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SIMULTANEOUS DETERMINATION OF TRACE AMOUNTS OF BROMIDE AND IODIDE BY METHYLATION WITH DIMETHYL SULPHATE AND ELECTRON-CAPTURE GAS CHROMATOGRAPHY

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SUMMARY

A specific and sensitive gas chromatographic method is described for the simultaneous determination of trace quantities of bromide and iodide. Bromide and iodide are methylated with dimethyl sulphate at 70°C to form methyl bromide and methyl iodide, respectively. The resulting methyl derivatives are simultaneously determined by gas chromatography with electron-capture detection. The detection limits are 0.1 μg/ml bromide and 0.5 ng/ml iodide. The interferences of several anions were investigated. The application of the method to the determination of bromide and iodide in spring-water is demonstrated. The results reveal that the recoveries are over 90% for both halides.

INTRODUCTION

Inorganic halide anions (*i.e.*, chloride, bromide, iodide, etc.) play important rôles in biological and environmental sciences. Therefore, their determination is very important, and various methods have been reported. Of these methods, several based on colorimetry[1] and ion-selective electrodes[2] have often been used. Each of these methods can be used for the determination of only one of the halide anions, but none can be used for the simultaneous determination of different halide anions. Recently, several techniques for the simultaneous determination of organic and inorganic anions by high-performance liquid chromatography have been published[3–9]. "Ion chromatography" developed by Small and co-workers[3–5] is very effective for the simultaneous determination of halide anions.

On the other hand, several gas chromatographic (GC) techniques have been reported for the determination of halide anions[10–14]. These methods are based on derivatization of halide anions to organic compounds detectable by GC. However, only one such method, developed by Stephen and co-workers[10,11], has been applied

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to the simultaneous determination of different halide anions. The method is based on the reaction of halide anions with trifluoromethylmercury(II) nitrate[10] or phenylmercury(II) nitrate[11] to form the corresponding organic mercury(II) halides which are subsequently determined by GC. Recently, we reported a new method to determine inorganic anions by flame-ionization GC[15,16]. The method is based on methylation or ethylation of the inorganic anions with reagents such as dimethyl or diethyl sulphate, methyl or ethyl *p*-toluenesulphonate and trimethyl or triethyl phosphate.

In this work, we have adapted the method to the simultaneous determination of trace quantities of bromide and iodide by using an electron-capture detector (ECD). In the previous studies[15,16], we reported that dimethyl sulphate is the most suitable reagent for the derivatization of bromide, whereas diethyl sulphate is the most suited for that of iodide. In this work, however, both bromide and iodide were methylated with dimethyl sulphate in order to determine them simultaneously.

EXPERIMENTAL

Apparatus

A Shimadzu (Kyoto, Japan) GC-4BM gas chromatograph equipped with a ^{63}Ni ECD was used. A stainless-steel column (1 m × 3 mm I.D.) was packed with Porapak P (80–100 mesh). Nitrogen was used as the carrier gas at a constant flow-rate of 50 ml min. The detector, injection port and column temperatures were maintained at 250, 250 and 125°C, respectively. The peak areas were measured by a digital integrator (Shimadzu Chromatopac EIA).

Materials

Dimethyl sulphate was a commercial grade reagent purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Benzene, a special grade reagent for liquid chromatography, was obtained from Wako (Osaka, Japan). Deionized water was distilled before use. All other reagents were of analytical reagent grade. The column packing material, Porapak P, was obtained from Waters Assoc. (Milford, MA, U.S.A.).

Procedure

The recommended procedure for the simultaneous determination of bromide and iodide at trace levels (below 25 μg/ml for Br^- and 0.1 μg/ml for I^-) was as follows. Dimethyl sulphate (0.05 ml) was added to a 1.0-ml aliquot of neutral aqueous sample in a reaction vessel (ca. 10 ml) with a glass stopper. The vessel used was brown to protect the contents from the light. It was sealed tightly with the stopper and shaken mechanically for 20 min in an incubator at 70°C. After cooling the reaction solution in an ice-bath, 1.0 ml of benzene was added. Then the derivatized methyl bromide and methyl iodide were extracted by shaking the vessel for 10 min at room temperature (18°C), and the organic layer was separated from the aqueous layer. An aliquot of the organic layer (0.3 μl) was injected into the gas chromatograph equipped with an ECD. In the case of the analysis of basic or acidic samples, a neutralization step is necessary before analysis.

