



High-precision isotope ratio analysis of inorganic bromide by continuous flow MC-ICPMS

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ABSTRACT

The study proposes a new method for the high-precision determination of bromine isotope ratio in inorganic samples. In the suggested method, inorganic bromide is wet-oxidized into molecular bromine and transferred into the MC-ICPMS by continuous flow of helium. Analysis of natural inorganic bromide samples from various sources revealed identical $\delta^{81}\text{Br}$ values within the range of the method uncertainty.

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1. Introduction

Halides are the major components of most brines and usually considered conservative tracers in groundwater system. Natural distribution of chlorine isotope composition in groundwater, marine and sedimentary formation waters as well as in fluid inclusions and crystalline brines were investigated by several research groups [1–4], and using Br isotope ratio as a tool in differentiating water types and evaluating geochemical and hydrogeological processes became an issue of interest currently [5,6]. Although first efforts to evaluate stable isotope composition of bromine were made in the beginning of the 20th century [7–9], a reliable high-precision method for its determination has remained a challenge until recently. During the last decade several research groups reported on the use of continuous-flow isotope ratio mass spectrometry (CF-IRMS) for this purpose [10,11]. It was demonstrated that the method could be applied to samples containing down to $1\ \mu\text{mol}$ of Br^- and allow achieving precision of $\pm 0.06\%$ [11]. Employment of this technique for the analysis of natural inorganic bromides revealed a variation of $\delta^{81}\text{Br}$ from -0.8% up to $+3.35\%$ relative to standard mean ocean bromide (SMOB) in formation waters [5]. However, a complex sample preparation that includes off-line conversion of inorganic bromide into methyl bromide by multi-step synthesis represents a major limitation of the proposed method. The synthesis is time-consuming, requires the use of toxic chemicals and must be

performed by well-experienced technician to achieve good analytical results.

The present study aimed to develop a simpler and less laborious technique for the routine isotope ratio determination of bromine in inorganic samples by MC-ICPMS.

Generally, this technique, combining superior ionization efficiency and high sensitivity, potentially allows precise isotope ratio determination for wide range of elements, including halogens. For instance, successful precise determination of the Br isotope ratio in organic compounds by gas chromatograph MC-ICPMS (GC-MC-ICPMS) has been recently demonstrated [12,13]. However the use of MC-ICPMS for high-precision Br isotope analysis of inorganic samples still remains a challenge, apparently, due to difficulties associated with sample introduction system. For example, introduction of inorganic bromide into the MC-ICPMS by aqueous solution nebulization causes a sharp increase in m/z 79 and 81 signals ($^{40}\text{Ar}^{38}\text{ArH}^+$ and $^{40}\text{Ar}^{40}\text{ArH}^+$) due to excess of hydrogen atoms in the plasma, interfering with both Br isotopes. On the other hand, introduction of a bromide solution via a desolvation system results in a signal loss due to the escape of volatile bromine species through the desolvation membrane.

In the present study we propose a more feasible method for the precise measuring Br isotope ratio in inorganic compounds using on-line oxidation of bromide into bromine and its subsequent introduction into MC-ICPMS by the continuous He flow.

2. Experimental

The system for the Br isotope analysis in inorganic compounds is schematically represented in Fig. 1.

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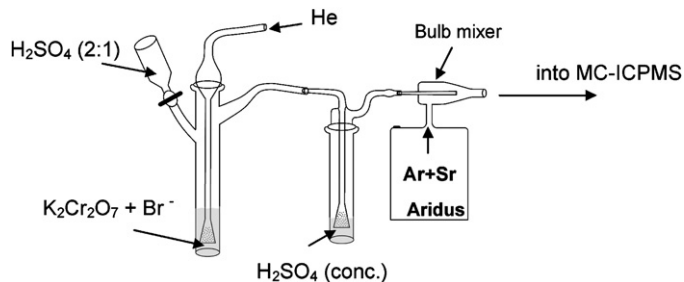


Fig. 1. Schematic representation of the system for Br isotope analysis.

Table 1
Instrumental parameters for the MC-ICPMS measurement.

MCICPMS parameters	
RF power	1200 W
Coolant flow	12 L/min
Auxiliary flow	1.13 L/min
Nebulizer gas flow	0.51 L/min
Interface cones	Nickel
Instrument resolution	~300
Nebulizer	PFA 70 μ l/min
Spray chamber temp.	75 °C
Desolvator temp.	160 °C
Sweep gas (argon)	3.61 L/min
Integration time	0.5 s

The following procedure was used for the bromide oxidation: a reaction vessel was charged with 1 ml of aqueous solution containing ~0.02 mg of bromide and 2 ml of 1 N $K_2Cr_2O_7$. The system was purged by helium (99.999%; flow of 40 ml/min) for several minutes followed by addition of 3 ml of 2:1 H_2SO_4/H_2O to initiate oxidation.

