

A Problem in the Determination of Trihalomethane by Headspace-Gas Chromatography/Mass Spectrometry

Yasuo Takahashi,^{*,a,b} Sukeo Onodera,^c Masatoshi Morita,^d and Yoshiyasu Terao^b

^aThe Tokyo Metropolitan Research Laboratory of Public Health, 3–24–1, Hyakunincho, Shinjuku-ku, Tokyo 169–0073, Japan, ^bGraduate School of Nutritional and Environmental Sciences, University of Shizuoka 52–1 Yada, Shizuoka 422–8526, Japan, ^cFaculty of Pharmaceutical Science, Science University of Tokyo, 12 Funagawara-machi, Ichigaya, Shinjuku-ku, Tokyo 162–0826, Japan, and ^dNational Institute for Environmental Studies, 16–2 Onogawa, Tsukuba-shi, Ibaraki 305–0053, Japan

(Received July 15, 2002; Accepted October 4, 2002)

The formation of trihalomethane (THM) from 37 organohalogen compounds, disinfection by-products, was measured by the headspace-gas chromatography/mass spectrometry (GC/MS) method. Among these 37 organohalogen compounds, 10, including trichloroacetones, trihaloacetone nitriles and trihaloacetic acids, produced THMs upon heating of aqueous solutions at 60°C for 30 min in a headspace sampler. The amounts and composition of THMs produced by heating depended on the position and number of the bound chlorine or bromine. In addition, the production of THMs from some of the organohalogen compounds upon heating was strongly affected by pH, temperature and heating duration. These results suggest that the headspace-GC/MS method overestimates the net concentration of THM due to positive errors.

Key words — trihalomethane, disinfection by-product, headspace-GC/MS method, trichloroacetone, trihaloacetone nitrile, trihaloacetic acid

INTRODUCTION

Chlorine has been used to treat water supplies since the beginning of the twentieth century, and this disinfection has markedly reduced the incidence of infectious diseases spread via water.¹⁾ However, in the mid-1970's, it was found that such treatment generates trihalomethanes (THMs),^{2,3)} and these by-products are closely related to carcinogenesis in humans and animals.^{4–8)} Among THMs, chloroform and bromodichloromethane have recently been classified as group 2B carcinogens by the International Cancer Research Institution.^{9,10)} Therefore, the trihalomethane content in the water supply is now the subject of attention and is often measured.¹¹⁾

The main methods used to quantify THMs are the purge and trap-gas chromatography/mass spectrometry (GC/MS) method, headspace-GC/MS method, headspace-electron capture detector/gas chromatography (headspace-GC/ECD) method and

hexane extraction-GC/ECD method. The first three of these methods¹²⁾ give positive errors in the quantification of THMs in drinking water derived from polluted rivers. In the headspace-GC/MS method, the major cause of such errors is thought to be heating and moisture.

In this study, we measured the formation of THM from 37 organohalogen compounds in aqueous solution upon heating, which simulated the headspace-GC/MS method, and investigated the effects of various experimental conditions on THM formation.

MATERIALS AND METHODS

Thirty-seven organohalogen compounds (Table 1), consisting of 9 haloacetic acids, 5 halopropionic acids, 8 haloacetone nitriles, 4 haloacetaldehydes, 6 haloacetones, 1 halonitromethane and 4 halophenols, were obtained from Hayashi Pure Pharmaceuticals Inc. (Osaka, Japan), Tokyo Kasei Inc. (Tokyo, Japan), Wako Pure Pharmaceuticals Inc. (Osaka, Japan) and Aldrich Inc. (Milwaukee, WI, U.S.A.). These compounds were dissolved in hexane or, if not dissolved, supplemented with metha-

To whom correspondence should be addressed: The Tokyo Metropolitan Research Laboratory of Public Health, 3–24–1, Hyakunincho, Shinjuku-ku, Tokyo 169–0073, Japan. Tel.: +81-3-3363-3231; Fax: +81-3-3368-4060; E-mail: yasuo@tokyo-eiken.go.jp

Table 1. Thirty-seven Organohalogen Compounds Investigated and THM Potential Formation in Neutral Solution upon Heating 60°C for 30 min

