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Short communication

High precision determination of bromine isotope ratio by GC-MC-ICPMS

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ABSTRACT

This work presents a new methodology for the precise determination of bromine isotope ratio in individual organic compounds based on the simultaneous introduction of brominated organic compounds and strontium as an external spike into MC-ICPMS. Using the proposed methodology, an external precision (2σ) up to 0.1‰ has been attained. The new approach for the bromine isotope ratio analysis could be applied for the investigating the fate of the organobromine compounds in the environment.

1. Introduction

Brominated organic compounds occur widely in the environment. Nowadays, more than 1600 natural organobromine compounds produced by marine organisms are known [1]. Synthetic brominated organic compounds are often applied as flame retardants and as disinfecting and protecting agents [2,3]. Due to a possible toxic effect of these compounds on human health, investigation of their biogeochemical cycle in the environment is of the utmost importance. In this sense, the examination of isotopic composition of bromine in the individual organic compounds may serve as a powerful tool for understanding their origin and fate in the environment.

Based on the fact that mass difference between isotopes ^{81}Br and ^{79}Br is small, it could be assumed that isotope fractionation of bromine in organic compounds as a result of different biotic and abiotic processes will be relatively small. Therefore, highly sensitive and highly precise techniques must be used for the bromine isotope ratio analysis of the individual compounds. Several techniques for the bromine isotope composition analysis in organic compounds have been developed recently [4,5], while the most promising one is the compound specific ^{81}Br/^{79}Br analysis by Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) coupled to Gas Chromatograph (GC) proposed by Sylva at al. [6]. Separation of organic mixtures by means of gas chromatography enables precise bromine isotope ratio analysis for individual organobromine compounds by MC-ICPMS. However, despite the high sensitivity of the method, its application is limited due to relatively low precision: 0.3‰ (1σ) when more than 0.3 nmol of Br are injected, and up to 4.6‰ (1σ) for smaller amounts of Br.

Another drawback of the method is its inability to determine true values of bromine isotope ratio due to the lack of bromine isotope standards and no instrumental mass bias correction.

In the present study we suggest a new methodology for the bromine isotope ratio determination of brominated organic compounds, applying ^{84}Sr/^{86}Sr isotope ratio as an external spike.

2. Experimental

Coupling of Gas Chromatograph (Hewlett-Packard 5890) and Aridus desolvation nebulizer to MC-ICPMS (Nu Instruments) is schematically represented in Fig. 1. The system was designed by analogy to the reported previously by Epov et al. [7] and Halicz et al. [8] Briefly, a capillary column of the GC passing through a specially designed heated transfer line (copper tube 1/8′ o.d.) was interfaced into the plasma through the injector tube of the commercially available standard torch. Strontium external spike (Standard Reference Material (SRM) 987—National Institute of Standards and Technology) was continuously injected into the system by Aridus desolvation nebulizer. Fine-tuning of the MC-ICPMS instrument 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 GC-MC-ICPMS system are listed in Table 1.

The following brominated organic compounds of the purity >98% were used in this study: 3-bromotoluene (BT) (Aldrich;

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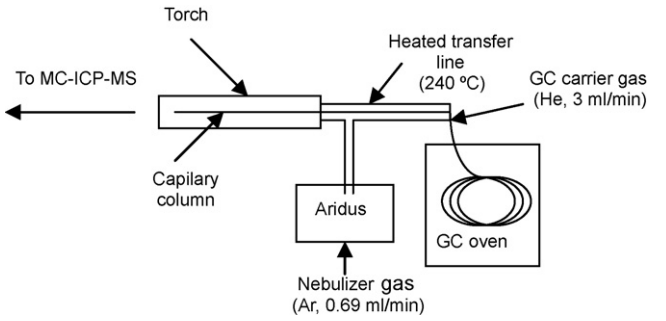

Fig. 1. Schematic representation of the GC-MC-ICPMS system.

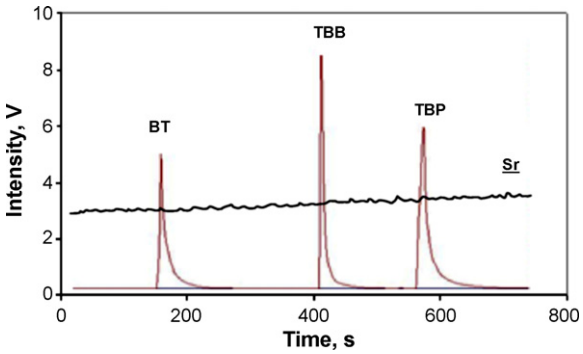

Fig. 2. Typical chromatogram for the solution of 3-bromotoluene (BT), tribromobenzene (TBB) and tribromophenol (TBP) in acetone, obtained by GC-MC-ICPMS.

