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Determination of boron isotope ratios by high-resolution continuum source molecular absorption spectrometry using graphite furnace vaporizers

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ABSTRACT

Boron isotope amount ratios n(^{10}B)/n(^{11}B) have been determined by monitoring the absorption spectrum of boron monohydride (BH) in a graphite furnace using high-resolution continuum source molecular absorption spectrometry (HR-CS-MAS). Bands (0 → 0) and (1 → 1) for the electronic transition $X^1\Sigma^+ \rightarrow A^1\Pi$ were evaluated around wavelengths 433.1 nm and 437.1 nm respectively. Clean and free of memory effect molecular spectra of BH were recorded. In order to eliminate the memory effect of boron, a combination of 2% (v/v) hydrogen gas in argon and 1% trifluoromethane in argon, an acid solution of calcium chloride and mannitol as chemical modifiers was used. Partial least square regression (PLS) for analysis of samples and reference materials were applied. For this, a spectral library with different isotopes ratios for PLS regression was built. Results obtained around the 433.1 nm and 437.1 nm spectral regions are metrologically compatible with those reported by mass spectrometric methods. Moreover, for the evaluated region of 437 nm, an accuracy of 0.15‰ is obtained as the average deviation from the isotope reference materials. Expanded uncertainties with a coverage factor of $k = 2$ range between 0.15 and 0.44‰. This accuracy and precision are compatible with those obtained by mass spectrometry for boron isotope ratio measurements.

1. Introduction

Boron is a naturally occurring element that can be found in several mineral forms in the earth crust [1]. This element presents two stable isotopes, ^{10}B and ^{11}B, with a natural abundance of 19.9% and 80.1% respectively [2]. It is due to their relatively large mass difference (~10%) that isotope fractionation leads to considerable isotope amount ratio variations n(^{10}B)/n(^{11}B) (hereafter referred as isotope ratios) in nature and in geological samples. These variations in the isotope ratio are expressed in δ^{11}B values relative to a standard reference material from the National Institute of Standards and Technology, NIST SRM 951a and natural variations can occur from −34.2‰ to +59.2‰ [3,4]. Therefore, variations in the isotope ratio due to isotope fractionation have been used as a proof of provenance of mineral [5,6] and biological samples [7,8], to estimate a contamination source [9] and to determine geological processes by erosion or subduction [10,11]. Additionally, boron is employed in the nuclear industry, because its isotope ^{10}B captures thermal-neutrons product of nuclear fission. Therefore, ^{10}B enriched boric acid solutions are used in the cooling system of thermonuclear facilities and in the alloying of steel and carbides for protective shielding [12]. Variations in the isotope ratio of boron in nuclear applications are therefore much higher than those found in natural environments.

Very small variations in the isotope ratios of boron have been routinely estimated by mass spectrometric methods with high accuracy and precision up to 1‰. These methods include multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [13], and thermal ionization mass spectrometry (TIMS), which so far is the most accurate method [14]. Additionally, inductively coupled plasma sector field mass spectrometry (ICP-SFMS) [15] and secondary ionization mass spectrometry (SIMS) [16] have been successfully documented. Variations in the sample introduction for isotopic analysis by MS methods like spark source (SS-MS), laser ablation ICP-MS and glow discharge (GD-MS) have been reported as well [17]. Further information about MS methods for determination of boron isotope ratios can be

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found in a recent review of Aggarwal et al. [18] Although atomic mass spectrometry dominates the field of isotope ratio analysis, alternative nondestructive methods like particle-induced gamma-ray emission analysis (PIGE) has been described [19].

In addition to mass spectrometric techniques, optical methods have been developed for the determination of the isotope composition of light elements like lithium and boron. Due to the relative wide mass differences of these elements and the mass dependency in transitions of the atomic energy levels, isotope effects have been observed in their atomic spectra [20–22]. For boron, the two main atomic absorption lines are shifted: at wavelength 249.8 nm (0.85 pm) and at 208.9 nm (2.5 pm) respectively. Therefore, using this principle, Hannaford et al. used graphite furnace atomic absorption spectrometry (GF-AAS) with two hollow cathode lamps, each of them enriched with one of the isotopes, for the estimation of the isotope amount in samples with an accuracy of 0.2% [23]. Later, Thangavel et al. report the determination of boron isotope ratios using Zeeman effect background correction by GF-AAS with comparable results to ICP-QMS and TIMS methods [24]. More recently, Wiltsche et al. developed a method using high-resolution continuum source flame atomic absorption spectrometry (HR-CS-FAAS), where they were able to determine the isotope composition of alloyed steel reference materials and boric acid by monitoring the isotope shift at the absorption line 208.9 nm of boron [25].