Chemical name	THM produced (mmol%)	Chemical name	THM produced (mmol%)
[Haloacetonitrile]		[Haloacetic acid]	
Chloroacetonitrile	0	Chloroacetic acid	0
Dichloroacetonitrile	0	Bromoacetic acid	0
Bromochloroacetonitrile	0	Dichloroacetic acid	0
Dibromoacetonitrile	0	Bromochloroacetic acid	0
Trichloroacetonitrile	0	Dibromoacetic acid	0
Bromodichloroacetonitrile	4	Trichloroacetic acid	2
Dibromochloroacetonitrile	2	Bromodichloroacetic acid	12
Tribromoacetonitrile	5	Dibromochloroacetic acid	21
[Haloacetone]		Tribromoacetic acid	100
Chloroacetone	0	[Halopropionic acid]	
Bromoacetone	0	α -Chloropropionic acid	0
1,1-Dichloroacetone	0	α -Bromopropionic acid	0
1,3-Dichloroacetone	0	β -Bromopropionic acid	0
1,1,1-Trichloroacetone	52	2,2-Dichloropropionic acid	0
1,1,3-Trichloroacetone	3	2,3-Dichloropropionic acid	0
[Halonitromethane]		[Halophenol]	
Chloropicrin	0	2,3,6-Trichlorophenol	0
[Haloacetaldehyde]		2,4,5-Trichlorophenol	0
Chloroacetaldehyde	0	2,4,6-Trichlorophenol	0
Dichloroacetaldehyde	0	2,4,6-Tribromophenol	0
Trichloroacetaldehyde	0		
Tribromoacetaldehyde	0		

THM: Trihalomethane

nol or methyl-t-butylether (MTBE) to prepare standard stock solutions (1000 mg/l). These solutions were diluted in methanol to make standard solutions (50 mg/l) every month. THM standard solution for the examination of water quality (Wako Pure Pharmaceuticals Inc.) was dissolved in methanol to prepare a standard solution (50 mg/l) every month. The standard stock solutions and standard solutions were stored in a freezer at -20°C .

Solutions and buffers for adjusting pH were prepared with pure grade reagents (Wako Pure Pharmaceuticals Inc.) as follows; 0.6 N hydrochloric acid for pH 1.0, 5.1 g/l potassium hydrogen phthalate for pH 4.0, 85 g/l potassium dihydrogenphosphate and 88.75 g/l disodium hydrogenphosphate for pH 6.9 and 1.9 g/l sodium tetraborate decahydrate for pH 9.2.

Methanol and hexane were of THM analysis grade (Wako Pure Pharmaceuticals Inc.) and MTBE was of HPLC analysis grade (Nacalai Tesque Inc. Kyoto, Japan).

Water purified by a Milli-RO/Milli-Q system (Nihon Millipore Inc., Tokyo, Japan) was boiled and cooled before use. Special grade sodium chloride

(Wako Pure Pharmaceuticals Inc.) was heated at about 450°C for 6 hr for the experiments.

Apparatus and Measurement Conditions — The equipment used included a GC (Type 5890-2, Hewlett Packard Inc., Tokyo, Japan), an MS (Type 5972, Hewlett Packard Inc.) and a headspace sampler (Type 7694, Hewlett Packard Inc.) (Table 2). THMs were quantified under the conditions shown in Table 2.

Quantification Methods — Three grams of sodium chloride, 10 ml buffer or 10 ml of 0.6 N hydrochloric acid, an indicated amount of organohalogen compound and a fixed amount of internal standard solution (4-bromofluorobenzene) were placed in a 22-ml vial which was then tightly closed. The vial was set in the headspace sampler adjusted to the indicated heating temperature for the indicated duration, and THMs were quantified by the headspace GC/MS method.

