APPLICATION OF ATMOSPHERIC PRESSURE HELIUM MICROWAVE INDUCED PLASMA ATOMIC EMISSION SPECTROMETRY WITH GAS-PHASE SAMPLE INTRODUCTION TO THE CONTINUOUS-FLOW DETERMINATION OF BROMINE IN SEAWATERS

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Abstract - A simple continuous-flow generation of volatile bromine by oxidation of aqueous bromide with 100 mM potassium persulfate in 5.0 M sulfuric acid has been applied to the determination of bromine in some coastal seawaters by atmospheric pressure helium microwave induced plasma atomic emission spectrometry. The results of the application of this technique with the use of both standard additions and calibration graph methods are in good agreement with those obtained by ion chromatography and inductively coupled plasma mass spectrometry.

Key words bromine, coastal seawaters, gas-phase sample introduction, atmospheric pressure helium microwave induced plasma, atomic emission spectrometry

Analytical plasmas such as the inductively coupled plasma (ICP) and microwave induced plasma (MIP) do show promise in the area of nonmetal determinations. The atmospheric pressure helium microwave induced plasma, in particular, has received considerable attention as an excellent source for atomic emission spectrometry (AES) [1]. Recently, we proposed a unique gas-phase sample introduction technique for the determination of iodine by MIP-AES[2-4]. More recently, the present authors[5] have described a similar continuous-flow determination of trace bromine by atmospheric pressure helium MIP-AES using the generation of volatile bromine from bromide and reported good detection limits of 29.5, 7.46 and 18.4 ng/ml for bromine at Br(I)447.78, Br(II)470.49 and Br(I)734.86 nm, respectively, with the use of an oxidizing solution of 100 mM potassium persulfate in 5.0 M sulfuric acid. The aim of this communication is to report the application of atmospheric pressure helium MIP-AES combined with continuous-flow gas-phase sample introduction to the determination of bromine in several coastal seawaters.

EXPERIMENTAL

The specifications of the instrumental components utilized in this study are exactly the same as described previously[5]. The complete analytical system with the gas/liquid separator and the optimized operating conditions used here have been depicted in the preceding paper[5]. The most sensitive Br(II) 470.79- and Br(I)734.86-nm lines were selected as the analytical ones for the determination of bromine in coastal seawaters.

All reagents were of analytical-reagent grade, and distilled and deionized water (Milli-Q water) was utilized throughout this work. A standard stock solution of bromine (1.000 mg/ml) was prepared on a daily basis by dissolving potassium bromide in Milli-Q water. From this standard solution, working standard solutions were prepared, just before use, by serial dilution with Milli-Q water. Synthetic seawater was made by dissolving the following five major constituents in Milli-Q water at their seawater concentrations, to give a salinity of approximately 3.5% as recommended by Kester et al. [6]: sodium chloride, magnesium chloride, sodium sulfate, calcium chloride and potassium chloride.

In a previous work[5], six methods for chemical vapor generation of elemental bromine from bromide were investigated. As a consequence, the use of three oxidizing solutions (i.e., 100 mM potassium persulfate in 5.0 M sulfuric acid, 10 mM potassium permanganate in 5.0 M sulfuric acid and 30 mM potassium perbromate in 5.0 M sulfuric acid) can give better limits of detection for bromine, while the remaining three oxidizing agents (i.e., potassium dichromate, sodium nitrite and hydrogen peroxide) produce less sensitivity when compared with the others (i.e., potassium persulfate, potassium permanganate and potassium perbromate). In this work, the above-mentioned three oxidizing solutions were used, in particular, for the interference study. The background emission intensity increased somewhat when diluted seawaters were introduced into the continuous-flow bromine generator. Therefore, background emission intensities were estimated by extrapolation using values measured in the immediate vicinity of both sides of the bromine line. Following background subtraction, the bromine content of the coastal seawaters was evaluated by the use of the method of standard additions and the matrix-matched calibration graph method in combination with the oxidation procedure with an oxidizing solution of 100 mM potassium persulfate in 5.0 M sulfuric acid for the elemental bromine generation.

RESULTS AND DISCUSSION

Using the Br(II)470.49- and Br(I)734.86-nm lines with the continuous-flow gas-phase sample introduction, we carried out a study of the effect of various concomitant ions on the emission intensity for 20 µg/ml bromine solutions. Several diverse species (i.e., cations or anions) and their concentrations were selected, taking the constituents of seawaters into consideration. The results of the effect of some diverse ions on bromine emission intensity at Br(II)470.49 nm by this procedure with the three oxidizing solutions mentioned above are shown in Table 1. Relative intensity is defined in this context as the ratio of the bromine emission

TABLE 1. Effect of diverse ions on bromine intensity at Br(II)470.49 nm

Species	Amount added (µg/ml)	Relative intensity*		
		Oxidizing solution†		
		K ₂ S ₂ O ₈	KMnO ₄	KBrO ₃
Li ⁺	100	97	100	98
Na ⁺	1000	99	100	97
Mg ²⁺	1000	97	103	92
K ⁺	1000	94	97	96
Ca ²⁺	1000	98	103	96
Ni ²⁺	100	100	99	101
Sr ²⁺	100	100	95	99
Al(OH) ₄ ⁻	100	100	101	101
Si(OH) ₄ ⁻	100	96	94	97
Fe(OH) ₄ ⁻	100	99	100	99
CuOH ⁺	100	93	101	102
NH ₄ ⁺	100	100	98	92
NO ₃ ⁻	100	100	101	101
B(OH) ₃	100	98	99	97
CO ₃ ²⁻	10	92	91	90
	100	66	69	71
HCO ₃ ⁻	10	96	99	99
	100	68	76	69
F ⁻	100	101	102	105
PO ₄ ³⁻	100	95	96	97
HPO ₄ ²⁻	100	102	95	101
H ₂ PO ₄ ⁻	100	101	98	99
Cl ⁻	100	102	107	96
	1000	105	92	83
I ⁻	1	95	100	98
	10	83	99	80
IO ₃ ⁻	100	101	103	99

* Compared to 100 for 20 µg/ml bromine as bromide alone.

