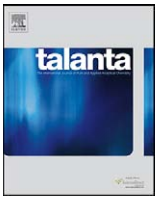
Talanta 81 (2010) 473–476

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta



Determination of iodine and bromine in coal and atmospheric particles by inductively coupled plasma mass spectrometry

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ARTICLE INFO

Article history:
Received 25 August 2009
Received in revised form
12 December 2009
Accepted 15 December 2009
Available online 23 December 2009

Keywords:
Bromine
Iodine
Atmospheric particles
Coal
ICP-MS
Memory effect

ABSTRACT

Bromine and iodine in atmospheric particles or coal can cause environmental problems such as destruction of ozone in the atmosphere; therefore, the presence of these compounds has recently received increased attention. Here, a rapid and reliable method for the simultaneous determination of total bromine and iodine using ICP-MS analysis is described. Samples were dissolved in mixtures of 5 mL of HNO_3 and 2 mL of H_2O_2 in a high pressure microwave digester. The solution was then oxidized by persulfate ($Na_2S_2O_8$) in addition to a small amount of silver nitrate, after which the total bromine and iodine were measured simultaneously by ICP-MS. The signal memory effects of bromine and iodine during analysis were effectively decreased by washing with a new mixture agent (2% alcohol acidic solution, pH 1–2 adjusted with HCl). The detection limits for bromine and iodine using this method were about 3.2 $\mu g\,L^{-1}$ and 1.1 $\mu g\,L^{-1}$, respectively. Additionally, the spike recoveries were between 78.7% and 121% for bromine and iodine analysis, while the relative standard deviations ranged from 4.3% to 9.7%, and from 1.5% to 3.4% for bromine and iodine, respectively. The results of this study indicate that the method described here is suitable for the analysis of micro-amounts of bromine and iodine in atmospheric particles and coal samples.

1. Introduction

Atmospheric particles in the atmosphere of cities account for a large percentage of the principal components of pollutants. According to the latest estimation of global atmospheric aerosol sources, natural aerosols account for 68–95% of the total and 58–65% of the fine particles in the PM10 and PM2.5 fractions [1]. These particles could be very harmful to human health. Bromine and iodine in aerosols (particles) play an important role in radiant balance, catalysis reactions in the O_3 layer, and other reactions in the atmosphere [2]. Accordingly, many studies have focused on the presence of Br and I in atmospheric particulate matter. For example, McElroy et al. [3] and Yung et al. [4] found that the BrO–ClO cycle reaction makes a considerable contribution to the loss of stratospheric ozone. Furthermore, Platt and Honninger [5] evaluated the role of halogen species in the troposphere, while Davis et al. [2] demonstrated that cycling of iodine in the atmosphere was an important route leading to ozone destruction in the marine troposphere. However, most data regarding atmospheric Br and I have been acquired by neutron activation analysis (INAA) and electro-chemical analysis [6], and very little information regarding the use of inductively coupled plasma mass spectrometry (ICP-MS) for Br and I analysis in aerosols is available.

Recently, trace levels of Br or I in plant samples, milk, urine and mineral deposits were reported using the ICP-MS method [7–11]. Additionally, Boulyg and Heumann [7] identified halogens in powdered geological and environmental samples using isotope dilution laser ablation ICP-MS. Furthermore, Reid et al. [8] determined the amount of iodine species by ICP-MS using different sampling-preparation methods, such as alkaline digestion with TMAH and the use of an ion-exchange column (loaded Pd^{2+}, Ca^{2+}) to retain selective iodide followed by elution with $(NH_4)_2SO_4$ solution. However, the effects of different valence states of Br and I on the signal intensities of ICP-MS have not yet been discussed, although several studies [8,12,13] have reported that iodine analysis using ICP-MS resulted in acute problems with signal memory due to the evaporation of iodine as I_2 or HI species from droplets in the spray chamber. Moreover, Li et al. [14] found that trace Br, As and I in geologic samples analyzed by ICP-MS produced different signals than anionic species of Br and I (in solution). Therefore, they developed an ICP-MS method for determination of Br or I in geologic samples, and decreased the memory effects of Br using NH_3OH_4 medium to a certain degree. Shi and Adams [15] developed a new rapid IC-ICP-MS method for analysis of iodoacetic acids, bromoacetic acids, bromate and other related halogenated compounds in water. However, they were not able to evaluate the total bromine or iodine species

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doi:10.1016/j.talanta.2009.12.026

Table 1
Typical operating parameters for the VG PQ-3 ICP-MS.

