in headspace analysis of volatile pollutants, *e.g.* trihalomethanes and trichloroethylene,²³⁾ is usually 20–30°C. However, higher headspace equilibration temperature is required for sensitive analysis of relatively nonvolatile compounds such as dichlorobenzenes. Kawata *et al.*²⁵⁾ reported that the measurement of volatile chlorinated hydrocarbons by headspace analysis at equilibration temperatures above 40°C is affected by condensation of water vapor in the syringe during sampling of the gas and also by dissolution of part of these compounds in this condensed water. The condensation and dissolution are caused by the difference between the headspace temperature and the syringe temperature, and the error of measurement is considered to increase with this temperature difference. Therefore, in the present method, the syringe was warmed to the headspace temperature in order to also obtain satisfactory reproducibility at temperatures above 40°C. In Table II, comparisons are made between the peak areas determined with FID from 0.5 ml headspace (60°C) gases of standard sample containing 10 ppb of compounds 1–10 in water using syringes kept at room tempera-

TABLE II. Effect of the Temperature of Gas Syringe on the Peak Areas of Various Compounds at 60°C for the Headspace Temperature

No.		Peak area (arbitrary units)		Ratio of (Room temp./60°C)
		Room temp.	60°C	
1	Benzene	12252	12620	0.97
2	Toluene	13197	13580	0.97
3	Ethyl benzene	14126	14663	0.96
4	<i>o</i> -Xylene	10750	11813	0.91
5	<i>m</i> -Xylene	13989	15082	0.93
6	<i>p</i> -Xylene	14265	15116	0.94
7	Monochlorobenzene	6404	6835	0.94
8	<i>o</i> -Dichlorobenzene	2148	2984	0.72
9	<i>m</i> -Dichlorobenzene	3506	3939	0.89
10	<i>p</i> -Dichlorobenzene	2746	3566	0.77

After equilibration for 2 h at 60°C, 0.5 ml of headspace gas of standard sample containing 10 ppb was injected into GC. Peak area was given by FID.

TABLE III. Effect of the Equilibration Temperature

No.		40°C		50°C		60°C
		R.P.A.	C.V.	R.P.A.	C.V.	C.V.
1	Benzene	0.87	3.8	0.93	3.9	3.6
2	Toluene	0.84	4.5	0.94	3.8	3.3
3	Ethyl benzene	0.84	4.0	0.98	4.5	3.9
4	<i>o</i> -Xylene	0.83	5.2	0.92	4.8	4.4
5	<i>m</i> -Xylene	0.82	3.8	0.96	3.0	4.1
6	<i>p</i> -Xylene	0.89	3.2	0.96	4.0	3.3
7	Monochlorobenzene	0.79	5.5	0.96	3.2	5.2
8	<i>o</i> -Dichlorobenzene	0.57	4.9	0.81	5.7	5.3
9	<i>m</i> -Dichlorobenzene	0.65	5.9	0.90	7.1	6.4
10	<i>p</i> -Dichlorobenzene	0.61	6.3	0.84	5.3	6.1

 $n=4$,

R.P.A.: relative peak area.

ture and those using syringes warmed to 60°C. Little difference between peak areas was observed at different syringe temperatures for highly volatile compounds such as benzene and toluene, but the difference was considerable for dichlorobenzenes, showing 72–89% for the ratios between them. This indicates that the measurement of dichlorobenzenes is subject to error as a result of the condensed water in the syringe, which was kept at room temperature. Moreover, the coefficients of variation (C.V.) in the determinations of dichlorobenzenes using syringes kept at room temperature were 10% or higher, while those of determinations using syringes at 60°C were 5.3–6.4%, showing the advantage of isothermal or consistent measurements.

Table III shows the coefficients of variation (C.V.) for the peak areas at the headspace equilibration temperatures of 40, 50, and 60°C using syringes warmed to the same temperatures, respectively, and the ratios of the peak areas obtained at 40 or 50°C for the headspace and syringe temperatures to those at 60°C or relative peak areas. The C.V. for the compounds examined were 3.2–6.3% at 40°C, 3.2–7.1% at 50°C, and 3.3–6.4% at 60°C, indicating a high reproducibility in this temperature range. Therefore, the precision of measurement was shown to be maintained even at the headspace equilibration tempera-

tures above 40°C, when the syringes were warmed to the same temperatures. Moreover, as indicated by the relative peak areas, the sensitivity of isothermal measurement was highest at the headspace and syringe temperatures of 60°C. On the basis of these results, we carried out the analysis at the temperature of 60°C.

2-2. Equilibration Time of Headspace Gas — Generally, during transport, the containers of sample water are cooled with ice to prevent evaporation of volatile compounds. To determine the optimal equilibration time at the headspace temperature of 60°C, vials containing 1–10 ppb standard solutions of target compounds were cooled first in a refrigerator (5°C), warmed in a water bath to 60°C and kept at that temperature for equilibration. After equilibration times of 10 min–6 h, the headspace gases (0.5 ml) in the vials were injected into the GC. The relative values of the peak areas after various equilibration times to the peak areas after 6 h for benzene and *o*-dichlorobenzene are shown in Fig. 2. The results with benzene, *o*-dichlorobenzene and the other compounds showed that the ratios after 1 h were above 90% for highly volatile compounds such as benzene, toluene and trichloroethylene, while at least 2 h was required before equilibration of relatively nonvolatile compounds such as dichloroben-

Fig. 2. Relationship between Equilibration Time and Peak Area

●—●: Benzene, ○—○: *o*-Dichlorobenzene.

Fig. 3. Relationship between Injection Volume and Peak Area

●—●: Benzene, ○—○: Monochlorobenzene.

a) Arbitrary units common to those in Table II.

zenes. For this reason, the equilibration time of 2–3 h was considered to be needed for this study.

