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Gas chromatographic–mass spectrometric determination of halogenated acetic acids in water after direct derivatization

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ABSTRACT

A previously developed difluoroanilide derivatization method was used for the determination of trace levels of halogenated acetic acids (HAAs), including bromoacetic acids, in water. The derivatives formed by the reaction were separated with a gas chromatograph–mass spectrometer equipped with a fused-silica capillary column and detected by selected ion monitoring. Five acids (chloro- and bromoacetic acids) in water could be determined at $\mu g\ l^{-1}$ levels. The recoveries for 10 $\mu g\ l^{-1}$ of analyte in natural waters (lake and sea waters) were greater than 85%. However, under the conditions used, tribromoacetic acid could be determined only at higher concentration levels. The proposed method was successfully used to determine concentrations of HAAs in a range of natural waters. HAA formation from raw river water was investigated by laboratory chlorination experiments.

INTRODUCTION

Dissolved organic compounds such as humic substances are known to form halogenated acetic acids (HAAs) in natural waters, especially chloroacetic acids (CAAs), by reaction with chlorine [1–4]. Among the chlorination products in drinking water, attention has been focused almost exclusively on volatile chlorinated organic compounds, particularly trihalomethanes (THMs) [1,5]. However, there has been an increased awareness that CAAs may represent potential hazards. CAAs seem to be the principal fraction of non-volatile chlorinated organic compounds in drinking water [2–4], with several researchers reporting concentrations of trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA) up to 160 $\mu g\ l^{-1}$ [6–11]. In Japan, both DCAA and TCAA have been found in drinking water at concentrations up to 35 $\mu g\ l^{-1}$ [12]. Specific regulation may be needed to control the formation of these chlorination by-products formed during disinfection of drinking water [13].

Previously, a novel but simple difluoroanilide derivatization method was developed for trace amounts of CAAs in water [14]. The CAA derivatives formed by a reaction with dicyclohexylcarbodiimide (DCC) and 2,4-difluoroaniline (DFA) were separated and determined by gas chromatography with electron-capture detection (GC–ECD). This method permits the CAAs in water to be converted into the derivatives suitable for GC analysis and extracted into an organic phase in one step. In practice, this method is convenient for the detection and determination of CAAs in tap water and wastewater after disinfection. However, the use of packed GC columns has limitations with respect to the separation of the derivatives.

In this work, the direct derivatization method was applied to bromoacetic acids (BAAs), which are expected to be formed during water chlorina-

tion in the presence of bromide ion [7,11]. A gas chromatographic–mass spectrometric (GC–MS) system fitted with a capillary column was used to separate the difluoroanilide derivatives of HAAs (CAAs and BAAs) and detect them selectively. This method was employed for tap water analysis, and laboratory chlorination experiments were conducted to investigate the formation of HAAs in the surface water of rivers.

EXPERIMENTAL

Apparatus

The system and operating conditions were as follows: gas chromatograph–mass spectrometer, JEOL JMS-AX505W; fused-silica capillary columns (J & W Scientific), DB-17 (15 m × 0.53 mm I.D., film thickness 1.0 μm) and DB-5 (15 m × 0.53 mm I.D., film thickness 1.5 μm); temperature programme, initially 100°C for 2 min, then increased at 8°C min^{-1} to a final temperature of 200°C; injection port temperature, 220°C; separator temperature, 230°C; ion source temperature, 260°C; ionization current, 0.3 mA; ionization voltage, 70 eV; and carrier gas, helium at a flow-rate of 20 ml min^{-1}. Aliquots of 2 μl of sample solution were introduced directly into the column.

A Shimadzu GC-6A gas chromatograph equipped with a ^{63}Ni electron-capture detector was used for the determination of THMs. A glass column (3 m × 3 mm I.D.) packed with 20% silicone DC-550 on Uniport HP was fitted. The column oven temperature was 90°C, the injection port temperature was 150°C and the carrier gas was nitrogen at a flow-rate of 30 ml min^{-1}. Aliquots of 5 μl of sample solution were introduced.