Riedel de Haen), tribromobenzene (TBB) (Aldrich), tribromophenol (TBP) (Aldrich), bromochlorobenzene (Aldrich), dibromoethane (Aldrich). Solutions of brominated organic compounds in acetone (GC grade, Fluka) were used for the bromine isotope analysis. SRM 987 strontium reference material solution in concentration of 1 mg/l was used as an external spike. Obtained continuous signal for ^{86}Sr was about 3 V.

3. Results and discussion

Our approach for the precise bromine isotope ratio determination in the organic compounds was based on the using strontium as an external spike. Although strontium and bromine have significantly different first ionization potential, we justified 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 [9,10] in ^{87}Sr/^{86}Sr determination by MC-ICPMS analysis, we supposed that integration of this technique into the GC-MC-ICPMS analysis will improve the precision of the measurements.

The new approach is based on the simultaneous introduction of the brominated organic compounds by GC and continuous introduction of Sr solution via desolvation nebulizer into MC-ICPMS. This 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-ICP-MS techniques [11]:

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

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}Sr/^{86}Sr ratio and R_{true} is the recommended ^{84}Sr/^{86}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}Sr ion beam was corrected for isobaric interferences from ^{86}Kr. For this, the ion beam of ^{83}Kr was monitored and the measured intensity at mass 86 was corrected for the ^{86}Kr contribution using the ^{86}Kr/^{83}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 the signals of about 2 and 2.5 mV intensity for the m/z 79 and 81, respectively.

This background was subtracted from each peak on the point-by-point basis. To test a possible contribution of proton derived from the organic compounds into the formation of ^{81}ArArH trimer, m/z 81 signals were measured upon injection of 1 μl of acetone which was used by us as a solvent in the solutions of bromoorganic compounds. No meaningful additional contribution to the m/z 81 signal was detected during the 15 min GC run. Since amounts of the analytes injected into GC are negligible compared to amount of solvent, their contribution to ArArH trimer formation could be neglected.

We assumed minimal matrix effect in determination of bromine isotope ratio due to the gas chromatographic separation of analytes prior to the MC-ICPMS analysis.

In contrast to that, when aqueous solutions of bromine containing compounds (organic or inorganic) were introduced into the MC-ICPMS by conventional nebulization (PFA nebulizer and cooling spray chamber), unstable and relatively high background signals of about 5 and 15 mV were observed for the m/z 79 and 81, respectively. This background obviously resulted from the formation of hydrides in the system and does not enable to perform a precise bromine isotope analysis. The possible way to decrease this background is to introduce a sample via desolvation nebulizer. However, in the case of bromine analysis significant loss of the element was observed probably, due to formation of volatile compounds.

Representative chromatograms obtained for the mixture of the brominated organic compounds are shown in Fig. 2. Typically, the injection of 0.2 nmol of Br resulted in a signal of 1 V intensity with full width at half-height (FWHH) about 6–8 s for all brominated organic compounds used in this study. As we suspected, the linear correlation between the peak areas and the amount of injected samples was observed.

Different approaches for the integration of the transient signals were applied to calculate Br isotope ratio. Fig. 3 compares precisions (2σ) of the isotope ratio values referring to 80, 90 and 95%

Table 1
Instrumental parameters for the GC-MC-ICPMS measurement.

GC parameters	
Injector temperature	300 °C, splitless 1 min
Column	Ultra 2; 25 m × 0.2 m; film thickness 0.33 μm
Oven temperature	60 °C (1 min), 10 °C/min to 250 °C
He carrier flow	3 ml/min
Transfer line temperature	240 °C
MC-ICPMS parameters	
RF power	1200 W
Coolant flow	12 ml/min
Auxiliary flow	1.45 ml/min
Nebulizer gas flow	0.69 ml/min
Interface cones	Nickel
Instrument resolution	~300
Nebulizer	PFA 70 μl/min
Spray chamber temp.	75 °C
Desolvator temp.	160 °C
Sweep gas (argon)	5.45 l/min
Integration time	1 s

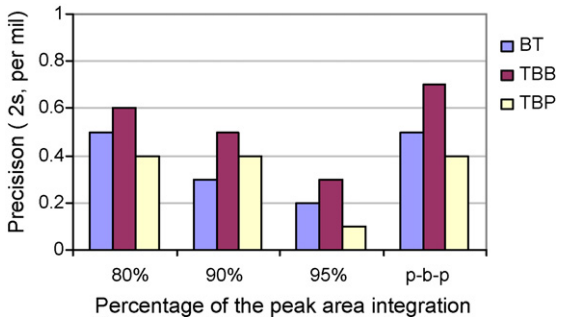

Fig. 3. Precisions for Br isotope ratio values of bromotoluene (BT), tribromobenzene (TBB), tribromophenol (TBP) using different integration approaches (acetone solution containing 1 nmol of Br of each organobromine compound was measured, $n = 3$).