When a sample contained bromate (BrO_3^-) and iodate (IO_3^-) ions, these species were reduced to bromide and iodide by sodium thiosulphate as follows. A 0.10-ml volume of sodium thiosulphate ($5.0 \cdot 10^{-2}$ *M*) was added to the sample (1.0 ml) in the reaction vessel, and allowed to stand for a few minutes at room temperature (18°C). The methylation and GC measurements were performed as described above, and total bromine ($Br^- + BrO_3^-$) and total iodine ($I^- + IO_3^-$) in the sample were thus determined.

RESULTS AND DISCUSSION

Optimum methylation conditions

In order to perform the methylation under optimum reaction conditions, the effects of reaction temperature, pH and reaction time on the methylation yields of bromide and iodide were investigated. In these studies, 25 μg/ml bromide and 0.10 μg/ml iodide solutions were used as the samples, and other reaction conditions used were identical to those described in the Experimental section.

The effects of reaction temperature on the peak areas of derivatized methyl bromide and methyl iodide were investigated. The peak areas do not vary between 50 and 70°C. However, when methylation was performed at temperatures lower than 50°C, the column deteriorated and the baseline fluctuated. Therefore, the reaction temperature was fixed at 70°C.

The effect of pH was examined as follows. To 1.0 ml of each aqueous solution of bromide and iodide, 0.1 ml of KOH or H_2SO_4 aqueous solution of different concentrations was added before the addition of dimethyl sulphate, and then the recommended procedure was performed. Fig. 1 shows the effects of KOH and H_2SO_4 concentrations on the peak areas of methyl bromide and methyl iodide. The maximum peak area of methyl bromide derivatized from bromide (25 μg/ml) or methyl iodide from iodide (0.10 μg/ml) was arbitrarily assigned a value of 100 throughout this paper. In Fig. 1, the peak areas decrease with increasing KOH concentration, but do not vary with H_2SO_4 concentration. Similar behaviour was observed in the case of methylation of these anions at 0.10 *M*[15]. On the basis of these results, dimethyl sulphate was directly added to the sample, as long as the sample was not

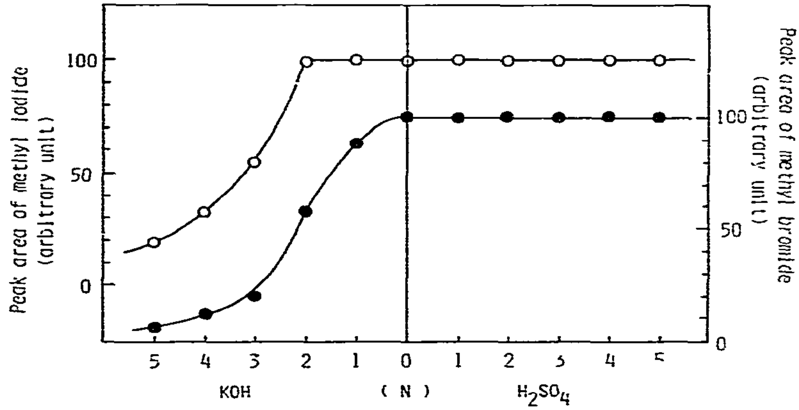

Fig. 1. Effect of normality of added acid or base on methylation of bromide (●, 25 μg/ml) and iodide (O, 0.10 μg/ml).