Reagents

DFA and DCC were used as 1 *M* solutions in ethyl acetate, as described previously [14]. Monochloroacetic acid (MCAA), DCAA and TCAA primary standards were prepared in distilled water at concentrations of 1000 μg ml^{-1} and stored in a refrigerator prior to use after appropriate dilution. Monobromoacetic acid (MBAA) and tribromoacetic acid (TBAA) were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). Dibromoacetic acid (DBAA) was obtained from Aldrich (Milwaukee, WI, USA). MBAA and DBAA primary standards were prepared and used as aqueous solutions in the same manner as the CAAs. Aqueous TBAA standards (1000 μg ml^{-1}) were used immediately after dilution and were not stored. A mixed standard solution of six HAAs was prepared from each standard solution (1000 μg ml^{-1}). [$^2H_8$]Naphthalene obtained from Cambridge Isotope Laboratories (Woburn, MA, USA) was dissolved in *n*-hexane. All organic solvents were of a suitable grade for pesticide residue analysis. Other reagents were of analytical-reagent grade.

Procedure

HAAs were derivatized as described previously [14]. Briefly, 1 g of sodium chloride and 0.4 ml of 10 *M* hydrochloric acid were added to a 50-ml water sample. After adding 0.4 ml of 1 *M* DFA solution and 0.4 ml of 1 *M* DCC solution, the mixture was vigorously shaken with 15 ml of ethyl acetate for 40 min. Following the addition of 5 g of sodium chloride, the aqueous layer was separated and then extracted with 5 ml of ethyl acetate. The combined organic layer was successively washed with 5 ml of 3 *M* hydrochloric acid, saturated sodium hydrogencarbonate solution and saturated sodium chloride solution and then dried over anhydrous sodium sulphate. The solution was concentrated to 10 ml and subjected to instrumental analysis.

A 50-μl volume of [$^2H_8$]naphthalene solution (2 μg ml^{-1}) was added as an internal standard to 2 ml of the sample solution and aliquots of this solution were injected into the GC–MS system. Quantification was by comparison of the sample peak area with that of the internal standard. For calibration, 0.05–10-μg amounts of each halogenated acid were added to 50 ml of distilled water with the mixed standard solution of six HAAs and the samples were subjected to the derivatization procedure.

Laboratory chlorination experiment

Surface water samples were collected during January 1991 from five rivers (A, B, C, D and E) flowing through the city of Nagano. The samples were vacuum filtered through glass-fibre filter

paper (Whatman GF/C). The formation of HAAs and THMs in these filtrates following chlorination in the laboratory without pH adjustment was investigated.

Sodium hypochlorite solution was added to 1 l of each of two filtered river water samples (from A and B) at an initial free chlorine concentration of 10 mg l^{-1} and kept in sealed bottles in darkness at 20°C. Sodium sulphite (to quench the chlorine residue in samples) was added to 50-ml water samples taken periodically from the bottles to follow the kinetics of CAA formation.

The formation of these compounds was also studied in eight surface water samples collected from the five rivers (A, B1, B2, C1, C2, D, E1 and E2). There were two sampling stations in rivers B, C and E, as indicated by the numbers 1 (upper) and 2 (lower). In each instance, the lower sampling station was several kilometres downstream from the upper one. Sample waters were chlorinated for 24 h at an initial free chlorine concentration of 5 mg l^{-1} under the same conditions as described above. HAA concentrations were measured according to the procedure outlined above. THM concentrations were measured by *n*-hexane extraction and GC–ECD [15]. Residual chlorine in the treated water was measured by the N,N-diethyl-*p*-phenylenediamine (DPD) method with a comparator [16].

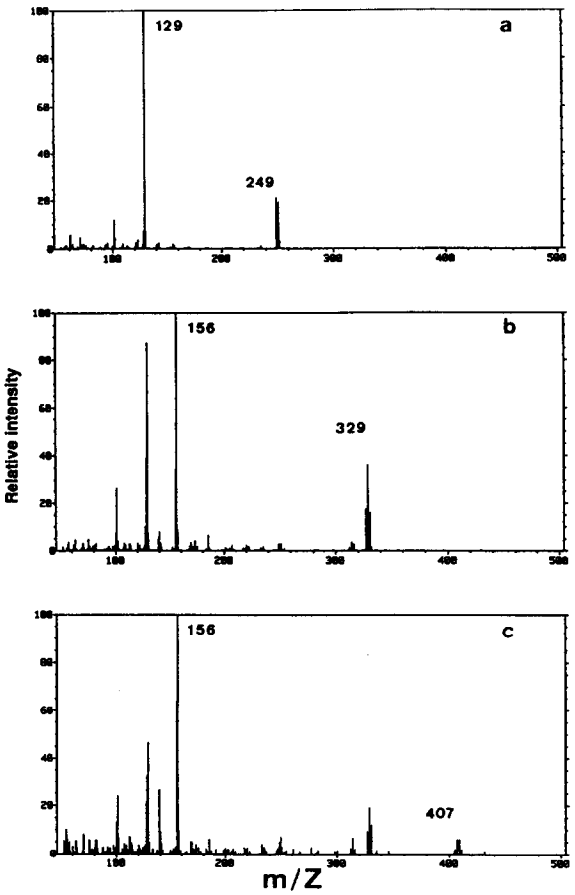

Fig. 1. EI mass spectra of the difuoroanilide derivatives of BAAs. (a) MBAA derivative (MBA-DFA); (b) DBAA derivative (DBA-DFA); (c) TBAA derivative (TBA-DFA).