The bromine formed in the reaction was transferred from the reaction vessel by the continuous purging with helium. The efficiency of the bromide removal was found $\geq 97\%$ (as determined by ICP-MS analysis of Br in the remained solution). The flow passed through the wash bottle containing concentrated sulfuric acid to remove moisture. After this stage, the flow of helium and bromine gas was combined with the argon stream from the Aridus desolvation nebulizer using a glass coaxial bulb mixer (Fig. 1). All vessels and lines in the apparatus are glass-made and do not contain any plastic parts. Toxic effect of the bromine produced over the course of the proposed procedure is minimal due to the small amounts of the bromide used in our experiments as well as its quantitative transfer into the torch of MC-ICPMS.

Instrumental mass bias was corrected by the Sr external spike (standard solution SRM 987, 1 mg/l) that was continuously injected into the system by Aridus desolvation nebulizer. Fine-tuning of the MC-ICPMS (Nu Instruments) was performed according to the maximum signal of Sr. Signals of $^{86}Sr^+$, $^{84}Sr^+$, $^{83}Kr^+$, $^{81}Br^+$, and $^{79}Br^+$ were simultaneously collected by Faraday cups. Operating parameters for the MC-ICPMS system are listed in Table 1. Bromide isotope

Table 2
Chemical composition of the analyzed samples in μ g/g.

Sample	Br (μ g/g)	Na (μ g/g)	K (μ g/g)	Ca (μ g/g)	Mg (μ g/g)	Cl (μ g/g)	Cl/Br (weight ratio)
IAPSO standard sea water	69	11,000	410	420	1330	19,800	287
Dead Sea water (Israel)	5600	35,900	7800	17,900	47,200	228,000	41
Hamei Tveria water (Israel)	250	6450	330	3650	640	17,900	72
Fulia water (Israel)	6.5	490	17	205	75	1020	157
KBr (superpure, Merck)	672,000	na	328,000	na	na	na	na
Karnalite (solid)	1500	na	120,000	350,000	75,000	150,000	100
NaCl (solid)	90	394,000	na	na	na	606,000	6700
NBS-977 bromide standard (solid)	776,700	223,000	na	na	na	na	na

na—not analyzed.

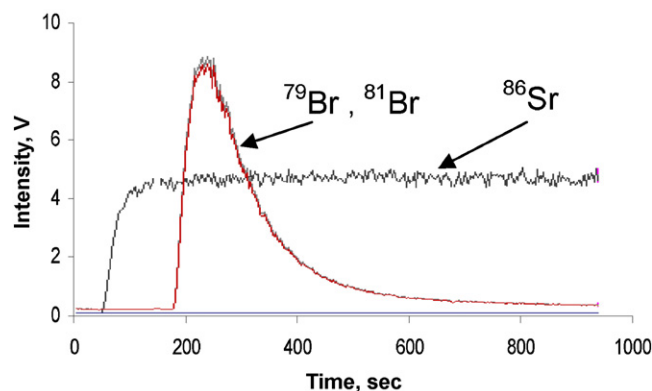


Fig. 2. Typical chromatogram of bromide isotope analysis by CF-MC-ICPMS.

composition was determined by the single data set integration of the bromine transient signal (Fig. 2).

3. Results and discussion

The study represents a new approach for bromine isotope analysis in inorganic compounds using continuous flow MC-ICPMS. Eight samples including natural waters and aqueous solutions of natural and industrial evaporates were analyzed using the proposed technique. Main chemical composition of the samples and bromide contents are represented in Table 2. As could be seen, the analyzed samples vary in their chemical composition and in their Cl/Br ratio, reflecting different extent of water evaporation and mineral precipitation processes.

As it was described above, the main problem of the precise isotope analysis of inorganic bromides by MC-ICPMS associated with a sample introduction. We assumed that this problem could be overcome if Br is introduced into the MC-ICPMS as a dry gas. One of the possible ways to realize it is to oxidize inorganic bromides into the volatile molecular bromine followed by its quantitative transfer to MC-ICPMS by helium purging. Solution of potassium dichromate and sulfuric acid was used in our method as an oxidizing reagent allowing selective oxidation of bromide over chloride. Taking into account that the natural samples contain high amounts of chlorides, “selective” bromide oxidation is expected to minimize a potential matrix effect on Br isotope ratio determination.

Based on the fact that comparable Br signal's area were obtained for the samples different in their chemical composition but containing equal amounts of bromide, we assumed that efficiency of the bromide oxidation was independent on the composition for all analyzed samples.

Linear relationship between amount of the analyzed bromide and transient signal's area was observed in the range of 1–10 V for all analyzed samples.

One of the ways to correct a mass fractionation and instrumental drift for Br isotopes in the MC-ICPMS is to compare it to the

external Br isotope standard (SMOB) [10], using “standard-sample-standard” bracketing technique [14].

However, internal (daily) precision for Br isotope ratio measurements varied from day to day reaching values up to 0.6‰ (1σ). One of the possible reasons to that is a relatively long analysis time (up to 15 min), causing an extended intervals between standard analyses and, consequently, to poor correction of the mass fractionation by “standard-sample-standard” technique. To eliminate this problem and to improve the precision of the analysis, we explored the use of instrumental mass bias correction using Sr external spike [13]. Although strontium and bromine have significantly different first ionization potential, we justify the choice of strontium as an external spike by its m/z value which is close enough to Br. Considering that Sr isotope ratio of stable isotopes is widely used as an internal standard for mass bias and matrix effect correction [15,16] in $^{87}\text{Sr}/^{86}\text{Sr}$ determination by MC-ICPMS analysis, we hypothesized that integration of this technique into bromine isotope analysis might improve the precision of the measurements.