RF power (W)	1350
Gases ($L\,min^{-1}$) Ar	
Cooling gas	13.6
Auxiliary	0.75
Nebulizer	0.85
Sampling cone orifice (Ni) (mm)	1.0
Skimmer cone orifice (Ni) (mm)	0.7
Number of sweeps	100
Channels per mass peak	3
Dwell time (ms)	3000
Operating vacuum pres. (Pa)	5×10^{-4}
The position of plasma $x/y/z$ (cm)	370/164/163
m/z for Br	81
m/z for I	127

directly by ICP-MS analysis without pre-treating the samples using techniques such as ion chromatography and filtration.

Here, we report a method of evaluating Br and I in atmospheric particulate and coal samples by ICP-MS. The Br and I in testing solution were oxidized by per-sulfates via the addition of one drop of Ag^+ (silver nitrate 0.5%); therefore, we investigated the oxidation conditions, observed the fluctuation in the background of blanks, and found an effective agent for washing and eliminating Br and I signal memory effects. Overall, a new method for the analysis of trace amounts of Br and I in coal and atmospheric particles was developed. Evaluation of the precision and accuracy of the method revealed that it provided good recovery and reproducibility.

2. Experimental

2.1. Instruments and reagents

A microwave digester (CEM corporation MARS) was employed for the digestion of coal, coke and atmospheric particles.

A VG PQ-3 (Thermo Elemental UK) was used in conjunction with a PC and the X-II series operating system. The typical operational conditions for the ICP-MS are shown in Table 1.

The experimental water used during analysis was de-ionized (18 MΩ) using a Millipore-Q corporation cartridge system and then was purified using sub-boiler stills prior to ICP-MS analysis. Stock solutions of ^{127}I and $^{79}Br/^{81}Br$ were prepared from corresponding isotopically enriched sodium bromate and iodate, which were purchased from Inorganic Ventures Corporation with the certified standard materials conformity.

2.2. Experiment method for ICP-MS analysis

All test solutions were prepared as follows prior to ICP-MS analysis: samples of coal or atmospheric particles (~0.05–0.1 g) were dissolved in 5 mL HNO_3, 2 mL H_2O_2 and 1 drop of $S_2O8_2{}^-$ (20% solution) using a high pressure microwave digester. The samples, which were clear, were then transferred to a 100 mL flask and diluted to ca. 30 mL with distilled water, after which 1 mL per-sulfate (20% $Na_2S_2O_8$) and 1 drop of silver nitrate (0.5% $AgNO_3$ solution) were added. The samples were then heated in a 45 °C water bath for 10 min, cooled to ambient temperature and diluted to 100 mL with distilled water. The blank solution was prepared as described above without the addition of target analytes.

The calibration standards, which consisted of I and Br with concentrations ranging from 1 $\mu g\,L^{-1}$ to 100 $\mu g\,L^{-1}$, were also prepared as blank solution' preparation procedure above.

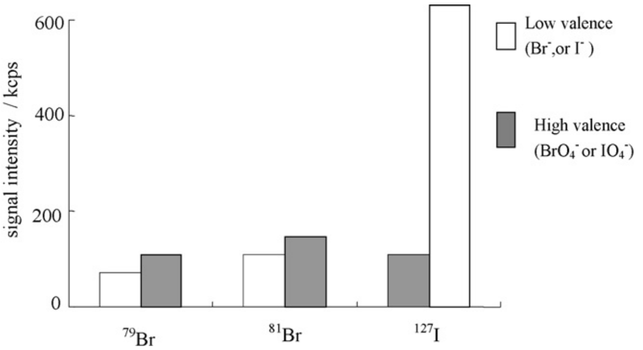

Fig. 1. Differences in the ICP-MS signals of I^- and $IO_4{}^-$ (c = 50 ppb, ~$\mu g\,L^{-1}$).