Table 2. Apparatus and Operational Conditions for GC/MS

HS sampler: HP7694(Hewlett Packerd)
Set point: Sample volume 10 ml, Loop volume 1 ml,
Oven temperature 40°C, Loop temperature 65°C, Transfer line temperature 100°C
Oven temperature 50°C, Loop temperature 100°C, Transfer line temperature 140°C
Oven temperature 60, 70, 80°C, Loop temperature 130°C, Transfer line temperature 140°C
Event time: Vial equilibration 3.8, 7.0, 15.0, 30.0, 45.0 min,
Pressure 10 psi, Pressurization time 0.5 min,
Loop fill time 0.01 min, Loop equilibration 0.05 min, Injection time 1.0 min
Gas chromatograph: HP5890-SeriesII (Hewlett Packerd)
Column: DB1301, 60 m long × 0.25 mm i.d., df = 0.25 μm
Oven temperature: 40°C(7 min)–5°C/min–180°C(0 min)–15°C/min–250°C(1 min)
Carrier gas: He 45 psi(1.0 min)–99 psi/min–15 psi(Constant flow)
Injection temperature: 200°C Injection system: Split(4 : 1) Interface temperature: 260°C
Mass spectrometer: HP5972 (Hewlett Packerd: quadropole type)
Ionsource temperature: 180°C Ionization energy: 70 eV
Monitor ion (<i>m/z</i>): Chloroform,Bromodichloromethane: 83,85 Dibromochloromethane: 129,127
Bromoform: 173,171 4-Bromofluorobenzene 174

RESULTS AND DISCUSSION

THM Formation from Organohalogen Compounds in Water upon Heating

The 37 organohalogen compounds shown in Table 1 are disinfection by-products using chlorine. Almost all of these organohalogen compounds are thought to be intermediates that eventually become THMs and dihaloacetic acids.¹³⁾ Neutral solutions (pH 6.9) of each of the 37 organohalogen compounds were prepared at a concentration of 300 ng/ml, and THMs produced by heating in the headspace sampler at a temperature of 60°C for 30 min were quantified by GC/MS. As shown in Table 1, THMs were detected from aqueous solutions of 10 of these 37 organohalogen compounds, including 2 trichloroacetones, 4 trihaloacetonitriles and 4 trihaloacetic acids.

THMs are likely produced by hydrolysis of 1,1,1-trichloroacetone and by decarboxylation of trihaloacetic acids. In the case of 1,1,3-trichloroacetone, chloroform may be produced via some chlorine migration, since no isomers were detected in a sample of 1,1,3-trichloroacetone by flame ionization detector/gas chromatography (GC/FID). The production of THMs from trihaloacetonitriles seems to occur by decarboxylation of the corresponding trihaloacetic acids formed by hydrolysis of the cyano group.

In the haloform reaction theory, trichloroacetaldehyde (chloral hydrate) is generated by the reaction between ethanol and chlorine, oxidation and

chlorination reaction, and then decomposed by hydrolysis to chloroform under basic conditions. However, Areguello¹⁴⁾ and Rook²⁾ did not detect chloroform originating from ethanol in the treatment of water with chlorine. This is likely due to the difficulty of hydrolysis of trichloroacetaldehyde to chloroform under neutral conditions. We also did not detect chloroform or bromoform in neutral solutions of trichloroacetaldehyde and tribromoacetaldehyde, respectively, by heating at 60°C for 30 min. However, under basic conditions, THMs were readily produced from trihaloacetaldehydes by hydrolysis, regardless of the heating temperature.

Effect of Experimental Conditions on THM Formation from Trichloroacetones, Trihaloacetonitriles and Trihaloacetic Acids

Aqueous solutions of the 10 organohalogen compounds from which THMs were produced were adjusted to pH 1.0 (strong acid), 4.0 (acid), 6.9 (neutral) or 9.2 (base). THMs produced by heating at different temperatures for different durations in the headspace sampler were quantified by GC/MS. The results for the 2 trichloroacetones, 4 trihaloacetonitriles and 4 trihaloacetic acids are shown in Figs. 1–3, respectively.

Figure 1 shows that the production of chloroform from 1,1,1-trichloroacetone was hardly affected by the heating temperature or duration tested in this study, but was markedly affected by the pH of the aqueous solutions used to prepare the samples. The amounts of chloroform produced under the basic