RESULTS AND DISCUSSION

Difluoroanilide derivatization of BAAs

The difluoroanilide derivatization method which was developed for CAA determination was tested here for its application to other HAAs. Aqueous solutions of BAAs produced derivatives when subjected to the same reaction conditions as applied to CAAs. Electron impact (EI) ionization mass spectra were measured for the products of the difluoroanilide derivatization of each of the BAAs (MBAA, DBAA and TBAA) (Fig. 1). Molecular ion peaks were observed at *m/z* 249, 327 and 405 for MBAA, DBAA and TBAA, respectively, which confirmed the formation of the difluoroanilide derivatives, 2,4-difluoromonobromoacetanilide (MBA-DFA), 2,4-difluorodibromoacetanilide (DBA-DFA) and 2,4-difluorotribromoacetanilide (TBA-DFA).

The MBAA derivative had a base peak at *m/z* 129, corresponding to a fragment ion $[M-76]^+$, which can be explained by the elimination of ketene from the rearranged molecular ion M^+. The derivatives of DBAA and TBAA, which possess two or more bromine atoms per molecule, exhibited base peaks at *m/z* 156, corresponding to a fragment ion $[CONH-C_6H_3F_2]^+$ which can be explained by cleavage of the carbon–carbon bond of the acetyl group. These base peaks for the derivatives of BAAs (from MBAA to TBAA) are similar to those observed for the CAA derivatives (from MCAA to TCAA). For the MCAA, DCAA and TCAA

derivatives, base peaks were observed at m/z 129, 156 and 156, respectively [14].

Separation and detection of HAA derivatives

In the previous study, difluoroanilide derivatives of CAAs were separated on packed columns with the stationary phases DEGS + H_3PO_4 and/or Apiezon grease L + H_3PO_4 [14]. In this study, fused-silica capillary columns with bonded stationary phases of slight polarity (5% diphenyl–95% dimethylpolysiloxane phase), DB-5, and of intermediate polarity (50% phenyl–50% methylpolysiloxane phase, equivalent to OV-17), DB-17, were tested for the separation of the HAA derivatives. Slight tailing of the chromatographic peaks was observed on both columns, especially for monohalogenated acetic acid derivatives. However, the intermediate polarity stationary phase yielded cleaner peak shapes.

With increasing number of chlorine and bromine atoms in an HAA molecule, the retention times of the corresponding CAA and BAA derivatives were prolonged (Table I). Monitoring ions for detection of the CAA [14] and BAA derivatives by selected ion monitoring (SIM) were chosen from the mass spectra (Fig. 2 is a typical SIM chromatogram obtained from a mixed standard solution of six HAAs at 200 μg l^{-1} each). The molecular ion peaks at m/z 205 and 249 or the fragment ion peak at m/z 129

TABLE I

COLUMN RETENTION OF THE DIFLUOROANILIDE DERIVATIVES OF HAAs

Acid	Relative retention time[a]	
	DB-5	DB-17
MCAA	1.00	1.00
DCAA	1.19	1.16
TCAA	1.40	1.34
MBAA	1.26	1.32
DBAA	1.66	1.74
TBAA	2.13	2.28

[a] Relative retention times were calculated on the basis of the retention time of the MCAA derivative on each column (15 m × 0.53 mm I.D.).