Isotope effects in molecular spectra are well known to be larger than those from atomic spectra, and specifically this is true for diatomic transient molecules, like those found in recombination processes during element atomization at high temperatures [26]. Russo et al. introduced laser ablation molecular isotopic spectrometry (LAMIS) for the determination of isotope ratio of boron and other elements like hydrogen, carbon, nitrogen, oxygen, chlorine, strontium and zirconium [27–29]. The emission spectrum of an analyte element from the laser induced plasma can be described as the spectra of the recombination of an analyzed element (X) with atmospheric nitrogen and/or oxygen to form a transient XN and/or XO molecule if the plasma is cooling down. If X has n isotopes, the resulting spectrum would be a linear combination of n isotopologues spectra and the amount of each component (isotope) can be estimated by a regression. The same principle was recently applied by Nakadi et al. by means of absorption spectrometry using a high-resolution continuum source graphite furnace molecular absorption spectrometer (HR-CS-GF-MAS) for the determination of chlorine $^{35}Cl/^{37}Cl$ and bromine $^{79}Br/^{81}Br$ isotope ratios by monitoring the isotopic shift on the molecular spectra of AlCl and CaBr respectively [30, 31]. The clear advantage of the latter analytical method is the lower instrumentation and operating costs in comparison with those for mass spectrometric techniques as well as the simplicity of its routine operation. Moreover, Resano et al. reported for the period of 2002 (introduction of the instrumentation) to 2014 the exponential increment of HR-CS-AAS/MAS publications in a review of scientific literature [32], including new applications of non-metal analysis [33] and isotope ratio analysis [30,31].

In this work, we explore the viability of HR-CS-MAS for the determination of boron isotope ratios by monitoring the molecular spectra of boron monohydride (BH) during its vaporization in a graphite furnace. To prove this concept, pure boric acid solutions were employed for this study. The results here are compared with those reported by mass spectrometric methods.

2. Experimental

2.1. Reagents and materials

A Milli-Q water purification system was used for water purification (Millipore gradient, Merck Millipore, Darmstadt, Germany) and ultrapure deionized water (18 MΩ cm) was employed for all dilutions. HNO_3 was purified by sub-boiling in PFA devices. A standard solution (Sample A) of 1 mg mL^{-1} of boron (Certipur®, Merck, Germany) was used for a temperature and gas flow program optimization. As chemical modifier, a 2 mg mL^{-1} solution of $CaCl_2$ in 1% HNO_3 was used and prepared by dilution of an appropriate amount of $CaCl_2$ (Emsure®, Merck, Germany) in 50 mL of water. A 5% (m/V) solution of D(-)mannitol (Merck, Germany) was made by dilution of 250 mg in 50 mL of water. A solution of 1% Triton® X-100 (Merck, Germany) was prepared by dilution in water. Enriched isotope spikes of ^{11}B and ^{10}B in form of boric acid solution 1 mg mL^{-1} were employed for $^{10}B/^{11}B$ ratios of 0.0; 0.25; 0.50; 0.70; 0.75; 0.80; and 1.0. For method validation, certified isotope reference materials from BAM (ERM-AE102a, ERM-AE103) and NIST (NIST SRM 951a) in form of boric acid were used. Isotope ratio of enriched ^{11}B and ^{10}B solutions and boron standard solution were determined by TIMS as previously described by Vogl et al. [34]

As primary gas, a Gas Mixture (A) of 2% (v/v) hydrogen with a 99.999% purity (N5.0) in argon N5.0 (Air Liquide, Krefeld, Germany) was used. Only for comparison, argon N5.0 (Air Liquide, Krefeld Germany) was employed as primary and secondary gas in some experiments. The following gas mixtures of halogenated hydrocarbons in argon N5.0 were used as secondary reactive gases during certain program steps: Gas Mixture (B) 1% (v/v) hydrogen N5.0 and 1% (v/v) chlorodifluoromethane N3.0 and Gas Mixture (C) 1% (v/v) trifluoromethane N5.0 (Air Liquide, Krefeld, Germany and GHC Gerling, Holz & Co. Hamburg, Germany).

2.2. Instrumentation

All measurements were carried out using a High-Resolution Continuum Source Atomic Absorption Spectrometer (HR-CS-AAS) contrAA 600 (Analytik Jena AG, Jena, Germany) with a transversely heated graphite furnace. The instrument is equipped with a 300 W xenon short-arc lamp operating in a hot-spot mode as a continuum source for wavelengths from 190 nm to 900 nm, a high-resolution double-monochromator, consisting of a prism pre-monochromator and an echelle grating monochromator equipped with a linear CCD-array of 200 pixels and spectral resolution of $\lambda/\Delta\lambda = 50{,}000$. Pyrolytically coated standard graphite tube with pin-platform (Analytik Jena, Part no. 407-A81.025) and a tailored autosampler (Analytik Jena AG, Jena, Germany) were used throughout this investigation. A detailed description of this instrumentation was made by Welz et al. [35]

2.3. Measurements

Prior to analysis, the graphite tube was permanently modified with a zirconium coating using 40 μL of 1% zirconyl chloride solution in 50% methanol and applying a similar temperature program to that listed in

Table 1
Optimized temperature and gas flow program for the BH vaporization in a graphite furnace.

Step	Temperature (°C)	Heating rate (°C s^{-1})	Hold time (s)	Gas flow	
				Primary gas[a]	Secondary gas[b]
Drying 1	80	6	20	Max	–
Drying 2	90	3	20	Max	–
Drying 3	120	5	10	Max	–
Pyrolysis	700	300	10	–	On
Auto zero	700	0	5	–	–
BH vaporization	2500	1000	18	–	–
Cleaning 1	2600	1000	4	Min	On
Cooling down	100	NP[c]	5	Min	On
Cleaning 2	2500	1500	4	Max	–
Cooling down	100	NP[c]	5	Max	–

[a] 2% H_2 in Ar (Max = maximal-gas flow 2.0 L min^{-1}, Min = minimal-gas flow 0.1 L min^{-1}).
[b] 2% CHF_3 in Ar (gas flow 0.5 L min^{-1}).
[c] NP: no power.