† 100 mM potassium persulfate in 5.0 M sulfuric acid, 10 mM potassium permanganate in 5.0 M sulfuric acid and 30 mM potassium perbromate in 5.0 M sulfuric acid.

intensity obtained in the presence of the diverse ion to that obtained when no diverse ion was present in the analyte solution. Quite similar results to those shown in Table 1 were obtained by using the Br(I)734.86-nm line. It should be mentioned, in particular, from the results shown in Table 1 that the presence of iodine as iodide in the concentration higher than 10 $\mu\text{g/ml}$ causes a relatively large depressing interference with the bromine determination. This depressing interference may be attributed to the fact that a part of the oxidizing agent might be consumed by the iodide ion, resulting in the possible generation of elemental iodine. However, the concentration of iodine as iodide present in seawaters is much lower than those investigated in this interference study (i.e. in the ng/ml concentration range rather than the $\mu\text{g/ml}$ one)[4].

The accuracy and precision of the present continuous-flow gas-phase sample introduction method for atmospheric pressure helium MIP-AES were established by analyzing several coastal seawaters as typical natural waters. To this end, the following procedure was followed for the determination of bromine concentrations in some coastal seawaters sampled in the adjacent sea of Japan (several locations in Tokushima, Ishikawa and Fukui Prefectures)

The presence of some components of the samples would be expected to cause more or less interferences in the bromine determination by the proposed method according to whether or not the gas-phase sample introduction procedure and the off-peak background correction technique are used. Recovery studies, therefore, were made by adding known amounts of bromine as bromide to the diluted samples and applying the recommended procedure with 100 mM potassium persulfate in 5.0 M sulfuric acid. As a consequence, the mean recoveries were found to be in the range from 95.0 to 104.5%, depending on samples of coastal seawaters. For accurate determination of bromine, therefore, both the method of standard additions and the calibration graph method. A sample was filtered through a No. 2 filter paper (Toyo Roshi Kaisha, Ltd., Tokyo), and the filtrate was analyzed for bromine after spiking with bromine in the ranges of 5-20 $\mu\text{g/ml}$ for the standard additions method. The calibration graphs for bromine were constructed by matrix matching with use of a synthetic seawater[6]. Dilution factor of 20 was used for the determination of bromine in the coastal seawaters. The results obtained by the present method of several samples of coastal seawaters are given in Table 2. At the same time, the bromine concentration in the

TABLE 2. Determination of bromine ($\mu\text{g/ml}$) in several coastal seawaters

Sample*	This work†					
	Standard additions method		Calibration graph method		Other methods	
	Br(II)470.49 nm	Br(I)734.86 nm	Br(II)470.49 nm	Br(I)734.86 nm		
A	33.4 $\pm$ 0.6 (n=6)	33.6 $\pm$ 1.6 (n=6)	29.6 $\pm$ 2.1 (n=8)	31.3 $\pm$ 2.2 (n=8)	31.0§	30.5¶
B	55.5 $\pm$ 1.7 (n=6)	56.7 $\pm$ 1.5 (n=6)	54.8 $\pm$ 2.0 (n=8)	55.6 $\pm$ 2.0 (n=8)	52.9§	57.1¶
C	60.2 $\pm$ 1.8 (n=6)	56.4 $\pm$ 2.0 (n=6)	56.3 $\pm$ 2.3 (n=8)	60.0 $\pm$ 1.9 (n=8)	57.8§	59.8¶
D	63.3 $\pm$ 0.9 (n=6)	64.4 $\pm$ 1.5 (n=6)	65.4 $\pm$ 1.4 (n=8)	67.4 $\pm$ 1.7 (n=8)	64.0§	66.9¶
E	54.4 $\pm$ 2.1 (n=6)	55.2 $\pm$ 2.1 (n=6)	55.2 $\pm$ 1.7 (n=8)	57.2 $\pm$ 1.0 (n=8)	55.8§	56.7¶

* Taken at (A) Shirahama (Tokushima Prefecture), (B) Ohama (Tokushima Prefecture), (C) Mitsukehama (Ishikawa Prefecture), (D) Senrihama (Ishikawa Prefecture) and (E) Takahama (Fukui Prefecture).

† Mean $\pm$ standard deviation (number of determinations).

§ Mean of three determinations by ion chromatography.

¶ Mean of three determinations by inductively coupled plasma mass spectrometry.

samples was determined by means of an ion chromatograph (Yokogawa Model IC-7000) and an inductively coupled plasma mass spectrometer (Seiko Model SPQ 6500) and the results are also shown in Table 2. It should be noted in Table 2 that there is little or no significant difference in the bromine concentration between the Br(II)470.49- and Br(I)734.86-nm lines and between the method of standard additions and the matrix-matched calibration graph method and that the results obtained by the present method are in good agreement with those obtained by other methods such as ion chromatography and inductively coupled plasma mass spectrometry. In addition, as shown in Table 2, the concentration of bromine in the sample A was lower

than those in other samples, because it was taken at the estuary. The lower concentrations of chloride, fluoride and sulfate as well as bromide were confirmed by means of ion chromatography.

In conclusion, the proposed method has been successfully applied to the determination of bromine in samples of coastal seawaters.

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