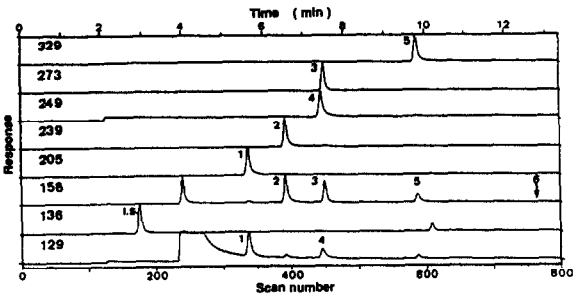

Fig. 2. SIM chromatogram of the difluoroanilide derivatives of HAAs obtained from a standard solution (200 μg l^{-1} of each acid). Peaks: 1 = MCAA; 2 = DCAA; 3 = TCAA; 4 = MBAA; 5 = DBAA; 6 = TBAA; I.S. = [$^2H_8$]naphthalene (internal standard).

were monitored for the MCAA and MBAA derivatives, respectively. The DCAA, TCAA, DBAA and TBAA derivatives were monitored by the fragment ion peak at m/z 156. HAA calibration graphs were prepared by normalizing the area of the ion peaks to the area of the molecular ion peak of the internal standard. Good linearity was shown by both the CAA derivatives over the range examined and by the MBAA and DBAA derivatives at concentrations of several μg l^{-1}. However, the TBAA derivative gave no peak at such low concentration levels. The detection limits of MCAA, DCAA, TCAA, MBAA and DBAA were 0.5, 0.5, 0.5, 2 and 1 μg l^{-1}, respectively, in a 50-ml water sample. TBAA could be detected only at concentrations higher than *ca.* 100 μg l^{-1} under these conditions. Monitoring at m/z 156 was of interest for the detection of HAAs with two or more halogen atoms, as mentioned above. Five HAA derivatives eluted with retention times from 5.5 to 10 min and the TBAA derivative eluted at 12.8 min (Fig. 2).

Stability of derivatives

A mixed standard solution of six acids (20 μg l^{-1} each) was derivatized and stored in a glass tube under various conditions to compare their stabilities (expressed as a percentage of the concentration remaining in an identical solution stored in darkness at 4°C) (Table II). TBAA could not be detected at the concentrations tested in this experiment and no data were obtained for it.

TABLE II

STABILITY OF THE HAA DIFLUOROANILIDE DERIVATIVES

Percentage of the concentrations measured in a standard solution stored in darkness at 4°C.

Acid	Darkness[a] (48 h)	Fluorescent lamp[a] (24 h)	Sunlight[a] (3 h)
MCAA	105	104	91
DCAA	101	90	83
TCAA	97	82	68
MBAA	86	80	90
DBAA	93	69	54
TBAA	–	–	–

[a] The derivatives were kept in darkness at 20°C for 48 h.
[b] At 20°C under 2000 lx illumination provided by a white fluorescent lamp for 24 h.
[c] Outdoors in direct sunlight for 3 h.

The other five HAA derivatives were stable in darkness at 20°C, but exposure to light diminished their peak area even at a constant temperature. When the analytical solution was allowed to stand for 1 day exposed to the light from a fluorescent lamp, most of the derivatives were reduced to 70–90% of the original concentrations. Exposure to direct sunlight reduced all the derivatives to 50–90% of the original concentrations after only 3 h.

The halogen atoms in HAAs appeared to affect the stability of the HAA derivatives. Acids with an increasing number of halogen atoms tended to form derivatives of lower stability. BAA derivatives were less stable than CAA derivatives in light. The analytical solution should be protected from light as much as practical and, if stored, it should be kept in a refrigerator.

Recovery experiments and tap water analysis

Six acids were added to lake and sea water samples at a concentration of 10 $\mu g\ l^{-1}$. The concentrations of these acids were then determined according to the procedures described above. In the analysis of sea water, the initial addition of sodium chloride to the sample water was omitted. Five HAAs showed recoveries of greater than 85% in both lake and sea water (Table III). Apparently inorganic salts other than sodium chloride in sea water exert hardly any influence on the derivatization reaction.

Drinking water was collected in winter in Nagano city at a water supply services tap. Residual chlorine in that sample was decomposed with sodium sulphite. DCAA and TCAA were detected in drinking water at concentrations of 4.5 and 7.5 $\mu g\ l^{-1}$, respectively (Fig. 3). MCAA was measured at 0.8 $\mu g\ l^{-1}$. However, no BAAs were detected.

TABLE III

RECOVERY OF HAAs FROM SPIKED NATURAL WATER

Lake water and sea water stored at 4°C were spiked with HAAs and analysed ($n = 3$).