3. Results and discussion

3.1. Purification of water

Millipore-Q water de-ionized at 18 MΩ still has a high background intensity at the mass of ^{81}Br and ^{127}I; therefore, the Millipore-Q water was prepared in advance and then subjected to distillation in a sub-boiler made of quartz or of PTFE material. The distilled water samples were then compared with each other and with de-ionized water. The water blank background-signal intensities at the Br′ and I′ mass positions of the sub-boiler distilled water were much lower than that of the Millipore-Q water. Furthermore, the background intensity of the water prepared using the PTFE sub-boiling system (50–80 $mL\,h^{-1}$) was much lower than that of the water prepared using the quartz system (400–600 $mL\,h^{-1}$). However the distillation yield by using PTFE sub-boiling system (50–80 $mL\,h^{-1}$) is much less than by using quartz system (400–600 $mL\,h^{-1}$).

3.2. Oxidization of bromine and iodine

The ICP-MS display varies greatly for different valence states of bromine and iodine species in solution, particularly for iodine species. Indeed, as shown in Fig. 1, the MS signals of I^- and $IO_4{}^-$ clearly differed. It is different to correctly determine the iodine concentration in unknown samples when there is such great variation in the calibration standards. Differences such as those shown in Fig. 1 have been reported in several other studies [14]. Indeed, Reid et al. [8] recently conducted an investigation of iodine species formed using oxone oxidizing agent for oxidation and subsequent determination of the level of iodine in milk samples with a view to controlling the iodine chemistry. However, they determined the amount of iodine species by ICP-MS using different sampling-preparation methods and pretreatment procedures, such as the ion-exchange column technique. No final solution for the determination of the total iodine or bromine levels with different valences has been suggested to date. In this study, hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$) and sodium per-sulfate ($Na_2S_2O_{8)}$ were selected as the oxidizing agents in an attempt to oxidize the different low valence iodine species.

When using H_2O_2 for oxidizing agent, we found that the ICP-MS signals at ^{127}I of different valence species of iodine (such as I^-, $IO_4{}^-$, and the mixture of $I^- + IO_4{}^-$) were not same. These findings imply that H_2O_2 is not capable of sufficiently oxidizing the lower valence species of iodine (such as I^-) to produce high valence species of iodine (iodinates) and that it cannot produce a stable oxidization solution for analysis. This was because H_2O_2 was not stable in solution and also easy to cause disproportionating reaction.

The oxidizing agent $KMnO_4$ can oxidize the lower valence iodine species mixtures according to its electro-chemistry potential the-

Table 2
Detection limits and precision of Br and I.

Element	Detection limits ($\mu g\,L^{-1}$)	RSD/%	
		$n=7$ ($10\,\mu g\,L^{-1}$)	$n=7$ ($60\,\mu g\,L^{-1}$)
Br	3.2	9.7	4.3
I	1.1	3.4	1.5

ory, but it can only maintain this higher valence state for 30 min observed here. The standard electro-potential of E^0 (MnO_4^-/Mn^{2+}) and E^0 (IO_4^-/I^-) were ~1.51 V and ~1.24 V, respectively.

The half electro-chemistry reactions would be as follows:

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O \qquad (a)$$

$$IO_4^- + 8H^+ + 7e \rightarrow I^- + 4H_2O \qquad (b)$$

It is clear to deduce the electro-potential of whole reaction with (a) and (b), $\Delta E = E_a - E_b = 0.27\,V + \Delta$, where Δ value will depend on the concentration of oxidizing agent of [$KMnO_4$], [H^+] ion concentration, as well as [IO_4^-] and [I^-] concentration. The test solution here on ICP-MS analysis contains a large amount of [$KMnO_4$ ~2%] and micro-amount of [IO_4^-] and [I^-] (about $mg\,L^{-1}$ level). So $\Delta E > 0.27 \gg 0$, the micro-amount of iodine can be oxidized by $KMnO_4$ according to the Nernst equation calculation (assumption at 25 °C).