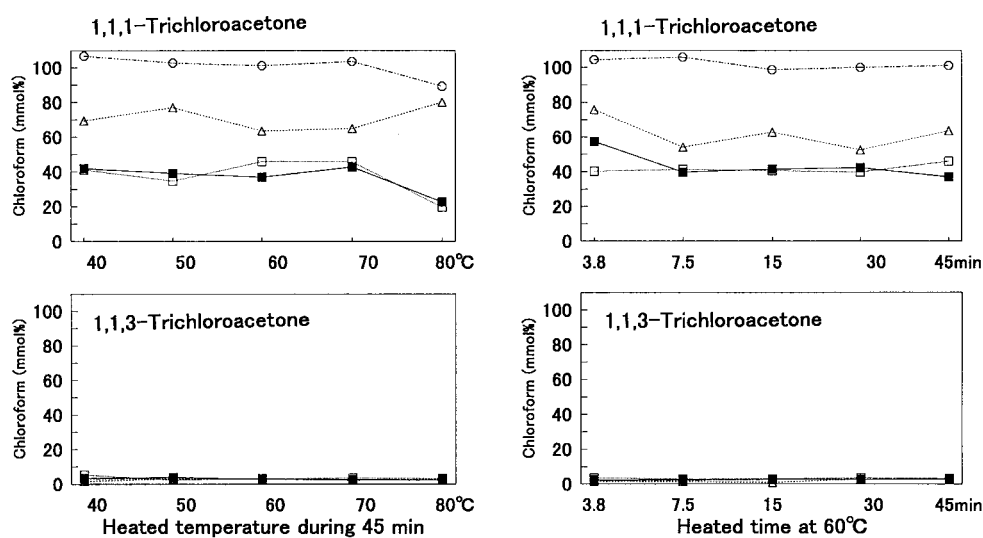


Fig. 1. Amount (mmol%) of Chloroform Produced from 1,1,1-Trichloroacetones and 1,1,3-Trichloroacetones in Aqueous Solution with Heating at Different Temperatures for Different Durations under Different pH Values

—■— String acid (pH 1.0), ----□---- Acid (pH 4.0), ----△---- Neutrality (pH 6.9), ----○---- Base (pH 9.2).

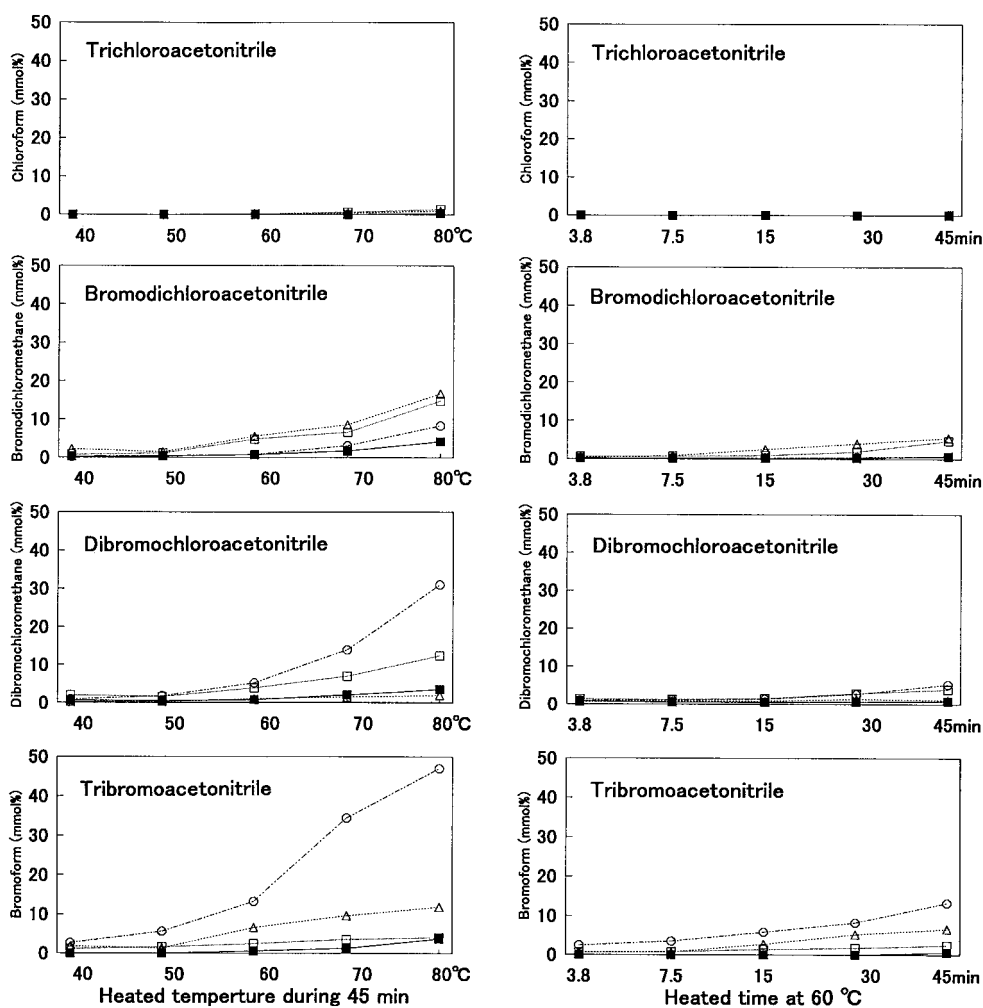


Fig. 2. Amounts (mmol%) of Trihalomethanes Produced from Trihaloacetonitriles in Aqueous Solution with Heating as Described in Fig. 1