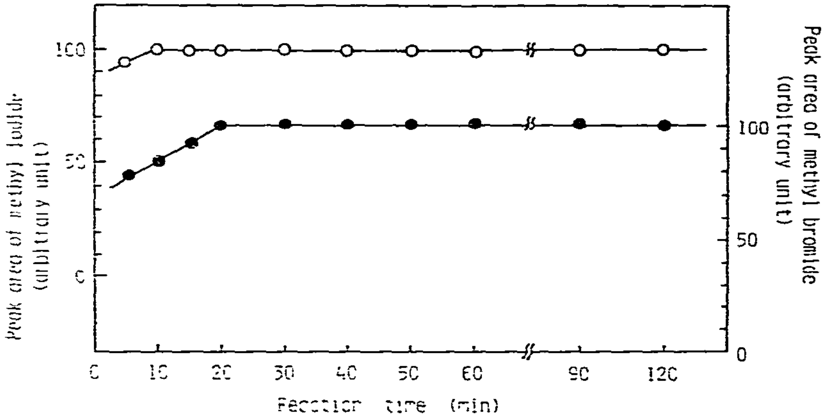

Fig. 2. Effect of reaction time on methylation of bromide (●) and iodide (○).

basic or acidic. The effects of reaction time were also examined, and the results are shown in Fig. 2. The times required to obtain methylated products at constant yields are around 20 min for bromide and 10 min for iodide. The reaction time, therefore, was fixed at 20 min.

From these results, the procedure described in the Experimental section was adopted. The methylation yield of iodide was determined by a similar method to that reported in our previous papers[15,16]. A yield of 76.3 ± 0.4% was found for $7.87 \cdot 10^{-7}$ *M* (= 0.10 μg/ml) iodide. This value agrees satisfactorily with that obtained when 0.10 *M* iodide was methylated and its yield evaluated by flame-ionization GC (73.2 ± 1.8%)[15]. The yield of bromide cannot be estimated exactly because of the difficulty in preparing standard solutions of methyl bromide (b.p. 3.6°C).

Analytical calibration

Calibration curves were constructed by plotting the peak areas of methyl derivatives *vs.* the concentrations of bromide and iodide (Fig. 3). Good linear relationships are obtained in the concentration ranges of 2.5–25 μg/ml bromide and 0.01–0.10 μg/ml iodide. The calibration curve for bromide passes through the origin, whereas that for iodide does not. This is due to the very small unknown peak given by the blank without iodide and to the difficulty in separating the blank peak from the peak of methyl iodide. A commonly accepted definition of the detection limit is the concentration of analyte giving a signal twice the average noise. According to this definition the detection limit of bromide was 0.1 μg/ml. On the other hand, the detection limit of iodide could not be obtained by the above definition, because the peak of methyl iodide overlapped the small blank peak. A detection limit of 0.5 ng/ml iodide was obtained as follows. The mean value (M) and standard deviation (S.D.) of the blank peak area were obtained by performing five replicate analyses. The detection limit in this case was defined as the concentration of iodide giving a peak area of (M + 2 S.D.). It is possible to detect several times lower concentrations of bromide and iodide than the detection limits by injecting a volume of the benzene extract slightly higher than 0.3 μl into the gas chromatograph or by decreasing the volume of benzene added in the extraction procedure. The determination level and the detection limit of bromide are a few hundred times higher than those of iodide. This behaviour is based

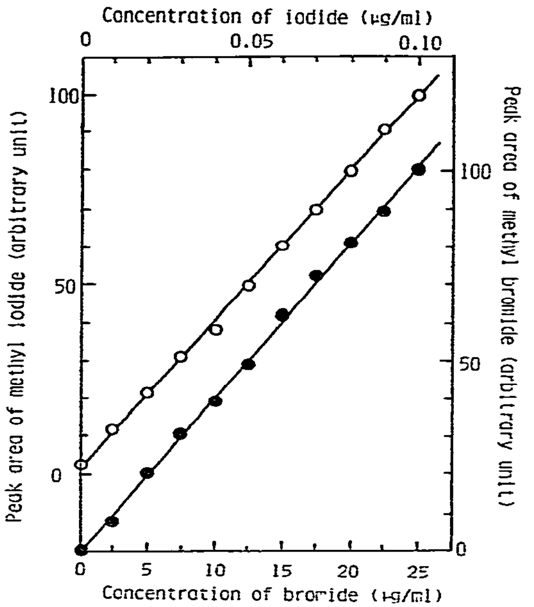

Fig. 3. Calibration curves for bromide (●) and iodide (○).

on the difference in the responses of methyl bromide and methyl iodide to an ECD. Generally, the concentration of bromide is several hundred times higher than that of iodide in environmental and biological samples, which is all the more convenient for applying the proposed method to the simultaneous determination of bromide and iodide in those samples.