2-3. Injection Volume of Headspace Gas — To determine the optimal volume of the headspace gas to be injected into the GC, the peak areas of target compounds were measured with injection volumes of 0.1, 0.2, 0.5, and 1.0 ml by splitless injection (0.5 min). Fig. 3 shows the peak areas obtained with 10 ppb standard solutions of benzene and monochlorobenzene at various injection volumes.

TABLE IV. Detection Limits of Target Compounds by Dual Detection

No.		Detection limit (ppb)	
		FID	ECD
1	Benzene	0.4	
2	Toluene	0.3	
3	Ethyl benzene	0.3	
4	<i>o</i> -Xylene	0.3	>100
5	<i>m</i> -Xylene	0.3	
6	<i>p</i> -Xylene	0.3	
7	Monochlorobenzene	0.5	
8	<i>o</i> -Dichlorobenzene	1.5	0.3
9	<i>m</i> -Dichlorobenzene	1.1	0.2
10	<i>p</i> -Dichlorobenzene	1.2	0.6
11	1,1,1-Trichloroethane	2.1	0.005
12	Trichloroethylene	1.8	0.02
13	Tetrachloroethylene	1.5	0.005

The injection volume of 1.0 ml resulted in a marked peak area loss of 21% for benzene and 27% for monochlorobenzene. The peak areas of all compounds examined were nearly linear against injection volumes of 0.1–0.5 ml, but a marked loss of 21–30% and widening of the peak were observed at 1.0 ml. This indicates that the injection volume of 1.0 ml was an excessive load to this GC system that may cause errors of determination. The injection volume of 0.5 ml was therefore considered appropriate.

3. Detection Limits by Dual Detection

In general, volatile compounds must be analyzed as soon as possible after sampling because of their high volatility. Dual detection by a combination of FID and ECD yields more information by a single injection than that with using a single detector and is advantageous for simultaneous determination of various compounds. Table IV shows detection limits of the target compounds by dual detection. FID was sensitive to all aromatic hydrocarbons (1–6) and monochlorobenzene (7) at 0.3–0.5 ppb, while ECD was poorly sensitive to them. By contrast, ECD was highly sensitive to chlorinated hydrocarbons (11–13) and aromatic chlorinated hydrocarbons except monochlorobenzene (8–10) with detection

TABLE V. Reproducibility for Drinking Water Spiked with Standard Solutions

No.	Detector	20 ppb		10 ppb		1 ppb	
		P.A.	C.V.(%)	P.A.	C.V.(%)	P.A.	C.V.(%)
1 Benzene	FID	26019	4.6	12935	4.2	1322	5.3
2 Toluene		28314	5.0	14030	5.1	1487	5.1
3 Ethyl benzene		28996	3.4	14687	4.2	1480	5.6
4 <i>o</i> -Xylene		24212	4.7	12555	4.7	1198	5.5
5 <i>m</i> -Xylene		29788	4.1	15151	5.3	1493	6.1
6 <i>p</i> -Xylene		31210	3.7	15225	4.7	1533	4.9
7 Monochlorobenzene	ECD	13907	4.9	7098	5.9	682	5.8
8 <i>o</i> -Dichlorobenzene		127539	5.5	63003	5.7	6289	6.9
9 <i>m</i> -Dichlorobenzene		263500	4.8	130096	5.7	12938	6.8
10 <i>p</i> -Dichlorobenzene		89432	5.6	45499	5.3	4615	6.2

No.	Detector	1 ppb		0.1 ppb	
		P.A.	C.V.(%)	P.A.	C.V.(%)
11 1,1,1-Trichloroethane	ECD	2353591	5.0	228380	7.4
12 Trichloroethylene		326160	5.1	33186	5.5
13 Tetrachloroethylene		1653233	4.4	162162	5.7

 $n=4$,

P.A.: peak area (arbitrary units common to those in Table II).

Fig. 4. Gas Chromatograms of Sample Water Spiked with Standard Solutions

No. 1—10: 10ppb, No. 11—13: 1 ppb.

The peak numbers correspond to those in Table I.

limits of 0.005–0.02 and 0.2–0.6 ppb, respectively, while FID was poorly sensitive to them. As a whole, dual detection by FID and ECD allowed microdetection of all the target compounds to detection limits of 0.005–0.6 ppb.

4. Reproducibility of Standard Samples

The target compounds were added at the concentration range of 0.1–20 ppb to the tap water in our laboratory, which had been confirmed to be free of contamination by the compounds, and then examined (Table V). Detection was made on FID for all aromatic hydrocarbons (1–6) and monochlorobenzene (7), and on ECD for chlorinated hydrocarbons and aromatic chlorinated hydrocarbons except monochlorobenzene (11–13 and 8–10). Fig. 4 shows chromatograms obtained with FID and ECD for tap water samples spiked with 10 ppb aromatic hydrocarbons and aromatic chlorinated hydrocarbons and 1 ppb chlorinated hydrocarbons. Measurements

of the target compounds by both detectors were scarcely affected by other compounds coexisting in the water such as trihalomethanes. The coefficients of variation (C.V.) ($n=4$) of aromatic hydrocarbons and aromatic chlorinated hydrocarbons were 3.4–5.6% at 20 ppb, 4.2–5.9% at 10 ppb, and 4.9–6.9% at 1 ppb with good reproducibility. Linearity of calibration curves was found for all these compounds in the above concentration ranges. The values of C.V. for chlorinated hydrocarbons showed satisfactory results with 4.4–5.1% at 1 ppb and 5.5–7.4% at 0.1 ppb.

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