When sodium per-sulfate ($Na_2S_2O_8$) was used as the oxidation agent instead of H_2O_2 or $KMnO_4$, the difference in ICP-MS signals corresponding to iodine with different valence levels was very little; therefore, we could determine the concentrations of different iodine species regardless of the species of iodine in the solution.

The best results of experiments conducted using different amounts of $Na_2S_2O_8$, different oxidizing temperatures and different oxidizing times were obtained under the following conditions: 1 mL $S_2O_8^2$ (20% solution), 45 °C and 10 min. Additionally, we found that the addition of a micro-amount of silver nitrate (1 drop of 0.5% $AgNO_3$ solution) greatly increased the speed of the reaction. Furthermore, the addition of Ag^+ resulted in determination of Br or I rapidly reaching the final stable values in 4–5 min. Moreover, the testing solution system that included $S_2O_8^{2-}$ and micro-amounts of silver ions prepared under the oxidization conditions above can remain stable for at least 2 h for ICP-MS analysis. The standard electro-potential of E^0 ($S_2O_8^{2-}/SO_4^{2-}$) (at 25 °C) was about 2.01 V, almost the strongest oxidizing agent within inorganic chemicals. The reaction of oxidizing the low valence iodine species to its periodate IO_4^- by $S_2O_8^{2-}$ would take place easily, especially in addition of Ag^+ ion as catalyst.

3.3. *The blank background and memory effects*

In this study, we generally found that the blank signals of ^{81}Br and ^{127}I ranged from 15 kcps to 50 kcps, when we observed the fluctuation of ^{81}Br and ^{127}I signals in sample blank solution over the course of nearly 6 months (from December 3, 2008 to April 15, 2009). The concentration of the blanks followed no clear pattern and varied from $0.2\,\mu g\,L^{-1}$ to $3.1\,\mu g\,L^{-1}$ and from $0.01\,\mu g\,L^{-1}$ to $1.8\,\mu g\,L^{-1}$ for Br and I, respectively. These findings suggest that the mean concentration of the blank used for Br or I (Br^- $1.61\,\mu g\,L^{-1}$, I^- $0.8\,\mu g\,L^{-1}$) should be eliminated prior to calculation of the sample concentration during practical sample analysis. From the point of view of analytical chemistry statistics theory, this is because it is more accurate to subtract the mean arithmetical blank value than the value of the blank at a single point. The mean arithmetical value of blank calculated from many times (at least 7 or 11 more times) should be subtracted for more accurate results when making sample analysis.

Table 3
Analysis of actual samples and recovery of spiked samples by ICP-MS.

Samples	Br, $mg\,kg^{-1}$ ($n=3$)		I, $mg\,kg^{-1}$ ($n=3$)	
(coal/source[a])	Measured	Recovery %(std)[b]	Measured	Recovery %(std)
I-1/Australia	8.0	107 (30)	3.9	101 (30)
I-2/Indonesia	15	120 (10)	2.1	82 (30)
I-4/Vietnam	27.1	78.7 (100)	4.1	99 (30)
E-2/China	17.6	121 (30)	1.3	95 (30)
E-4/China	9.2	89 (100)	1.0	86 (10)
Samples	Br, $\mu g\,L^{-1}$ ($n=3$)		I, $\mu g\,L^{-1}$ ($n=3$)	
TSP-Aerosols	Measured	Recovery% (std)	Measured	Recovery% (std)
Sh-1/spring	16.6	90 (10)	11.9	90 (10)
Sh-2/summer	11.2	99 (10)	7.0	107 (10)
Sh-3/autumn	40.7	110 (30)	9.8	120 (10)
Sh-4/winter	26.4	95 (10)	16.8	104 (30)
Samples	Br, $\mu g\,L^{-1}$ ($n=3$)		I, $\mu g\,L^{-1}$ ($n=3$)	
PM10-aerosols	Measured	Recovery %(std)	Measured	Recovery %(std)
Sh-1/spring	16.8	96 (10)	8.8	120 (10)
Sh-2/summer	17.3	nd[c]	6.1	nd
Sh-3/autumn	32.9	nd	9.4	nd
Sh-4/winter	24.5	95 (30)	12.2	117 (30)

