



Advancing the analytical capabilities of laser ablation molecular isotopic spectrometry for boron isotopic analysis



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ABSTRACT

Laser ablation molecular isotopic spectrometry (LAMIS) recently has been investigated for analysis of the boron isotopic composition in ambient air at atmospheric pressure. The initial precision of 100–400‰ (2σ) for the $^{10}\text{B}/^{11}\text{B}$ isotopic ratio was less than results obtained from other analytical methods like TIMS or ICP–MS. This paper describes how accuracy and precision for boron isotopic ratio using LAMIS can be improved to the few per mil level. Several optimization procedures, viz., spectral region of analysis, effect of flicker noise from matrix, spectral normalization and pre-treatment procedures, were studied. This paper reports a precision of 9‰ (2σ) for the $^{10}\text{B}/^{11}\text{B}$ ratio using alternative spectral normalization and pre-treatment procedures.

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1. Introduction

Existence of two naturally occurring stable boron isotopes (^{11}B and ^{10}B) was first reported by F.W. Aston as early as 1920 employing a Positive Ray Spectrograph [1]. Due to the presence of a relatively large mass difference (~9.48%) between the two isotopes, high mobility in aqueous media and high volatility, significant boron isotopic composition variations occur in nature ($\delta^{11}\text{B} \sim 90\%$; $\delta^{11}\text{B} = \{[(^{11}\text{B}/^{10}\text{B})_{\text{Sample}} / (^{11}\text{B}/^{10}\text{B})_{\text{NIST SRM-951}}] - 1\} \times 1000$) [2]. As per the IUPAC, the range of natural variation in boron isotopic composition is 18.927–20.337% for ^{10}B and 81.073–79.663% for ^{11}B [3]. The large natural $\delta^{11}\text{B}$ makes it a widely applicable signature or tracer element in geochemistry, isotope hydrology, oceanography, environmental sciences, etc. [4–13]. In addition to having large mass difference, ^{10}B has a very high neutron absorption cross-section of 3837 b, which has made it a crucial element for the nuclear power industry [14]. More precisely, natural or enriched boron is used in the primary coolant system of pressurized water reactors (PWRs) in the form of boric acid to control the reactivity in the core; as a control rod in the form of B_4C in pressurized heavy water reactors (PHWRs). Boron is also used as a source for the short range α particles in cancer treatment known as boron neutron capture therapy (BNCT) [15]. Depending upon the application, analytical methods for boron isotope analysis have been developed to permit the study of various types of samples with high accuracy and precision within the specifications of various instruments.

The most accurate and precise analysis of boron has been achieved by the use of thermal ionization mass spectrometry (TIMS), either PTIMS (positive-TIMS) or NTIMS (negative-TIMS) which allows isotope

ratio measurements to a precision of 0.5‰ (2σ) [16,17]. The precision can be further improved to 0.05‰ using a long analysis period of ~24 h [18–20]. Inductively coupled plasma quadrupole mass spectrometry (ICP–QMS) has much faster throughput than TIMS and does not require complete purification of boron. The tradeoff of the ICP–QMS is 14‰ (2σ) precision compared to 0.5‰ (2σ) with TIMS and the results highly depend on the matrix composition [21]. ICP–QMS precision can be increased to 1‰ (2σ) by applying common analyte internal standardization (CAIS) chemometric technique using $^6\text{Li}/^7\text{Li}$ [22]. Multiple collector inductively coupled plasma mass spectrometry (MC–ICP–MS) has been used effectively for boron isotope ratio measurements with precision of 0.2‰ [21]. However, there is an inherent memory problem in ICP for boron analysis and the presence of a significant background in ICPMS that restricts sample handling to only a few nanograms of boron [6]. Several other mass spectrometric methods also have been applied for boron isotopic analysis. A complete evaluation of different mass spectrometric techniques can be found in Aggarwal and Palmer [23]. Briefly, Chaussidon et al. used secondary ionization mass spectrometry (SIMS) for analyses of boron directly in solid with a precision of 4‰ (2σ) [24]. Lukaszew et al. used spark source mass spectrometry (SSMS) with a precision of 100‰ (2σ) [25]. Manoravi et al. utilized an in house laser–RTOF mass spectrometry system for direct determination of boron isotopic ratios in irradiated B_4C pellets of control rod of nuclear reactor with a precision of 50‰ (2σ) [26].

