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Matrix effects in laser ablation molecular isotopic spectrometry

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ABSTRACT

Recently, it has been shown that laser-induced breakdown spectroscopy (LIBS) can be used for the detection of isotopes of elements via isotopic shifts in diatomic species in a technique known as laser ablation molecular isotopic spectrometry (LAMIS). While LAMIS works quite well for isotopic analysis of pure compounds under optimal conditions, it is desirable for it to be applicable for a variety of compounds and matrices. However, the LIBS plasma emission associated with LAMIS depends on several parameters, including the applied electric field of the laser pulse, the physical properties of the material being investigated, and the presence of additional elements other than the element of interest. In this paper, we address some of the pitfalls arising from these dependencies when using LAMIS for the determination of the relative isotopic abundance of boron-containing materials with varying chemical matrices.

1. Introduction

Investigation of the isotopic composition of simple molecules dates back to the earliest days of molecular spectroscopy. Mulliken performed isotopic analyses of boron oxide (BO) using analysis of vibronic emission spectra in 1925 [1], while Jenkins et al. performed one of the first relative abundance analyses on the same molecule using both rotational and vibrational features [2]. Other studies of optical spectra of molecular isotopologues such as metal hydrides [3], silicon hydride [4], copper halides [5], iodine monochloride [6], carbon monoxide [7], and many other molecules containing isotopes of lower natural relative abundances were later demonstrated. These later analyses utilized microwave and infrared spectroscopy to obtain rotational and vibrational emission spectra produced from chemical reactions, thermal desorption, electrical breakdown, and a variety of other vaporization/ionization methods of vapors or gases [8].

Although spectroscopists were aware of the molecular isotopic composition influence on the rotational, vibrational, and electronic spectra in these studies, most experiments were not designed to precisely measure the relative abundance of isotopes. Instead, only molecules made of the isotopes of the highest abundances for a given element were studied without enrichment because the major isotope makes up more than 92% of all atoms for most lighter elements [9]. For the inquiry of lower abundance isotopologue spectra, chemicals were enriched in the lower abundance isotopes to help elucidate spectroscopic parameters such as vibrational force constants or rotational constants [10–12]. However, the 19.9% and 80.1% natural abundances of ^{10}B and ^{11}B and the 76.8% and 24.2% natural abundances of ^{35}Cl and ^{37}Cl occurred in proportions such that multiple isotopes could be studied simultaneously without enrichment or purification. As a result, the ratio of intensities of features in optical spectra of isotopologues of boron and chlorine compounds was sometimes used to justify assignments of transitions, thereby not only showing an early awareness of relating optical spectra back to relative abundances of isotopes but also demonstrating the limitations of utilizing the information from isotopologues below a certain abundance threshold [13,14].

More recently, a method called laser ablation molecular isotopic spectroscopy (LAMIS) seeks to expand this use of optical emission for the determination of the relative abundance of isotopes in a sample via laser-induced breakdown spectroscopy (LIBS) [15–20]. Like LIBS, LAMIS begins with a high-fluence, high-power laser pulse that induces ablation, decomposition, and ionization of a (usually solid) sample. This process initially creates atoms and elemental ions from a target [21], but LAMIS avoids looking at these species because the energy separation between isotopes from atomic emission is often smaller than 10 GHz, which is narrower than the broadening caused from the strong electric fields of the LIBS plasma [22,23]. Instead, the technique focuses on molecules that eventually materialize through recombination processes under favorable plasma conditions [24]. Once molecules form, the analysis of rovibronic bands of isotopes of diatomic molecules in

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the plasma that can have vibrational isotopic shifts of 100 GHz or more resolves the relative abundance of isotopes in a solid sample [25].

Due to technological improvements to LIBS-associated equipment over the past decade, the LAMIS technique has the potential to supplant commonly utilized technologies for isotopic analysis [16,20]. Current methods for abundance measurements include but are not limited to accelerator mass spectrometry (AMS), multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), gas source mass spectrometry and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). However, these systems tend to be prodigious, complicated, and time-consuming. The availability of compact lasers and spectrometers now means that a LIBS instrument, including the power supply, can be small enough to be field-portable for in-place, non-contact sampling [26,27]. LIBS also has short analysis times, taking less than a second, as well as having simple experimental setups [28,29]. It requires no expendables and could function several tens of meters from a target in almost any phase [30,31]. Very few techniques can compete on this last point, which may be very important if potentially radioactive samples are to be probed for isotopic information with the LAMIS technique from a safe distance.

Because of this ability for non-contact, standoff sampling, the advantages of LAMIS are most capably demonstrated for the analysis of non-volatile, pure solids, but careful consideration of both the material being analyzed for a given instrument setup is still paramount to unlocking the full potential of this technique.. Laser-induced breakdown can produce many diatomic species suitable for isotopic analyses [32], though the amount of material that is ablated or entrained into a plasma depends not only on the applied electric field from the laser but also on the physical properties of the material under study [33–36]. Any additional elements that are present in a plasma other than the element of interest – including additional elements in pure compounds – can affect the extent of ablation and quality of spectra [37,38]. These additional elements potentially obscure or aid in the relative abundance assessment for a given element [39,40]. Collectively, the elements not being analyzed form a sort of matrix that can include more than just the elements in the starting compound. For example, the surrounding atmosphere can also contribute atoms to the plasma, and these atoms are necessary for LAMIS to be applicable in some cases [15,41]. The total amount of ablated sample, chemical composition, density, thermal conductivity, and other chemical and physical properties of a material results in similar issues for isotopic analysis as well. Changes to the signal-to-noise and signal-to-background ratio lead to inevitable adjustments to instrument settings for a given sample to ensure that molecular spectra are observed [42,43]. Addressing these potential problems is a necessary step in helping LAMIS become a more robust technique for the analysis of the relative abundance of isotopes in a sample.