[a] Country of origin.
[b] Concentration of standard bromine or iodine added.
[c] nd: not determined.

Indeed, the high memory effects of Br and I that result from contamination with a high concentration of Br and I would break down very slowly in response to washing with water, which would lead to difficulty in returning blank signals after a normal washing uptake time. (More were observed and illustrated in our previous work for analysis of Br in electric plastics [16].) This was because different Br and I species were not easily washed out of the spray chamber, even after washing for long periods of time. In this study, many attempts were made to decrease the memory effects by washing the spray chamber with water, various washing agents and gases. Fig. 2 shows the effects of washing with air, N_2, water, and washing agent (2% alcohol, acidic solution of pH 1–2) on the elimination of

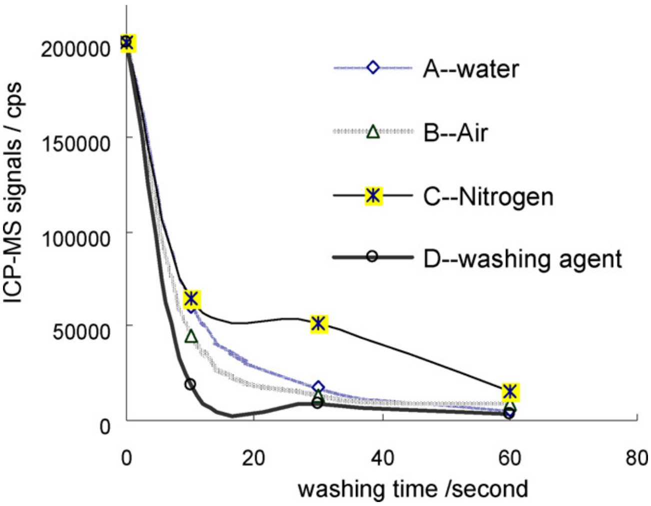

Fig. 2. The memory effects of bromine species eliminated by washing. ($100\,\mu g\,L^{-1}$ bromate solution was evaluated by ICP-MS, after which the sampler was washed with A–D in turn, where A indicates that the sampler was washed with water; B indicates that the sampler was washed with air (through pipe connection); C indicates that the sampler was cleaned using a connected nitrogen pipe; D indicates that a washing agent comprised of 2% alcohol acidic solution (pH 1–2, adjusted with HCl) was used to clean the sampler. The results obtained when the iodate testing solution was used were similar to those reported above.)

Table 4
Determined value of Br and I in soil certified reference materials by ICP-MS.

Sample (s-CRM)[a]	Br ($\mu g\,g^{-1}$)		I ($\mu g\,g^{-1}$)	
	Certified	Found ($n=3$)	Certified	Found ($n=3$)
GBW07406(GSS-6)	8.0	9.1, 8.3, 10.0	19.4	17.1, 21.3, 18.9
GBW07408(GSS-8)	2.5	1.9, 3.0, 2.9	1.7	2.2, 2.6, 2.0
Recovery (%) ($n=3$)	112, 101, 117		97.0, 99.0, 107	
(mean)(Added 10 $\mu g\,L^{-1}$ of standard solution of Br and I in digested sample solutions)	(110)		(101)	

($n=3$) represents three times test.