The ability to perform online and remote analysis is one of the great advantage of emission based spectroscopic (i.e., emission or fluorescence) measurement technique over mass spectrometry. Though mass spectrometric techniques are widely used for boron isotopic analysis, atomic/ionic emission spectroscopic boron isotopic analysis has not been widely reported in the literature [27]. Optical methods can be applicable for elements which have a significant isotopic shift in their

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emission line spectra. In the case of boron, the isotopic shift of ^{11}B relative to ^{10}B for the main resonance lines at 249.7 nm and 208.9 nm is +0.00085 nm and -0.0025 nm respectively [28]. Due to the small isotopic shifts, traditional emission spectroscopic methods are generally not suitable for isotopic analysis of boron. To the best of our knowledge, there is only one report by Zolfonoun et al. on the application of ICP-optical emission spectrometry (OES) for the determination of boron isotopic ratio using multivariate curve resolution with alternating least squares (MCR-ALS) algorithm. Using a spectral resolution of 3 pm, the method yields a precision of 11.8% (2σ) [27].

Isotopic shifts in molecular emission can be orders of magnitude larger than that observed in atomic/ionic spectra [29]. Zhiglinskii and Kochemirovskii in 1963 applied this concept of molecular isotopic shifts for the determination of boron isotopic composition by studying the BO molecular band emitted from a hollow cathode tube [30]. Zakorina et al. used the same principle to calculate the boron isotopic ratio in a high-frequency electrode-less discharge with gaseous BF_3 introduced into the discharge tube [31]. Both papers report a relative random error of 100–200% (2σ). Niki et al. in 1998 demonstrated the possibility of using laser induced breakdown spectroscopy (LIBS) for the determination of boron isotopic ratio with an ~5% tolerance limit by monitoring the BO molecular band isotopic splitting [32]. The concept of molecular isotopic shifting in BO for standoff applications came in 2011, when Russo et al. showed the application of molecular emission generated from a laser induced plasma for isotopic analysis, known as laser ablation molecular isotopic spectrometry (LAMIS) [33,34]. Both reports showed 20–90% (2σ) precision on the determination of ^{11}B percentage composition, which propagates to 100–400% (2σ) precision for the $^{10}\text{B}/^{11}\text{B}$ isotopic ratio. Yee et al. recently reported a similar study using femto-second LAMIS of boron with ~60% (2σ) precision on the determination of ^{10}B percentage composition [35], which propagates to 125% (2σ) precision for the $^{10}\text{B}/^{11}\text{B}$ isotopic ratio. The error propagation equation is discussed in Appendix A.

LAMIS involves the initiation of an optical emission source (laser-induced plasma) by laser ablation, and monitoring the molecular emission as the plasma expands and cools. The method has several advantages over other methods discussed above for determination of boron isotopic composition; such as, real time analysis at atmospheric pressure, no sample preparation, no consumable, opens path standoff measurements, direct solid analysis etc. But the initial reported precision of the method was less competitive with results obtained from traditional methods like TIMS, MC-ICP-MS or ICP-QMS.

The present manuscript reports a detailed discussion on the advancement of LAMIS to achieve <10% (2σ) precision for boron isotopic ratio analysis. The influence of spectral emission region and matrix effects is studied and reported in the manuscript. Different spectral pre-treatment methods before analysis with the PLSR algorithm were carried out. The manuscript also discusses the effect of spectral data accumulation on the precision of the method.

2. Instrumentation and measurements

A 1064-nm Nd:YAG laser, with pulse width of 5 ns and energy of 40 mJ, was focused onto a sample surface with a fused-silica lens to a measured spot diameter of approximately 475 μm . The plasma molecular emission was collected through a fused-silica lens onto the entrance of an optical fiber bundle coupled to a Czerny–Turner spectrometer (focal length = 1.25 m) (Horiba JY 1250M) with an intensified charge-coupled device (ICCD) (Princeton Instruments, PI MAX 1024 Gen II) as detector. The grating, with groove density 1200 per mm was used and the corresponding measured spectral resolution was ~35 pm full width at half maxima (FWHM). The detection system provides a spectral window of 16 nm. Operating parameters of the ICCD were as optimized in our previous work; acquisition delay of 4 μs and a gate width of 30 μs [34]. The gain of the ICCD (Unigen II intensifier) was set at 200.

