Estimation of boron isotope ratios using high resolution continuum source atomic absorption spectrometry

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ABSTRACT

In the production of ^{10}B enriched steels, the production–recycling process needs to be closely monitored for inadvertent mix-up of materials with different B isotope levels. A quick and simple method for the estimation of boron isotope ratios in high alloyed steels using high resolution continuum source flame AAS (HR-CS-FAAS) was developed. On the 208.9 nm B line the wavelength of the peak absorption of ^{10}B and ^{11}B differs by 2.5 pm. The wavelength of the peak absorption of boron was determined by fitting a Gauss function through spectra simultaneously recorded by HR-CS-FAAS. It was shown that a linear correlation between the wavelength of the peak absorption and the isotope ratio exists and that this correlation is independent of the total boron concentration. Internal spectroscopic standards were used to compensate for monochromator drift and monochromator resolution changes. Accuracy and precision of the analyzed samples were thereby increased by a factor of up to 1.3. Three steel reference materials and one boric acid CRM, each certified for the boron isotope ratio were used to validate the procedure.

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1. Introduction

High alloyed ^{10}B steel is used in the nuclear industry due to the high neutron absorption cross section of ^{10}B ($3.8 \cdot 10^{-25}$ m^2 compared to $5 \cdot 10^{-31}$ m^2 for ^{11}B) [1].

As the mass difference of the two naturally occurring boron isotopes ^{10}B and ^{11}B is about 10%, a correction factor for the total boron content has to be applied, if the boron isotopic ratio of the calibration standards does not match the samples.

Foremost amongst the methods for boron isotope determination is mass spectrometry.

Amongst the different mass spectrometry techniques thermal ionization mass spectrometry (TIMS) is used for high precision determination of the boron isotopic ratio [2].

Inductively coupled plasma quadrupole mass spectrometry (ICP-MS) provides a relatively fast method for the isotope ratio determination although instrumental mass discrimination and matrix induced mass discrimination affect the final result [3]. Memory effects of boron in sample introduction systems are well known and several approaches to circumvent this problem have been published [4–6].

Other mass spectrometric approaches for the determination of boron isotopic ratios are spark source MS [7] (SS-MS), high resolution glow discharge MS [8] (HR-GD-MS) and high resolution magnetic sector ICP-MS [9] (HR-SF-ICP-MS).

The determination of isotopic ratios is also possible by other means than mass spectrometry. For the very light elements H, Li, B the relative mass difference between the isotopes is large and due to the mass dependency of the Rydberg constant a shift of the wavelength of the peak absorption [13] occurs. Heavy elements show isotopic shifts too. These are caused by differences of the nuclear charge distribution. Edelson et al. used the isotopic splitting of ^{239}Pu, ^{240}Pu and ^{242}Pu for the determination of plutonium isotope ratios using ICP-OES [16].

Of the two major boron absorption lines the less sensitive 208.9 nm line has a considerably larger isotopic shift (2.5 pm) than the in the AAS commonly used 249.8 nm line (0.85 pm) [10]. The nature of the involved electronic transitions has been described by Burke [11].

Hannaford and Lowe [10] determined the isotopic ratio of amorphous and crystalline natural boron using a water-cooled sputtering cell and two hollow cathode lamps each containing only a single boron isotope. A simplified procedure to approximate boron isotope ratios by flame AAS (FAAS) using a conventional boron hollow cathode lamp is also described in this publication.

Recently Thangavel et al. [12] used Zeeman background correction graphite furnace AAS (GFAAS) for the determination of boron isotopic ratios and compared this method with ICP-MS and TIMS. The inherent limitation of this simplified procedure is the requirement of a constant total boron concentration (<5%) in both, the sample and the calibration solutions. In order to correct the isotopic ratio, according to Hannaford and Lowe and Thangavel et al., the total boron content must be known and should be determined at the boron line 249.8 nm which is not strongly affected by the isotopic composition.

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Table 1
Operation conditions for the HR-CS-FAAS.

Burner	5 cm with scraper for automatic burner cleaning after each sample
Fuel	C_2H_2 (230 L h^{-1})
Oxidizer	N_2O
Ratio C_2H_2/N_2O	0.544
Integration time	3 s
Number of detector illuminations within integration time	20
Replicates measured	6
Simultaneously recorded detector pixels	200 pixel
Resolution of the monochromator at 208.9 nm	1.3 pm/pixel
Instrument software version	ASpect CS 1.1.B (includes automated export of recorded spectra)

The production process of boron alloyed steel with up to 2% total boron is a challenging task. Amongst ferroboron and other ferroalloys different types of scrap are used as raw material. Out of the internal production route, a certain amount of high and low level enriched material has to be recycled. Unintentional mix-up of [10]B enriched material with natural or low [10]B materials tremendously increases reject costs.

To avoid such a mix-up during this recycling process a fast and cheap method for material identification according to the level of [10]B is desirable.