Interference study

The interferences of several anions in the determination of bromide and iodide were investigated (see Table I). The anions selected are those normally found with bromide and/or iodide in environmental and biological samples. The concentrations of the anions added to the standard solution containing bromide (25 μg/ml) and iodide (0.10 μg/ml) are much higher than those in environmental and biological samples. Except for chloride and nitrate, the anions do not interfere with this analysis. Chloride at a very high concentration (20,000 μg/ml = 2.0%; corresponding to the concentration in sea-water) gives a slightly negative interference with the bromide determination. In this case, the gas chromatogram shows a small peak of methyl bromide on the tailing of the peak of methyl chloride produced by methylation of the large amount of chloride. Therefore, the peak area of methyl bromide seems to be slightly underestimated by the integrator. However, such interference is not observed at a chloride concentration of 100 μg/ml. On the other hand, the interference of nitrate (100 μg/ml) in the iodide determination is due to a small peak of a by-product derivatized from nitrate. The retention time of this by-product is the same as that of methyl iodide. The by-product is probably methyl nitrate, although it has not been identified. This interference is negligible when the nitrate concentration is reduced to 10 μg/ml. In addition, nitrite and acetate are also methylated with dimethyl sulphate

TABLE I

INTERFERENCE STUDY

Concentrations of bromide and iodide are 25.0 μg ml and 0.10 μg ml, respectively.

Anion	*Concentration (μg ml)*	*Added as*	*Peak area**	
			Methyl bromide	*Methyl iodide*
Standard	–	–	100.0 ± 1.2	100.0 ± 1.7
Cl^-	20.000	NaCl	91.6 ± 2.6	100.6 ± 2.7
Cl^-	100	NaCl	101.3 ± 2.2	98.4 ± 1.0
F^-	100	NaF	98.1 ± 1.6	99.3 ± 0.9
Br^-	100	NaBr	–	100.4 ± 2.0
I^-	100	NaI	98.0 ± 1.2	–
CH_3COO^-	100	CH_3COOK	99.4 ± 2.4	99.9 ± 2.9
SO_4^{2-}	100	Na_2SO_4	98.7 ± 1.6	100.6 ± 0.8
CO_3^{2-}	100	K_2CO_3	101.2 ± 1.3	102.5 ± 1.6
NO_3^-	100	$NaNO_3$	100.3 ± 1.9	**
NO_3^-	10	$NaNO_3$	–	99.3 ± 2.0
NO_2^-	100	$NaNO_2$	100.4 ± 2.2	100.1 ± 3.6

* Mean ± S.D. of five replicate analyses.

** The peak area of unidentified product from nitrate is not negligible.

in low yields[15]. In the test of nitrite interference, two new peaks were observed in addition to the peaks from the standard solution (Fig. 4A), but these do not interfere with the analysis because of the good separation of the two peaks from the peaks of methyl bromide and methyl iodide. On the other hand, the peak of methyl acetate derivatized from acetate was not observed because of its very low ECD response.

Applications

This method was applied to the determination of bromide and iodide in spring-water. Recovery tests for bromide and iodide added to the spring-water samples were

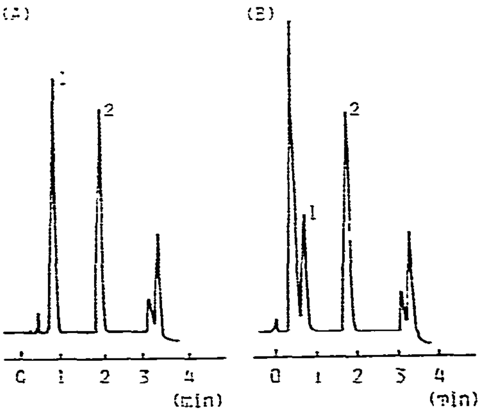

Fig. 4. Typical gas chromatogram obtained from standard solution (A), and gas chromatogram obtained in the analysis of spring-water sample (B). Peaks: 1 = methyl bromide; 2 = methyl iodide.