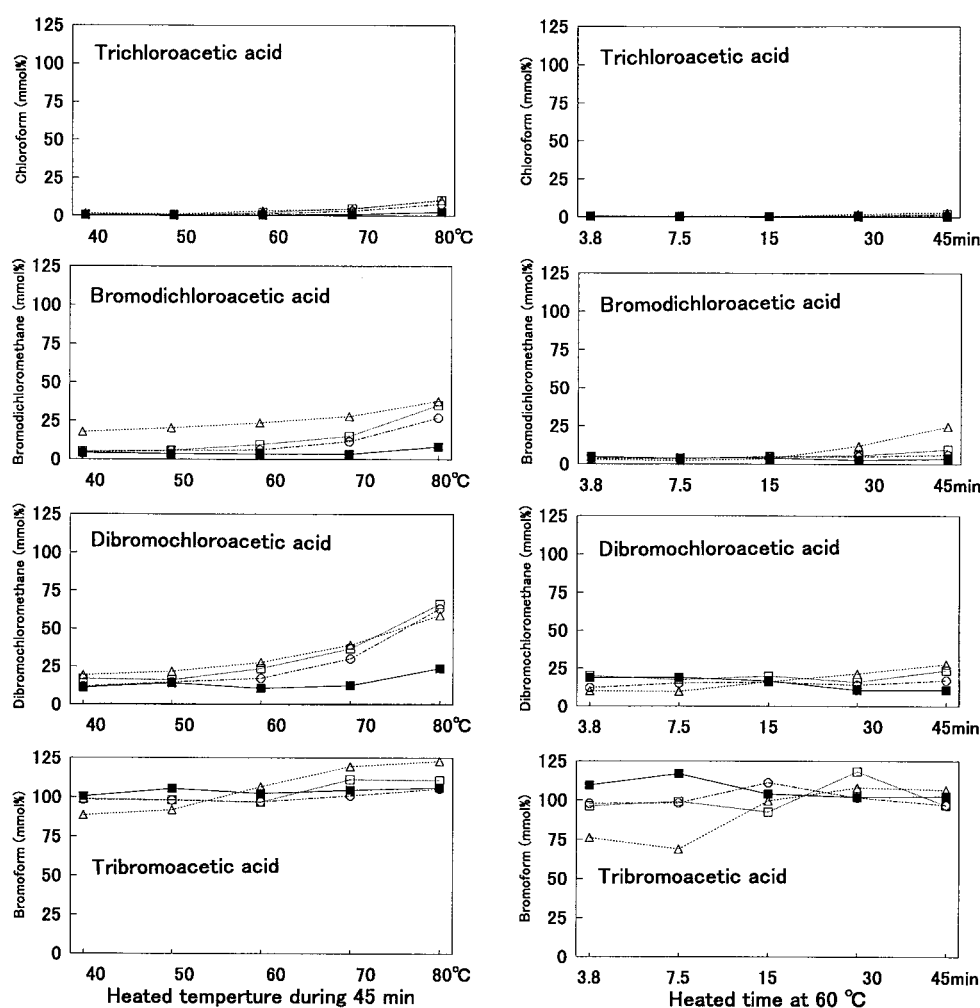


Fig. 3. Amounts (mmol%) of Trihalomethanes Produced from Trihaloacetic Acids in Aqueous Solution with Heating as Described in Fig. 1

condition was almost 100 mmol%, but this was reduced under the neutral condition, followed by the acidic and strongly acidic conditions. On the other hand, 1,1,3-trichloroacetone produced chloroform in about 3 mmol%, regardless of the heating temperature, duration time or pH tested in this study.

