



Measurement of boron isotopic ratio with non-gated molecular spectroscopy of femtosecond laser-produced plasma

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ABSTRACT

Laser-induced breakdown spectroscopy can be augmented by concurrent spectroscopic measurements of molecules and molecular ions resulting from recombination of laser-ablated plasmas with the ablated sample and surrounding environment. Molecular emissions can exhibit significantly greater isotopic shifts than atomic emissions, making this approach attractive for isotopic characterization of nuclear materials. We describe a measurement of boron isotopic ratios in four boron-containing samples utilizing the emission from boron monoxide radicals formed in the expanding laser-induced ablation plume. Femtosecond laser excitation is used and the emission in the 532–540 nm region of interest is studied, where a linear superposition of characteristic spectra for two boron isotopes has been applied for reconstruction of the boron isotopic ratio. It is also demonstrated that the use of non-gated measurements of emission spectra suffices for accurate isotopic characterization using this method. The application of multivariate regression to deconvolve the isotopic ratio from the measured emission spectra is discussed in detail, including the limitations and subtleties of this approach.

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1. Introduction

Isotopic analysis is a critical component of material characterization in many areas of research, industry, and security. Some examples include determining the geographic origin of drug samples [1], doping detection in sports [2], hydrology studies [3], and carbon dating of paleontological artifacts [4]. Notably, isotopic ratio measurement plays a pivotal role in nuclear forensics. For example, the relative abundances of the U^{234} , U^{235} , U^{236} , and U^{238} isotopes in uranium samples provide information on the intended use of the material (e.g. nuclear power vs. nuclear weaponry), its production process, and its history of neutron irradiation [5]. This isotopic information would aid law enforcement officials in attributing intercepted material or collected post-detonation debris to their sources [6], allowing for a prompt and appropriate response.

It is worth considering the potential of laser-induced breakdown spectroscopy (LIBS) for performing isotopic measurements. LIBS is a minimally destructive material characterization technique with inherent and widely demonstrated in-situ capabilities. Numerous prior studies have highlighted its remote analysis capability [7], especially in harsh, inaccessible environments, such as the interior of a steel furnace [8], the steam generator tubes in a nuclear reactor [9], and even the

Martian surface [10]. Unlike ionizing radiation detectors, LIBS can be used to analyze the composition of nonradioactive materials. This feature can be of significant value in nuclear forensic applications.

Recent studies [11–14] have demonstrated the extension of LIBS to isotopic analysis through a technique termed laser ablation molecular isotopic spectroscopy (LAMIS). A major obstacle to performing spectroscopic analysis with good isotopic sensitivity has been the relatively small isotopic shift of atomic emission lines, as the variation in the number of neutrons in a nucleus usually has minimal effect on electronic transitions [11]. This isotopic shift is frequently smaller than the Stark broadening of the emission lines. The issue of relatively large Stark broadening obscuring the isotopic shift at ambient pressure can be addressed by collecting and analyzing molecular emission spectra, in addition to the usual collection of atomic emission spectra in LIBS. In recent work by R.E. Russo et al. [11–13] and H. Niki et al. [14], the molecular emissions of diatomic radicals exhibiting various isotopic compositions have been studied. These radicals can originate directly from the sample and/or from plasma assisted chemical reactions as plasma expands into the surrounding air rich in nitrogen and oxygen. Diatomic oxides have been of particular interest [11]. This approach thus circumvents the requirement for vacuum ambient conditions normally required for LIBS isotopic analysis. In fact, presence of ambient gas for the formation of radicals can even be required if the reactants are not already present in the sample [11]. The improvement of the capability to measure isotopic abundance using molecular emission spectra compared to the use of atomic emission spectra arises from the stronger dependence of molecular energy levels on nuclear masses compared to atomic energy levels. [11].

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Extensive use of detectors with ability to provide time gating on the order of ns, such as intensified CCDs (iCCDs), is common in LIBS. Recent experiments that relied on the analysis of molecular emission spectra have also utilized iCCDs [11–14]. Laser-induced plasmas exhibit several stages of emission, with the first being continuum emission resulting from recombination of free electrons with atoms. These continuum emissions generally do not provide useful information on the ablated material composition and, instead, can reduce the signal-to-noise ratio for desired discrete atomic or molecular emissions in time-integrated spectral measurements. When ns-pulsed lasers are used, intensified detectors with gate widths on the order of a few nanoseconds are needed to effectively reject the continuum emissions that dominate in earlier stages of plasma evolution. Recent studies, however, have shown that the use of fs pulses in LIBS results in reduced continuum emissions compared to the use of ns or ps pulses [15–20]. As a result of the short time-scale of their interaction with targets, fs pulses can perform ablation without subsequently heating the induced plasma, which would normally further increase the continuum background emission [21].

Although non-destructive methods are usually an order of magnitude less accurate than destructive methods [22], it has been shown that molecular emission spectra can be used to measure isotopic ratios to within 1–5% accuracy [11–14]. Current techniques such as ICP-MS and radiochemical separation methods can take up to a week or a month to perform [6]. In contrast, a laser ablation-based spectroscopic system, using the aforementioned mobile capabilities, can provide nearly instantaneous measurements in the field. While other (destructive) techniques can lead to greater accuracy, the field of nuclear forensics can significantly benefit from the rapid analysis available with this technique, even at the present level of accuracy.