The simultaneous introduction of the gaseous bromine and Sr external spike into MC-ICPMS enables determination of bromine isotope ratio through correction an instrumental mass bias during the sample run.

External normalization of the mass bias correction was done using the following approximations which is commonly used in TIMS and in MC-ICPMS techniques [17]:

$$F = \frac{\log(R_{\text{true}}/R_{\text{obs}})}{\log(m_{84}/m_{86})} \quad (1)$$

F is the correction factor per atomic mass unit; m_{86} and m_{84} are the exact masses of ^{86}Sr and ^{84}Sr isotopes respectively; R_{obs} is the measured $^{84}\text{Sr}/^{86}\text{Sr}$ ratio; R_{true} is the recommended $^{84}\text{Sr}/^{86}\text{Sr}$ value equal to 0.05655 [12].

$$\left(\frac{^{81}\text{Br}}{^{79}\text{Br}}\right)_{\text{Sr-corr}} = \left(\frac{^{81}\text{Br}}{^{79}\text{Br}}\right)_{\text{obs}} \times \left(\frac{m_{81}}{m_{79}}\right)^F \quad (2)$$

m_{81} and m_{79} are the exact masses of ^{81}Br and ^{79}Br isotopes respectively.

The measured $^{86}\text{Sr}^+$ ion beam was corrected for isobaric interferences from ^{86}Kr . For this purpose, the ion beam of $^{83}\text{Kr}^+$ was monitored and the measured intensity at mass 86 was corrected for the $^{86}\text{Kr}^+$ contribution using the $^{86}\text{Kr}/^{83}\text{Kr}$ ratio of 1.52. No mass discrimination correction was needed due to the low level of Kr ion beam.

Examination of the background prior to the isotopic analysis showed signals of about 30 and 32 mV intensity for the m/z 79 and 81, respectively. This background was subtracted from each peak on the point-by-point basis.

Applying Sr as an external spike for instrumental mass bias correction, allowed us to achieve precision up to 0.1‰ (1 std) for $^{81}\text{Br}/^{79}\text{Br}$ ratio for signals with amplitudes in the range of 1–10V. An accuracy test was performed using NBS-977 standard ($\delta^{81}\text{Br}_{\text{SMOB}} = -0.64\text{‰}$ [11]). Bromine isotope ratio $\delta^{81}\text{Br}_{\text{SMOB}} = -0.7\text{‰}$ ($1\sigma = 0.1$) was obtained for this standard in the present study.

The results of the analyses are summarized in Fig. 3. As could be seen, $\delta^{81}\text{Br}_{\text{SMOB}} = 0\text{‰}$ was obtained for all analyzed natural water samples as well as for evaporates containing bromide. These results could be well explained if a conservative behavior of Br is taken into the consideration. Due to the fact that bromides are not involved in precipitation–dissolution processes in the natural waters, any meaningful Br fractionation is not expected. Assuming that bromide salts could be produced by sea water evaporation, identical in the range of the method uncertainty isotope ratio of KBr and sea water may indicate that there is no fractionation of Br during evaporation process.

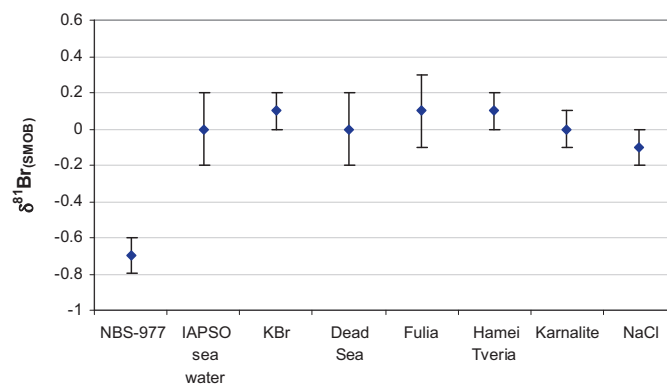


Fig. 3. Bromine isotope composition of the analyzed samples ($n=3-8$).

The results of our measurements agree with the results obtained by Eggenkamp and Coleman [10], who determined very close Br isotope composition of sea water and two industrial NaBr reagents.

4. Conclusions

In the present study we proposed a new analytical method for the determination of the bromine stable isotope ratio in inorganic compounds by continuous flow MC-ICPMS technique. Identical results for bromine isotope composition of NBS-977 standard obtained in the present study and earlier reported in the literature can serve as a proof of the method accuracy. Although the precision of the method is slightly worse than the precision obtained by CF-IRMS analysis, the proposed method might be preferable in many cases due to its simplicity, high sensitivity and lower toxicity of chemicals used. Analysis of inorganic samples from different natural sources performed in the present study, resulted in identical within the range of the method's uncertainty $\delta^{81}\text{Br}$ values. Further optimization of the method and its application to bromine isotope analyses in inorganic samples are in progress.

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