[a] The certified reference materials was from Geophysics Institute of China.

bromine species effects. The elimination of iodine species memory effects by washing was similar to that of bromine; therefore, they were omitted from the figure. The washing agent comprised of 2% alcohol acidic solution (pH 1–2) eliminated the Br and I memory effect in approximately 10–15 s and maintained the stability of the analytical results. This might be due to the reduction in plasma gas temperature, species excitation temperature and a decline in the electron density of the plasma and ionization temperature [17]. Of course, the small amount of alcohol in the washing water likely lowered the surface-tension of the uptake washing solution, which facilitated the removal of Br and I species from the spray chamber.

4. Detection limits, precision and accuracy

The method detection limits for Br and I in 5% HNO_3 medium are shown in Table 2. The detection limits (DL) of Br and I were 3.2 $\mu g\,L^{-1}$ and 1.1 $\mu g\,L^{-1}$, respectively, based on three times the standard deviation obtained from measurement of the seven spike samples (Table 2).

The precision of the method was tested by multiple spiked sample blank analysis under two levels of concentrations (spiked with 10 $\mu g\,L^{-1}$ and 60 $\mu g\,L^{-1}$). The relative standard deviation (RSD) of Br and I ranged from 4.3% to 10% and from 1.5% to 4%, respectively (Table 2), which indicates that the method developed here is sufficient for the analysis of micro-amounts of Br and I.

To evaluate the accuracy of the method, the recoveries of different concentrations of Br and I (10 $\mu g\,L^{-1}$, 30 $\mu g\,L^{-1}$, 100 $\mu g\,L^{-1}$) added to the test solution was evaluated (Table 3). The recoveries of Br and I ranged from 78.7% to 121% and from 82% to 120%, respectively. The accuracy of the method was well within the generally accepted range of 70–130% indicated in ISO 5725 [18]. Taken together, these results indicate that the method developed here would be satisfactory for microanalysis of analytes by ICP-MS.

The validation results for soil certified reference materials (s-CRM) is shown in Table 4. The determined contents of Br and I in s-CRM by this method were accurate with comparison of certified value. Moreover that average recoveries of Br and I, 110% and 101% respectively, were quite well.

5. Atmospheric particulate and coal samples analysis

Both aerosol samples collected in Shanghai and coal from import and export countries were evaluated by ICP-MS. As shown in Table 3, the coal samples from different countries contained different levels of bromine and iodine. Additionally, the coal samples generally contained higher concentrations of bromine than iodine. For aerosol samples, the highest levels of bromine in autumn were 40.7 $\mu g\,L^{-1}$ in the TSP aerosol sample and 32.9 $\mu g\,L^{-1}$ in the PM10 aerosol sample. The highest iodine levels during winter were 16.8 $\mu g\,L^{-1}$ and 12.2 $\mu g\,L^{-1}$ for TSP and PM10, respectively. Conversely, the lowest concentrations of bromine in the TSP and PM10 samples were 11.2 $\mu g\,L^{-1}$ in summer and 16.8 $\mu g\,L^{-1}$ in spring, respectively. The lowest levels of iodine were 7.0 $\mu g\,L^{-1}$ and 6.1 $\mu g\,L^{-1}$ for the TSP and PM10 samples collected during summer. All sample recoveries of Br and I were within the accepted range of 78.7–121% (Table 3). The correlation between the concentration of Br or I in different samples collected within the same seasonal time period and atmospheric pollution caused by Br and I should be evaluated in detail in another paper.

6. Conclusion

The effective and sensitive simultaneous method of detecting bromine and iodine by ICP-MS was developed using the addition of per-sulfate solution as the oxidizing agent. Coal and four seasonal aerosol particles were then digested and treated in a high pressure microwave digester and the levels of Br and I were then determined successfully with no other sampling pre-filtration or preparation steps required. In addition, the high memory effects of bromine and iodine were greatly reduced using a new washing agent (2% alcohol acidic solution). The procedure of ICP-MS has been validated by certified reference material. Besides that, the method described here has fairly good precision and accuracy as well as a low detection limit, which meets the requirements for microanalysis by ICP-MS.

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