Acid	Concentration ($\mu g\ l^{-1}$)	Lake water		Sea water		Monitored ion (m/z)
		Average recovery (%)	R.S.D. (%)	Average recovery (%)	R.S.D. (%)	
MCAA	10	95	1.5	97	4.1	129
DCAA	10	99	0.7	102	1.6	156
TCAA	10	96	1.9	103	2.5	156
MBAA	10	87	6.6	86	4.0	129
DBAA	10	104	1.8	92	1.5	156
TBAA	10	–	–	–	–	156

Laboratory chlorination experiments

The time course of CAA formation by chlorination was followed in river water from sampling sites A and B (Fig. 4). Immediately after sodium hypochlorite had been added to filtered river water, the CAA concentrations increased rapidly. The formation rate slowed after about 6 h. However, the concentrations of CAAs were still increasing even 1–2 days after chlorination. The two different river water samples showed similar time courses of CAA formation. The ratio of DCAA to TCAA was almost constant (*ca.* 1:2) and was independent of reaction time. This ratio (DCAA/TCAA) has been reported to be dependent on the chlorine-to-carbon ratio, that is, relatively large amounts of DCAA were formed in comparison with TCAA during chlorination under low chlorine-to-carbon ratio conditions [3]. For this experiment, the observed DCAA/TCAA ratio is consistent with a high chlorine-to-carbon ratio during chlorination.

The potential formation of HAAs in different river waters was compared by measuring the HAA concentrations after a given period following chlorination (Table IV). After 24 h, the residual chlorine concentrations were not less than 10% of the initial concentration (5 mg l^{-1}). CAA formation totalled 2.9–11 μg l^{-1} for DCAA and 4.5–25 μg l^{-1} for TCAA. MCAA formation was considerably less, below 1 μg l^{-1}. DBAA was undetected except for one river water sample collected from site C2 (discussed below). In the rivers from which both upstream and downstream samples were collected, CAA formation tended to increase longitudinally downstream.

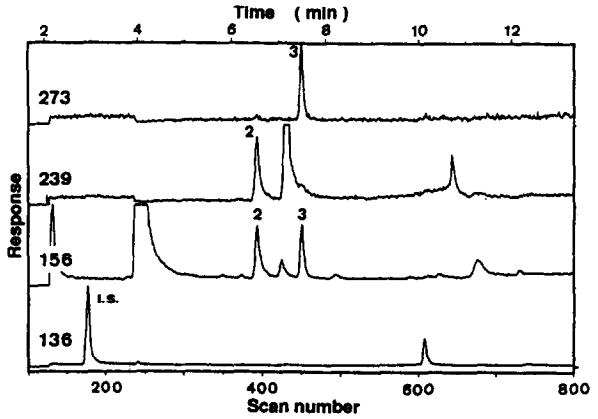

Fig. 3. SIM chromatogram for tap water. Peak numbers as in Fig. 2.

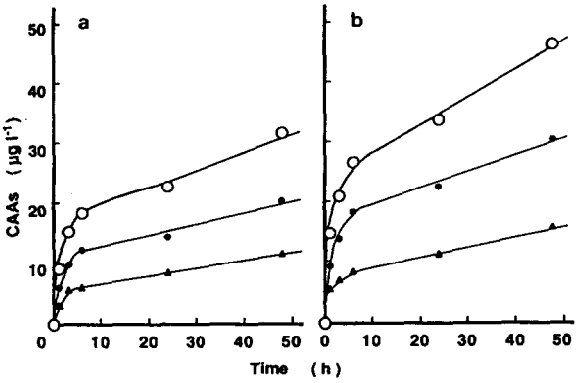

Fig. 4. Formation of CAAs as a function of reaction time from filtered river water samples collected at (a) site A and (b) site B. ● = TCAA; ▲ = DCAA; ○ = total CAAs. The pH values of the river samples were 7.3 and 7.4 at sites A and B, respectively. Reaction conditions: 10 mg l^{-1} chlorine dose; in darkness at 20°C. Residual free chlorine concentrations after treatment for 48 h were (a) 1.8 and (b) 2.8 mg l^{-1}.

River water with high THM formation rates also had high HAA formation rates. There was a strong correlation between chloroform formation and total CAA formation (MCAA + DCAA + TCAA) represented by the equation [total CAAs] = 1.2[chloroform] −1.1 (units = μg l^{-1}, $r^2 = 0.949$; Fig. 5). The correlation between major components of total CAAs and chloroform was also high, *e.g.*, [TCAA] = 0.87[chloroform] −2.4 (μg l^{-1}, $r^2 = 0.936$) and [DCAA] = 0.31[chloroform] +0.64 (μg l^{-1}, $r^2 = 0.970$).