As shown in Fig. 2, the production of chloroform from trichloroacetonitrile was not detected under the various conditions tested. The production of THMs from trihaloacetonitriles containing bromines tended to increase with an increase in the heating temperature, especially at a temperature above 60°C, and with an increase in the number of bromines. Trihalomethane production was clearly pH-dependent in the case of dibromochloroacetonitrile and tribromoacetonitrile, which produced the greatest amount of THMs under the basic (pH 9.2) condition. The amount of bromoform produced from tribromoacetonitrile was about 50 mmol% under the

basic condition. The strongly acidic (pH 1.0) condition inhibited THM formation.

As shown in Fig. 3, the production of THMs from trihaloacetic acids with 0–2 bromines increased with an increase in the number of bromo substituents. Tribromoacetic acid produced bromoform in almost 100 mmol%, regardless of the pH. Since bromodichloroacetic acid and dibromochloroacetic acid contained other trihaloacetic acids as an impurity, THMs other than bromodichloromethane were formed in bromodichloroacetic acid solution, and accounted for less than 5 mmol% of the bromodichloromethane detected. Dibromochloroacetic acid also produced THMs other than dibromochloromethane, and accounted for less than 5 mmol% of dibromochloromethane detected.

The production of THMs from trihaloacetic acids by heating at 60°C was almost constant, regardless of the heating duration and pH. These results

Table 3. Comparison of Trihalomethane and Organohalogen Concentrations in Drinking Water Obtained by Headspace-GC/MS with Those Obtained by Hexane Extraction-GC/ECD

Chemical name	Concentration($\mu\text{g/l}$)	
	Headspace-GC/MS method	Hexane extraction-GC/ECD method
Chloroform	12.6 (11.5)	10.7
Bromodichloromethane	14.0 (12.9)	12.7
Dibromochloromethane	9.0 (8.4)	8.0
bromoform	2.0 (2.0)	1.0
Total trihalomethane	37.6 (34.8)	32.4
1,1,1-Trichloroacetone	—	1.7
1,1,3-Trichloroacetone	—	0.1
Trichloroacetonitrile	—	n.d.
Bromodichloroacetonitrile	—	n.d.
Dibromochloroacetonitrile	—	n.d.
Tribromoacetonitrile	—	n.d.
Trichloroacetic acid	—	9.2
Bromodichloroacetic acid	—	4.5
Dibromochloroacetic acid	—	2.7
Tribromoacetic acid	—	1.0

Drinking water Tap water sample collected from the Tokyo metropolitan reserach laboratory of public health in Oct. 25 1996. (Values in parentheses): The trihalomethanes values estimated on the basis of trihalomethane production during headspace-GC/MS measurement (heating at 60°C for 30 min) of strongly acidic solution of the organohalogen compounds are added to those in tap water determined by hexane extraction-GC/ECD method. —: Impossible determination.

suggest that trihaloacetic acids with 0–2 bromo substituents are easily decarboxylated with an increase in the heating temperature to become THMs. On the other hand, trihaloacetic acid with three bromines was easily decarboxylated, regardless of the heating temperature and duration and pH, and all of the tribromoacetic acid became bromoform.

Measurement of THMs by the Headspace-GC/MS Method

A typical procedure for measuring THMs by the headspace-GC/MS method,¹⁵⁾ which is the official method, is as follows. A 10 ml water sample is placed in a 22-ml vial, adjusted to pH2, and 3 g sodium chloride is added. The water sample is agitated in a headspace sampler-GC/MS at 60°C for 30 min, and THMs are quantified. Kajino *et al.*¹⁶⁾ indicated that the production of THMs from intermediate organohalogen compounds is suppressed by acidification of the water sample. However, as shown in Figs. 1–3, THMs were produced by 30 min of heating at 60°C under the strongly acidic condition.

We examined halogenated disinfection by-products^{17,18)} in water samples collected from a water service pipe in the Tokyo metropolitan area by a multi-component systematic analytic method,¹⁹⁾ which is a kind of hexane extraction-GC/ECD method that we developed. Table 3 shows that sev-

eral organohalogen compounds other than THMs were detected in the water supply by the hexane extraction-method. However, with the headspace-GC/MS method, such compounds were not detected but the concentration of THMs was overestimated because of positive errors due to THMs produced in the analytical procedures. Furthermore, there may be more organohalogen compounds that cause positive errors than those tested in this study. Therefore, the headspace-GC/MS and -GC/ECD methods are inappropriate for the official measurement of THMs.