In this paper the application of a commercially available high resolution continuum source flame AAS (HR-CS-FAAS) for the rapid estimation of the B isotope ratios in highly alloyed steels is described.

2. Experimental

2.1. Instrumentation and operation conditions

All measurements were carried out on a ContrAA300 (Analytik Jena AG, Germany) HR-CS-FAAS. The operating conditions are listed in Table 1. A description of a monochromator equivalent to the one used in the ContrAA300 is given by Heitmann et al. [17].

2.2. Reagents and standards

Enriched boric acid was obtained from EaglePicher Technologies LLC (USA).

Except for Fe and B single element stock solutions (10 g L^{-1}, Specpure, Alfa Aesar, Germany) were used throughout. A 40 g L^{-1} Fe solution was prepared from Fe powder (pa, Merck, Germany), HCl and H_2O_2.

SRM 952 (Enriched Boric Acid Standard) was obtained from NIST (Gaithersburg, USA).

Milli-Q water (Millipore, Bedford, USA) was used throughout.

2.3. CRMs

As up to now no steel with a certified boron isotopic ratio is available, in house reference materials from Böhler Edelstahl GmbH and synthetic steel solutions spiked with NIST SRM 952 were used for method validation. The boron isotopic ratios in the Böhler reference materials were determined by Q-ICP-MS, MC-ICP-MS and TIMS prior to this investigation. The B isotopic ratios are given in Table 2 and the major constituents are given in Table 3.

Table 2
Reference material: B isotopic ratio (mean value ± standard error [19]).

	S20	S35	S97
Abundance of [10]B, %	19.85 ± 0.07	34.70 ± 0.09	97.07 ± 0.03
Total B, %	1.80 ± 0.05	1.84 ± 0.05	1.79 ± 0.05

Table 3
Reference material: informative values for matrix elements.

Element	Fraction, %
C	0.02
Cr	19.7
Fe	Balance
Mn	1.1
Ni	12.3

2.4. Sample decomposition

The steel sample (0.5 g) was treated with 10 ml HCl (36%, suprapur, Merck, Germany). After 10 min 2 ml HNO_3 (65%, suprapur, Merck, Germany) and 0.5 ml HF (40%, suprapur, Merck, Germany) were added and a microwave assisted sample decomposition was carried out as previously reported [14]. After digestion the solution was made up to a final volume of 50 ml.

Following an internal laboratory procedure suprapur grade acids were used. Acids of lower purity may also be used if no increase in the boron blank level is caused.

2.5. Calibration for isotope ratio determination

Aqueous calibration standards with different [10]B isotope ratios were made gravimetrically by mixing appropriate amounts of [10]B stock solution (500 mmol L^{-1} boric acid 99.71% [10]B, EaglePicher Technologies LLC, USA), [11]B stock solution (500 mmol L^{-1} boric acid 99.97% [11]B, Eagle Picher Technologies LLC, USA), Fe (40 g L^{-1}) and Ni (10 g L^{-1}, Alfa Aesar) stock solution, diluted to 50 ml with water. The total B concentration was kept constant in these solutions.

3. Results and discussion

3.1. Isotope shift

Johansson et al. [20] investigated the isotope shift of the boron UV2 multiplet at 209.0 nm. They report emission wavelength of 208.95898 nm for [10]B and 208.95650 nm for [11]B for the $2s^2 2p^2 P_{3/2}$–$2s2p^2\ ^2D_{5/2}$ transition used in this investigation.

Although the used HR-CS-FAAS instrument has a relatively high optical resolution compared to other currently commercially available atomic absorption or atomic emission spectrometers, the resolution of the monochromator is still not sufficient to obtain a full separation of the two boron isotope absorption signals as calculated by Hannaford and Lowe [10]. When plotting the absorption signal vs. the wavelength
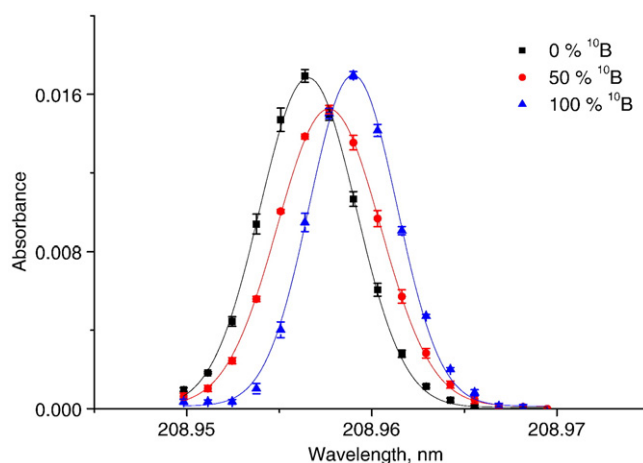

Fig. 1. Spectra and Gauss fit of three different isotope ratios; aqueous solution of boric acid; total B: 20 mmol L^{-1}; no spectral correction applied (error bars: standard deviation calculated from 120 individual spectra).