HAAs were not detected in the raw river water before treatment but were detected after treatment. Among BAAs, DBAA formation was found (at trace levels) only in the sample from station C2 (Fig. 6). Unlike all the other river samples, bromine-substituted THMs dominated total THM formation (31 μg l^{-1}) at site C2. During water chlorination in the presence of bromide ions, chloroform formation is suppressed and there is a shift towards the forma-

TABLE IV

LABORATORY CHLORINATION OF RIVER WATER

Chlorination conditions: 5 mg l^{-1} chlorine dose; in darkness at 20°C for 24 h.

Sampling station[a]	pH	Residual free chlorine (mg l^{-1})	HAAs ($\mu g\ l^{-1}$)					THMs ($\mu g\ l^{-1}$)[b]			
			MCAA	DCAA	TCAA	MBAA	DBAA	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
A	7.1	2.8	N.D.[c]	4.1	7.2	N.D.	N.D.	11	4.8	1.9	N.D.
B1	7.8	3.9	N.D.	9.6	24	N.D.	N.D.	30	4.0	0.4	N.D.
B2	8.4	3.3	N.D.	11	25	N.D.	N.D.	32	5.5	0.8	N.D.
C1	7.5	4.2	N.D.	2.9	4.5	N.D.	N.D.	8.8	5.7	3.3	N.D.
C2	7.4	2.4	0.7	3.3	6.5	N.D.	Trace	8.0	10	10	2.8
D	7.9	3.9	N.D.	8.2	21	N.D.	N.D.	25	6.8	1.4	N.D.
E1	8.9	3.2	0.9	5.6	7.7	N.D.	N.D.	17	7.5	3.4	N.D.
E2	8.1	0.6	0.7	7.0	14	N.D.	N.D.	17	8.6	3.9	N.D.

[a] 1 and 2 indicate the upstream and downstream sampling stations in each river, respectively.
[b] Detection limits of THMs: chloroform = 0.5 $\mu g\ l^{-1}$; bromodichloromethane = 0.1 $\mu g\ l^{-1}$; dibromochloromethane = 0.2 $\mu g\ l^{-1}$; bromoform = 1 $\mu g\ l^{-1}$.
[c] N.D. = Not detected.

tion of brominated THMs [17–19]. Non-volatile brominated organic compounds are also produced under such conditions [20], and these might include BAAs. It can therefore be assumed that there was a comparatively high concentration of bromide ions in the river water at site C2 before treatment. DBAA has been found to be the most prominent HAA in Dutch drinking waters prepared from surface waters [11].

In conclusion, the difluoroanilide derivatization method is applicable to BAAs. Five HAAs (except TBAA) were determined by GC–MS at the $\mu g\ l^{-1}$ level and good recoveries from natural waters were obtained in the recovery

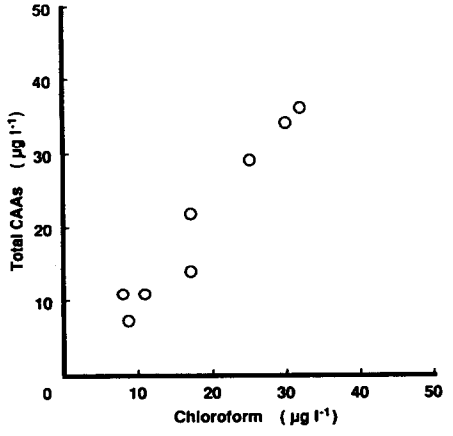

Fig. 5. Relationship between the formation of chloroform and total CAAs in filtered river water samples. Reaction conditions: 5 mg l^{-1} chlorine dose; in darkness at 20°C for 24 h.

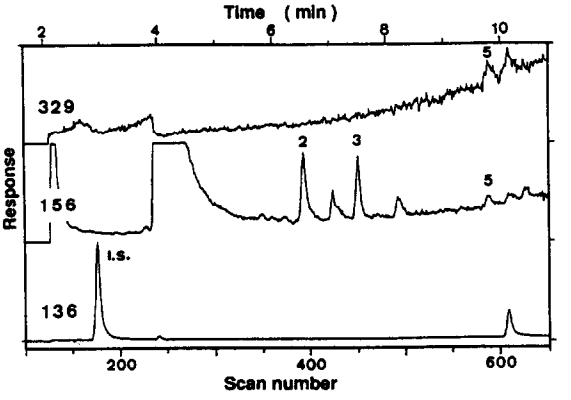

Fig. 6. SIM chromatogram obtained from the chlorinated surface water collected at site C2. Peak numbers as in Fig. 2.

experiments. The proposed method is useful for the simple determination of HAAs in water. However, the problem of the very high detection limit of TBAA remains to be solved.

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