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Analytical Note

Boron isotopic measurements from spectrally filtered non-gated molecular spectra induced by laser ablation

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ABSTRACT

Spectral analysis of molecular emissions from laser-produced plasmas can augment laser-induced breakdown spectroscopy measurements, in which only atomic spectra are typically considered. Molecular isotopic shifts can be significantly greater than the respective atomic isotope shifts, enabling isotopic measurements with lower spectral resolution and in atmospheric pressure conditions. Successful isotopic measurements using molecular spectra have been made in the past by gating off the atomic emissions, or by the use of a femtosecond laser in conjunction with a non-gated detector. We report that it is possible to make accurate isotopic measurements by use of molecular emissions from non-gated spectral data even when nanosecond lasers are used. We demonstrate this capability by measuring the isotopic composition of boron-containing samples using 10-ns, 1064-nm pulses from an Nd:YAG laser and a non-gated detector. We investigate how the accuracy and precision of the multivariate calibration model used in the isotopic reconstruction is influenced by the spectral data analysis. The effect of the selection of the spectral region of interest for analysis and the optimization of a numerical spectral filter is studied. It is shown that the accuracy of isotopic reconstruction can be greatly improved by spectral filtering, and that it is relatively insensitive to laser pulse duration.

Recently, laser-induced breakdown spectroscopy (LIBS) capabilities have been extended to include measurements of optical spectra from molecular species in the laser-produced plasma for isotopic analysis [1–4]. Laser ablation molecular isotopic spectrometry (LAMIS) considers the contribution to optical emission originating from molecular excitations, with measurements typically performed in ambient atmosphere. Relatively large isotopic shifts can be present in molecular emission spectra, which can reduce the spectral resolution requirements in isotopic measurements. Intensified CCD detectors (ICCDs) with the ability to provide temporal gating, on the order of ns, are usually used to reject the broadband continuum and atomic emissions from the plasma that dominate at earlier measurement times. This enables an increase of the signal-to-noise ratio of molecular signals that contain both elemental and isotope-specific information. It has been shown recently that the use of non-gated measurements of emission spectra suffices for accurate isotopic characterization when femtosecond (fs) laser pulses are used [5]. The analysis method described in Ref. [5] has been reinvestigated to demonstrate that high-accuracy isotopic characterization is possible even when using nanosecond (ns) laser pulses and non-gated detectors. Our results are obtained from measurements of four boron carbide (B_4C) samples with a range of ^{10}B enrichments. Spectral data filtering has been previously used to improve the performance of multivariate calibration [6,7] and has also been employed and extended in this study. We compare the performance of two types of spectral filters and show that their use can significantly improve the accuracy of isotopic measurements. The results of the analysis are described for three spectral ranges in which high-accuracy calibration and reconstruction of boron isotope content was achieved.

We also compare the performance of our analysis method when ns and fs pulses are used. Ns lasers are most commonly used in LIBS measurements since they are simpler to operate and more accessible. Since different physical mechanisms govern the ablation process for ns and fs pulses, this could result in different characteristics of acquired spectra. For fs pulse duration, ablation is considered to be a direct transition from solid to plasma; for ns duration, reheating of the plasma can cause an increase in the broadband continuum emission and consequently a decrease of the signal-to-noise ratio. Prior studies have shown that the magnitude of continuum background in the ns regime can be several times greater than in the fs regime [8]. The results of the study reported here could contribute to the development of an effective LIBS system capable of isotopic analysis using molecular emissions with a ns laser source and a lower-cost detector.