Calibration of BO molecular spectra was carried out with in-house partial least squares regression (PLSR) algorithm written in LabVIEW (LabVIEW 2012, National Instruments). The algorithm used in this study is the same as previously described [36,37]. To correlate boron isotopic abundance to the relevant reference molecular spectra, a PLS regression coefficient matrix was calculated. For unknown boron isotopic abundance samples, a mathematical inversion of the pre-computed PLS coefficient matrix was applied to its spectra to determine the isotopic composition of the unknown sample.

3. Sample preparation

Certified enriched $^{10}\text{B}_2\text{O}_3$ (99% ^{10}B) and $^{11}\text{B}_2\text{O}_3$ (99.62% ^{11}B) powders were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). For preparation of isotopic standards, weighted amounts of the two enriched B_2O_3 samples were mixed in a ball mill and then pelletized by pressing them with 7 ton pressure for 4 min into 1 cm diameter pellets. Five standards were prepared with ^{11}B isotopic abundance of 1, 20, 50, 80, and 99.62%. Boron nitride (BN) pressed-powder disks with natural isotopic abundance were also used in the study. The BN disks were commercial sputtering targets designed for film deposition in the electronics and optical industry (Alfa Aesar, 99.99% purity).

4. Results and discussion

4.1. Wavelength region of analysis

BO molecular emission originates from four electronic transitions, $\text{C}^2\Pi_{(f)} \rightarrow \text{X}^2\Sigma^+$ (band origin, $\nu_{00} = 181$ nm), $\text{B}^2\Sigma^+ \rightarrow \text{A}^2\Pi_i$ ($\nu_{00} = 519$ nm), $\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+$ ($\nu_{00} = 233$ nm) and $\text{A}^2\Pi_i \rightarrow \text{X}^2\Sigma^+$ ($\nu_{00} = 422$ nm) [38]. The $\text{A}^2\Pi_i \rightarrow \text{X}^2\Sigma^+$ transition is the most intense and was used in this study. A recent study from this group showed that the prediction capability of PLSR calibration for LAMIS depends on the molecular isotopic shift of vibrational bands and their respective intensities in the emission wavelength region used for analysis [36]. To demonstrate the spectral band influence in this paper, LAMIS spectra with 30 laser shots accumulation were recorded in the 300–700 nm wavelength region using a BN sample (Fig. 1). Several vibration bands of the $\text{A}^2\Pi_i \rightarrow \text{X}^2\Sigma^+$ transition are visible in the laser plasma, which makes the 300–700 nm region a very molecular emission rich spectrum. The relative intensity of these bands depends on their Frank-Condon Factor (FCF) [39]. Comparing Fig. 1 and the FCF values of different vibrational bands with the degree of isotopic shift in the respective bands, four wavelength regions were selected for construction of the PLSR calibration curves, viz., (a) 434–448 nm, (b) 466–478.5 nm, (c) 503.5–516.5 nm and (d) 555.5–568.5 nm. These four regions have the

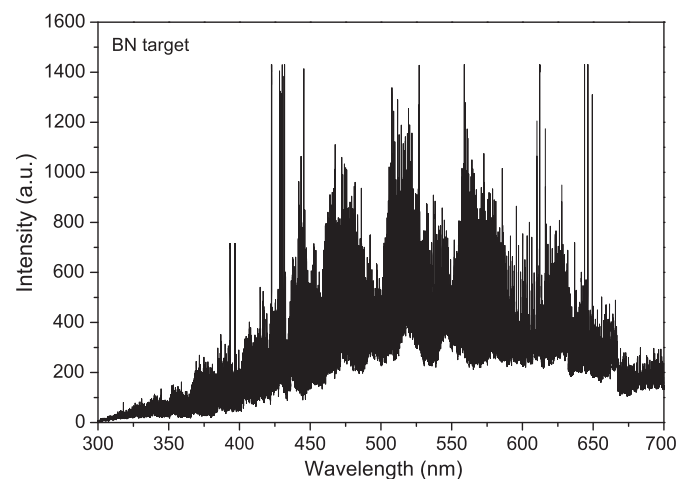


Fig. 1. 30 laser shot accumulation LAMIS spectrum of BN.

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