TABLE II

RESULTS OF ANALYSES OF SPRING-WATER SAMPLES WITH BROMIDE AND IODIDE RECOVERY TEST

Spring-water samples were diluted four-fold with water before analyses.

Sample No.	*Amount added (μg/ml)*		*Amount found (μg/ml)*		*Recovery (%)*	
	Bromide	*Iodide*	*Bromide*	*Iodide*	*Bromide*	*Iodide*
1	0.0	0.000	10.8* (0.38)	0.037* (0.0020)	–	–
	5.0	0.050	15.4	0.088	92.0	102.0
	10.0	0.100	19.8	0.136	90.0	99.0
	15.0	0.150	26.8	0.189	106.7	101.3
	20.0	0.200	30.6	0.236	99.0	99.5
2	0.0	0.000	7.7* (0.31)	0.034* (0.0013)	–	–
	5.0	0.050	12.3	0.081	92.0	94.0
	10.0	0.100	16.7	0.131	90.0	97.0
	15.0	0.150	22.4	0.186	98.0	101.3
	20.0	0.200	27.1	0.235	97.0	100.5

* Mean of five replicate analyses, with S.D. in parentheses.

performed. The results are shown in Table II, and Fig. 4B shows the gas chromatogram obtained in the analysis of the spring-water sample. The recoveries are all over 90 % for both anions and the relative standard deviations of the method are less than 6 % for both cases. Fig. 4A shows the gas chromatogram obtained from a standard solution prepared by dissolving potassium bromide and potassium iodide in water. In the gas chromatogram in Fig. 4B, the largest peak whose retention time is identical with that of methyl chloride appears very closely to the methyl bromide peak; the spring-water samples tested contain a large amount of chloride (*ca.* 3 %). Therefore, it seems possible to determine chloride together with bromide and iodide by this method. However, chloride cannot be determined precisely and sensitively because of the high volatility of methyl chloride (b.p. −24°C) and its low ECD response.

Determination of total bromine and total iodine

A sample may contain bromate and iodate ions together with bromide and iodide. In that case, it is impossible to determine accurately only bromide and iodide, if bromate and iodate are simultaneously derivatized to methyl bromide and methyl iodide, respectively. However, total bromine ($Br^- + BrO_3^-$) and total iodine ($I^- + IO_3^-$) seem to be analyzable by reducing them completely to bromide and iodide and then methylating. We have, therefore, investigated the reduction of bromate and iodate by using sodium thiosulphate as the reducing agent, and the results are given in Table III. A $1.5 \cdot 10^{-4}$ *M* bromate and $8.0 \cdot 10^{-7}$ *M* iodate solution was analysed by the procedure described in the Experimental section. The peak areas of methyl bromide and methyl iodide obtained from a solution containing bromide ($1.5 \cdot 10^{-4}$ *M* = 12 μg/ml) and iodide ($8.0 \cdot 10^{-7}$ *M* = 0.10 μg/ml) without adding the reducing agent were arbitrarily assigned a value of 100 in Table III. The direct derivatization

TABLE III

DERIVATIZATION OF BROMATE AND IODATE

Concentration of Br^- or BrO_3^- is $1.5 \cdot 10^{-4}$ *M*, and that of I^- or IO_3^- is $8.0 \cdot 10^{-7}$ *M*.

Anion	*Peak area**	
	$Na_2S_2O_3$ added	*Not added*
Br^-	100.0 ± 3.4	100.0 ± 1.2
BrO_3^-	100.0 ± 2.8	11.4 ± 1.4
$Br^- + BrO_3^-$	200.8 ± 3.2	115.3 ± 2.6
I^-	100.0 ± 1.0	100.0 ± 1.7
IO_3^-	99.3 ± 3.2	4.7 ± 0.2
$I^- + IO_3^-$	200.6 ± 4.2	105.3 ± 0.6

* Mean ± S.D. of five replicate analyses.

(no addition of sodium thiosulphate) of bromate and iodate to methyl bromide and methyl iodide proceeds in low yields. On the other hand, bromate and iodate are quantitatively derivatized by the addition of sodium thiosulphate. Therefore, the method proposed in this paper is applicable to the simultaneous determination of total bromine and total iodine.

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