A detailed description of our experimental setup and its performance has been presented elsewhere [9], and here we summarize its main characteristics. The fs experiments are carried out using a Ti:sapphire chirped-pulse amplification laser system (Amplitude Technologies), operating at 800 nm and producing 40-fs pulses at a repetition rate of 10 Hz. For ns experiments in this study we use an Nd:YAG laser (Spectra Physics Quanta-Ray) with a central wavelength of 1064 nm, pulse duration of 10 ns, and a repetition rate of 10 Hz. The pulsed laser beam is focused normal to the surface of

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the target using a 25-mm diameter lens with a 300-mm focal length. The light emitted from the plasma is focused onto the entrance slit of a 550-mm spectrometer (Horiba Jobin Yvon) using an 1800 grooves/mm grating. Emission from the plasma is detected using an open-electrode charge-coupled device (CCD, Horiba Jobin Yvon), with no ability to provide fast gating. A LabVIEW-based data acquisition system has been developed to provide the experimental timing through the interface to a delay generator (Stanford Research Systems), which triggers the laser control unit, a mechanical shutter, and the CCD camera. A motorized translation stage is also interfaced to LabVIEW and provides automated sample translation during data acquisition.

The spectra acquired in this study are averaged over 20 individual CCD images, with each image integrated over a 1020-ms interval (12 ablation shots at ~10 Hz, with two initial shots used for cleaning the sample surface prior to spectral acquisition and not included in data analysis). Two B_4C targets (Ceradyne), with ^{10}B enrichments of 50.37% and 97.35% (at.%), and hot-pressed B_4C sputtering target (Goodfellow), with 19.9% ^{10}B (natural, at.%), were ablated. A previously uncertified, nonradioactive B_4C sample originating from the Penn State's Breazeale Reactor was also used in our study. A separate, independent measurement by Ceradyne Inc. using inductively coupled plasma-mass spectroscopy indicated the ^{10}B abundance in our unknown sample was 88.33%. A continuous method of linear regression was used to analyze the collected spectral data [10].

Plasma emission was acquired from three spectral regions in both the fs and ns experiments. The results for the ns study were obtained using ~5 mJ laser pulses with an energy fluctuation of 1.8%, while the fs study utilized ~1 mJ laser pulses with 1.5% energy fluctuation. Sample experimental data is shown in Figs. 1 and 2. The background signal was collected while blocking the beam, which allowed the contributions of electronic noise and ambient light to the background to be separately subtracted.

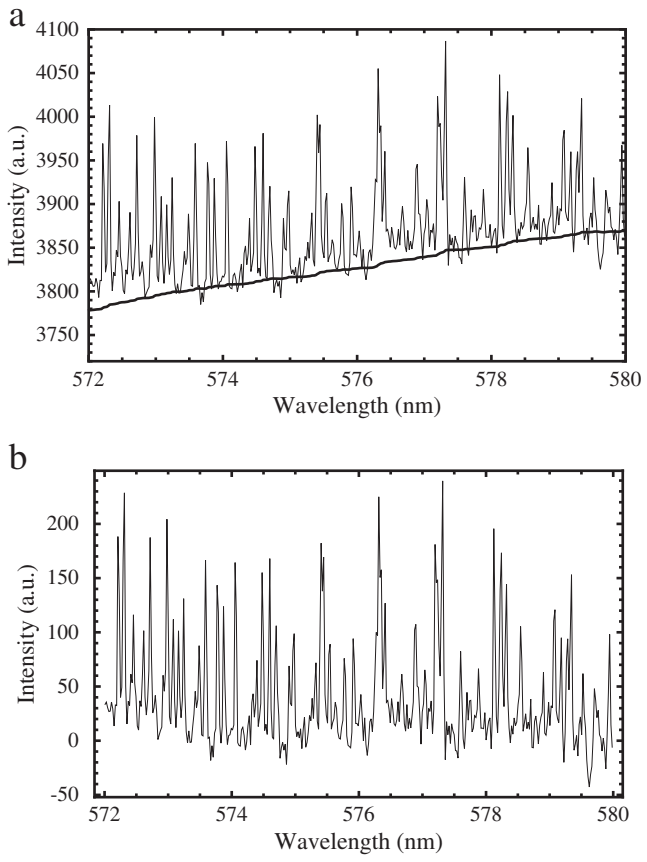

Fig. 1. Example of (a) an original fs spectrum with fitted baseline (thick line) and (b) spectrum after baseline removal when Filter 1 ($\alpha = 0.009$) is used for continuum suppression in spectra from the boron carbide sample with 97.35% ^{10}B abundance.