In conclusion of this study, we examined the formation of THMs by heating aqueous solutions containing 37 organohalogen compounds as by-products of halogen disinfection, and observed the generation of THMs from trichloroacetone, trihaloacetonitriles and trihaloacetic acids. These organohalogen compounds can be detected in water supplies and in swimming pool water after chlorine treatment. When THMs in such water samples are quantified by the headspace-GC/MS or -GC/ECD method, the concentration of THMs must be overestimated. This was actually demonstrated in an analysis of tap water in Tokyo.

Based on these considerations, we recommend the following hexane extraction-GC/ECD method for the measurement of THMs: After residual chlorine is removed, water samples are weakly acidi-

fied, and hexane extraction with 3 min of agitation is performed 2 times. The hexane extracts are combined and dehydrated, and subjected to GC/ECD for quantification of THMs.

REFERENCES

- 1) Ellis, K. V. (1991) Water disinfection: A review with some consideration of the requirements of the third world. *Environ. Control.*, **20**, 341–407.
- 2) Rook, J. J. (1974) Formation of haloforms during chlorination of natural water. *Water Treat. Exam.*, **23**, 234–243.
- 3) Beller, T. A., Lichtenberg, J. J. and Kromer, R. C. (1974) The occurrence of organohalide in chlorinated drinking water. *J.A.W.W.A.*, **66**, 703–711.
- 4) National Cancer Inst. (1976) Report on carcinogenesis bioassay of chlorination. *Bethesda, Md.*
- 5) Federal Register, FDA. (1976) *Chloroform as an ingredient of human food and cosmetic products.*
- 6) Cotrubo, J. A. (1980) THMs in drinking water. *Environ. Sci. Technol.*, **15**, 268–274.
- 7) Bull, R. J. (1981) Health effects of drinking water disinfectants and disinfection by-products. *Environ. Sci. Technol.*, **16**, 554a–559a.
- 8) Onodera, S. (1991) Characterization and determination of organic compounds in the mutagenic XAD-2 extracts of drinking water. *J. Chromatogr.*, **557**, 413–427.
- 9) International Agency for Research on Cancer (1987) Overall evaluations of carcinogenicity: an updating of IARC Monographs volumes 1–42. In *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Suppl. 7*, Lyon, pp. 152–154.
- 10) International Agency for Research on Cancer (1991) Chlorinated drinking-water; Chlorination by-products; some other halogenated compounds; cobalt and cobalt compounds. In *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 52*, Lyon, pp. 45–359.
- 11) Krasner, S. W. and McGuire, M. J., et al. (1989) The Occurrence of disinfection by-products in US drinking water. *J.A.W.W.A.*, **81**, 41–53.
- 12) Takahashi, Y., Nakagawa, J., Hosokawa, N. and Morita, M. (1996) Concentration of total trihalomethane in tap water as determined by official and other methods. *J. Environ. Chem.*, **6**, 357–362.
- 13) Takahashi, Y. and Morita, M. (1998) Change in the concentrations and compositions of halogenated disinfection by-products in tap water during heating. *J. Environ. Chem.*, **8**, 465–472.
- 14) Argullo, M. D., Chriswell, C. D., Fritz, J. S., Kissininger, L. D., Lee, K. W., Richard, J. J. and Svec, H. J. (1979) Trihalomethanes in water: A report on the occurrence, seasonal variation in concentration and precursors of trihalomethane. *J.A.W.W.A.*, **71**, 504–508.
- 15) Japan Water Works Association (1993) *Standard method for the examination of water (Volatile compounds)*. Tokyo, pp. 357–374.
- 16) Kajino, M. and Ashitani, K. (1981) Determination of trihalomethane in water supplies by headspace gas chromatography method. *J. Water and Waste*, **23**, 43–51.
- 17) Takahashi, Y. and Morita, M. (1998) Halogenated disinfection by-products in tap water. *J. Environ. Chem.*, **8**, 455–464.
- 18) Takahashi, Y. and Morita, M. (1999) Halogenated disinfection by-products in raw and tap water collected from some areas. *J. Environ. Chem.*, **9**, 685–693.
- 19) Takahashi, Y. and Morita, M. (1997) Simultaneous determination of halogenated chlorination disinfection by-products in water supply. *J. Environ. Chem.*, **7**, 495–506.