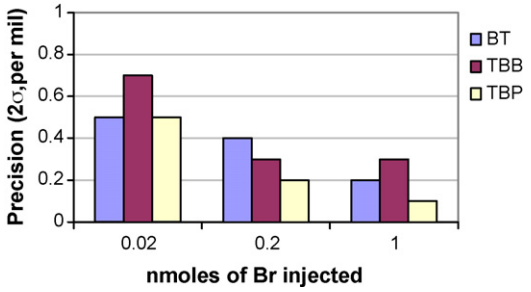

Fig. 4. Attainable precision (2σ) ($n = 3$) for Br isotope ratio of bromotoluene (BT), tribromobenzene (TBB), tribromophenol (TBP) versus injected amount of Br.

of the peak area as well as precision obtained using "point-by-point" (p-b-p) integration. As we observed, the best precision was achieved when applying integration of 95% of the chromatographic peak whereas the worse precision was obtained using "point-by-point" calculation. Therefore we decided to integrate 95% of the peak area for all Br isotope ratio measurements that we carried out in this work.

Precision (2σ) of the isotope ratio determination (corrected to Sr) of BT, TBB and TBP for signals equal to the 0.02, 0.02 and 1 nmol of Br are represented in Fig. 4. As could be seen from Fig. 4 precision of the measurements improved with the increase of the amount of bromine injected. Nevertheless the precision of the isotope ratio determination improved from 0.7‰ (2σ) for the 0.02 nmol of Br to 0.1‰ (2σ) for the signals representing 1 nmol of Br. It should be mentioned that higher standard deviations for the results were observed without correction to Sr. Thus attained precisions (2σ) for the signals representing 0.02 and 1 nmol of Br were 1.9‰ and 0.5‰, respectively.

The proposed analytical procedure was employed for Br isotope ratio analysis in a number of the industrially produced brominated organic compounds. Table 2 represents measured bromine isotope composition of the selected synthetic organobromine substances. Due to the lack of the available standard materials for bromine isotope ratio, accuracy of the results is still questionable. However, as it was postulated earlier by Eggenkamp and Coleman [5] in such cases reproducibility of the results, high yields and low blanks could serve the measures of accuracy.

In the present study measured values of Br isotope ratio were found independent on analyte and strontium concentration. This finding indicates the robustness of the used analytical method and points out usefulness of strontium correction.

Table 2
$^{81}Br/^{79}Br$ isotope ratio of analyzed synthetic brominated organic compounds ($n = 5$).

Compound	$^{81}Br/^{79}Br$–Sr corrected
3-Bromotoluene (Aldrich)	$(9762 \pm 1) \times 10^{-4}$
3-Bromotoluene (Riedel)	$(9763 \pm 2) \times 10^{-4}$
Tribromobenzene (Aldrich)	$(9768 \pm 3) \times 10^{-4}$
Tribromophenol (Aldrich)	$(9763 \pm 1) \times 10^{-4}$
Dibromoethane (Aldrich)	$(9744 \pm 4) \times 10^{-4}$
2-Bromochlorobenzene (Aldrich)	$(9759 \pm 2) \times 10^{-4}$

As could be seen from the results listed in Table 2, the isotopic variability for the brominated aromatic compounds (bromotoluene, tribromobenzene, tribromophenol and bromochlorobenzene) is very small and falls into the range of the standard deviations. A meaningful difference in Br isotope composition (about 2‰) of dibromoethane comparatively to the isotope composition of the brominated aromatic compounds was observed. We hypothesize that this variation results from the different synthetic routes used for the production of the compounds.

4. Conclusions

The new methodology for GC-MC-ICPMS analysis of bromine isotope ratio based on the simultaneous introduction of brominated organic compounds and strontium solution as an external spike into MC-ICPMS was developed. This study demonstrated that precision of the bromine isotope ratio analyses of brominated organic compounds by GC-MC-ICPMS could be improved through the use of Sr as an external spike. This study also demonstrates that choosing the right area integration strategy is critical to obtain the optimal precision.

Although an accuracy of the method is still questionable due to the lack of organic standard materials with known bromine composition, high precision of the analysis enables to investigate a bromine isotope fractionation in specific organic compound resulted from various biotic and abiotic processes. Despite the robustness of the proposed method proved by the independence of the bromine isotope composition values on the analyte and strontium concentration, additional work should be performed to validate method accuracy.

We believe that the proposed technique of measuring Br isotope composition by GC-MC-ICPMS gives a new opportunity to study the fate of brominated organic compound in the environment. Additional experiments applying the proposed techniques for Br isotope fractionation during abiotic and biotic environmental processes are in progress.

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