It should be noted that some effort has been devoted to make LAMIS applicable to multiple materials for isotopic analysis of the same element. The original LAMIS work demonstrated that emission from ^{13}C-enriched urea and natural-abundance graphite showed good separation in the C_2 and CN LIBS spectra, but relative abundance analyses were not published on these materials [15]. In addition, natural-abundance boron nitride and isotopically-enriched boric acid samples were used in a follow-up publication where the isotopic composition of boron in a natural abundance sample was determined with an error of about 3.7% for ^{11}B using a partial-least squares PLS model [16]. Even lower limits of detection of 9‰ (2σ) for ^{10}B were achieved using improved pretreatment algorithms applied to LAMIS of BN and B_2O_3 [20]. Similar analyses have been carried out on boron carbide (B_4C) samples that improved upon the first LAMIS analyses by demonstrating slightly lower limits of detection of ^{10}B around 1% with femtosecond lasers to reduce continuum [18,19]. Although these works represent some extension of the method to different matrices, training a PLS model on the same or extremely similar matrices that are to be analyzed does not necessarily demonstrate that the method is capable of dealing with matrix effects if the matrix is not known. Furthermore, these analyses were not performed in the same spectroscopic region as previous LAMIS work; instead, a different electronic transition of BO in the visible portion of the spectrum was used.

Other LAMIS work extracted strontium isotopic information from different halide salts of that element, but the same diatomic was not analyzed throughout [17]. Rather, the analyses of the emission from different strontium halide diatomics rather than strontium monoxide, which was produced through chemical reactions for each halide material, were demonstrated. This analysis illustrates the ability to extract isotopic information from different diatomics and shows the production of the same diatomic from different matrices, but it does not provide understanding of how the matrix can affect the analysis of a given diatomic.

Though using different regions of a molecular spectrum, deriving alternative modeling techniques, or extracting information from different molecules for similar substrates does not invalidate the application of LAMIS to different matrices, it does preclude comparison of the previous calibration-free methods to more empirical ones for the analysis of a given molecule as the matrix is changed. Moreover, calibration-free models can be used to deduce the influence of the matrix on plasma properties, such as the local thermodynamic equilibrium (LTE) temperature, which are integral to understanding plasma behavior under a given set of experimental conditions. Because no LAMIS work has yet been published on matrices that do not contain the element of interest (e.g., a boron LAMIS analysis on a mixture, of which some compounds contain no boron), it is reasonable to assume that these calibration free models may become more important as LAMIS is used on samples that are not chemically pure.

To extend the previous LAMIS studies with regard to matrix effects, the determination of the relative abundance of boron isotopes obtained from a study of BO emission spectra of multiple compounds and mixtures was examined in this work. LIBS spectra of boron oxide originating from different compounds, such as boron nitride (BN), boric acid (H_3BO_3), borax ($Na_2B_4O_7 \cdot 10H_2O$), anhydrous borax ($Na_2B_4O_7$), lanthanum borate ($LaBO_3$), and elemental boron (B) were acquired. In addition, LIBS was performed on impure B-containing samples where all ablated materials did not contain boron. Each of these materials had different physical properties and elemental composition in order to test possible matrix effects for the LAMIS method. A calibration-free model similar to that of the original LAMIS work was used to determine properties of the plasma as the matrix was changed. For each compound or matrix, the effects of elements other than boron and the physical properties of the sample on the efficacy of LAMIS to determine the relative abundance of boron under the same experimental sampling conditions were examined.

2. Methods and materials

An overview of the experimental setup for this work using LIBS is shown in Fig. 1. A Q-switched Nd^{3+}:YAG laser (Quantel Brilliant B) operating at 532 nm at either 20 mJ or 100 mJ of output energy with ~5 ns pulse duration was used. The beam was directed, expanded, and collimated using a set of mirrors and lenses, and before being focused using an achromatic lens (150 mm focal length) to a spot size of 1 mm at the sample surface. A photodiode connected to an oscilloscope was used to synchronize and monitor plasma onset and confirm detector settings (e.g., gate width and gate delay) after the onset of the nanosecond laser induced plasma. One mid-size fiber optic collimator with a focal length of 18 mm (Fiberguide Industries) was positioned orthogonal to the plasma to collect and direct light into an Acton Spectropro 750i (3600 gr/mm, 240 nm blazed grating) spectrometer with an Andor iStar 740 intensified charge-coupled device (ICCD) camera that was used for recording spectra. Before collecting spectra, the wavelengths of this spectrometer were offset corrected with an HG-1 (Ocean Optics) line source using a transition near 253.7 nm. To ensure that all samples maintained the same lens to sample distance, a helium–neon laser line level was used.