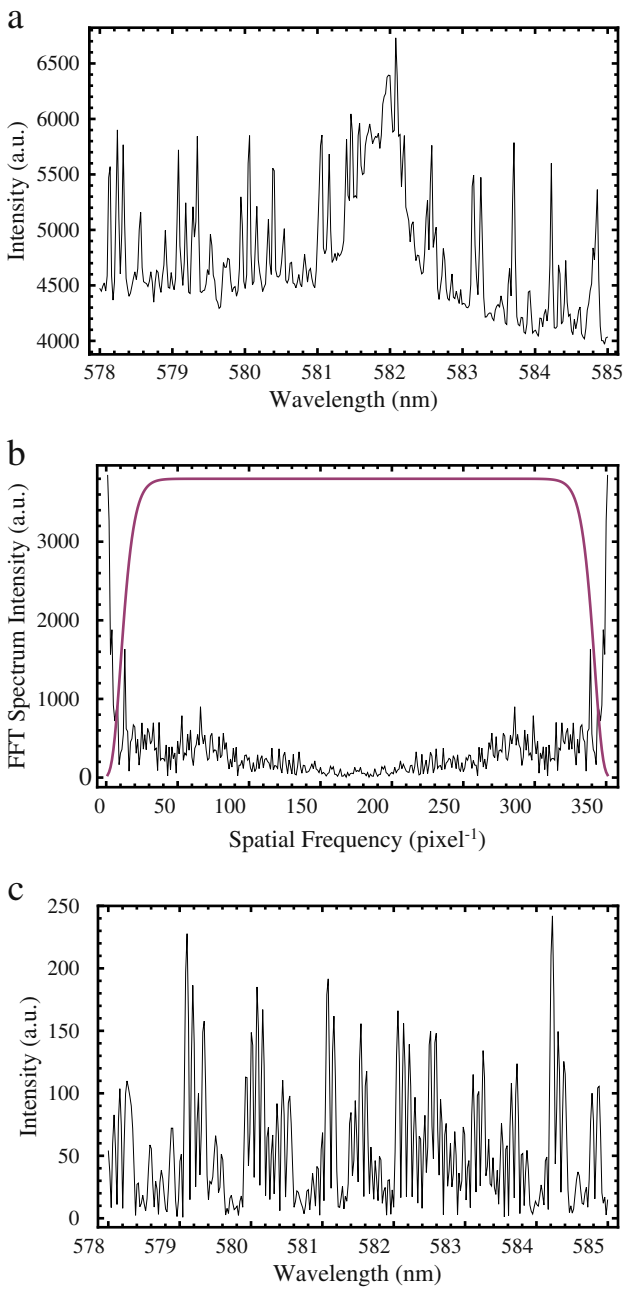

Fig. 2. Example of (a) an original ns spectrum from the boron carbide sample with 97.35% ^{10}B abundance. (b) Discrete Fourier filter of the spectrum in (a) (zero frequency component not shown) and the Filter 2 transfer function (thick line) with $f = 72.9\%$, and (c) filtered spectrum after Filter 2 is applied.

A discrete low-pass noise filter was used to smooth the slow-moving fluctuations in the signal (Filter 1). This filter utilizes the similarity in intensities of neighboring spectral samples, measurements of spectra at discrete wavelengths corresponding to CCD pixels on the detector, to suppress the variations in the continuum background. For a set of spectral samples ($i = 2, 3 \ldots n$), the algorithm

$$output[i] = \alpha\, input[i] + (1-\alpha) output[i-1] \quad (1)$$

returns a vector with reduced differential between adjacent points, effectively smoothing the original signal. The *input* is a vector of raw