Here we demonstrate that the measurement of isotopic ratio of boron using fs LIBS of molecular emission spectra is feasible even without the use of fast time-gated detectors, as a result of reduced continuum emission when fs pulses are used. We further demonstrate by the use of boron carbide samples that isotopic ratio measurements can be performed solely on the basis of oxide radicals formed from the interaction of the plasma with air, without the need for oxide presence in the sample. The choice of element and compound for this study was made based primarily on convenience, as enriched boron carbide targets are readily available, and emissions from the boron monoxide radicals have been thoroughly studied in the past. It is worth noting, however, that the isotopic composition of boron has great significance in the nuclear industry, where boron carbide is used in nuclear reactors as a control rod material, in radiation shielding, and in radiation detection applications. The ^{10}B isotope has a much greater absorption cross section for low-energy neutrons than the more abundant ^{11}B isotope. Ultimately, we believe that the method and analysis presented can easily be extended to many other elements.

Methods of linear regression are discussed in the context of analysis of our spectral data. Simpler, discrete multivariate regression methods are compared to a new continuous alternative suggested by Nielsen et al. [23] A brief description of Nielsen's continuous multivariate method, as well as a comparison of the advantages and disadvantages of the two methodologies for analysis of the spectral data, are presented.

2. Experimental setup and procedure

A 10-Hz Ti:sapphire chirped-pulse amplification laser system (Amplitude Technologies Trident) was used to produce pulses at a center wavelength of 800 nm, shaped temporally by a Fastlite Dazzler T3 acousto-optic pulse shaper. The pulse duration for this study was measured by single-shot autocorrelation to be ~ 42 fs. Laser pulses are focused onto the sample with a 300-mm lens and the plasma emission is collected with a 100-mm diameter collection lens at an angle of 45° with respect to the incident pulse. The collected pulses are focused and diverted in standard atmospheric conditions into a 0.55-m HORIBA iHR 550 Czerny-Turner spectrometer operating with a

1800 g/mm grating and slit width of 30 μm . While a scanning measurement of the spectrum is also possible, single-shot measurement of spectrum using a segmented detector is more desirable and is therefore adopted in our setup. An attached HORIBA Synapse time-integrated CCD produces an image with a resolution of ~ 0.02 nm. We note that this is significantly better resolution than needed to resolve molecular isotopic shifts, which can be on the order of nm [11], but insufficient to reliably resolve atomic isotopic shifts, which can be smaller by more than one order of magnitude [11].

A motorized three-axis translation stage is used to remotely translate the sample and expose fresh sample spots to the laser pulse. Reported spectra are averaged over 20 individual CCD images, with each image integrated over a 1020 ms interval (10 ablation shots at ~ 10 Hz). A LabVIEW interface, through a delay generator, allows for proper timing between the laser pulse, the laser shutter, the CCD camera, and the automated stage translation. Before the collection of spectra at each position, two "cleaning" shots, in addition to the 10 imaged ablation shots, are applied to the sample to reduce the effect of potential surface contamination. The automated data acquisition process is triggered on a pulse derived from the laser system. The shutter is then opened long enough to permit exactly 12 consecutive shots to pass to the sample, and the CCD camera is triggered such that data collection from the first two cleaning shots is not recorded. After the stage is translated, the process is repeated on a fresh spot of the sample surface.

Two 1-cm thick B_4C targets (Ceradyne), with ^{10}B enrichments of 50.37% and 97.35% (at. %), and a 4-mm thick hot-pressed B_4C sputtering target (Goodfellow), with 19.9% ^{10}B (natural, at. %), were ablated. Furthermore, an uncertified, nonradioactive B_4C sample originating from the Penn State's Breazeale Reactor was used in our case study. Pulse energies used in the experiments were $0.99 \text{ mJ} \pm 2.1\%$ for the measurement of the Ceradyne samples, $0.94 \text{ mJ} \pm 1.5\%$ for the natural sample, and $0.97 \text{ mJ} \pm 1.4\%$ for the uncertified reactor sample.

3. Experimental results and analysis

3.1. Collected spectra

The spectra collected from the four B_4C samples are shown in Fig. 1. Each spectrum shown has been obtained by summing the spectra measured at 20 sample spots (a total of 200 ablation shots). Background subtraction and filtering have been applied to the measured spectra. We first directly measure the background spectrum taken when the laser pulse is blocked, and subtract it from each individual spectrum measured. Subsequently, the broadband continuum emission is removed using a discrete low-pass Fourier filter, which is applied on each individual background-subtracted spectrum. As a result of application of Fourier filtering, the filtered spectral intensity can be negative. The vertical dotted lines in Fig. 1 highlight the emission lines where the differences in line intensities are particularly apparent for the three enrichments studied.

We originally sought to utilize the 579–584 nm spectral region, where successful studies were performed in the past [11–13]. However, the relatively high continuum background we observed in this region when making time-integrated measurements led us to consider other parts of the spectrum. We chose the 532–540 nm spectral region for our analysis on the basis of the experimentally observed greater ratios of intensities of discrete spectral lines to continuum background and significant differences among the spectra of samples with different enrichments. For many of the isolated peaks present in the spectra, their intensities generally scale linearly with the ^{10}B abundance. For example, the peak near 538.4 nm is likely associated with ^{10}BO . Its intensity is approximately halved in the sample containing 50.37% of ^{10}B when compared to the sample containing 97.35% of ^{10}B . Similarly, in the sample containing natural boron, intensity of this peak is reduced to approximately one-fifth of that present in the 97.35% ^{10}B sample. On the other hand, the peak highlighted at approximately 538.1 nm is likely

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