



Reduction of spectral interferences and noise effects in laser ablation molecular isotopic spectrometry with partial least square regression – a computer simulation study



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ABSTRACT

The fundamental analytical accuracies and precisions attainable by laser ablation molecular isotopic spectrometry (LAMIS), with emphasis on the impacts from spectral interferences and measurement noise, were investigated by means of computer simulation. The study focused on the analysis of a minor isotope at sub- to single-percentage abundance level. With a natural abundance about 1.1% for ¹³C, the C₂ Swan band (*d* ³Π_g–*a* ³Π_u) with Δ*v* = +1 was selected as a representative system. The characteristics (e.g., noise amplitude and distribution, signal strength, and signal-to-background ratio) of the simulated spectra were experimentally characterized. Partial least square (PLS) regression was used to extract isotopic information from the simulated molecular spectra. In the absence of any spectral interference and with the use of a calibration set consisting of eleven isotopic standards, the theoretical accuracies and precisions with signal accumulation from 100 laser shots are about 0.002% and 0.001%, respectively, in absolute percentage abundance of ¹³C. The theoretical analytical accuracies slightly degrade, but are adequate for many applications, to 0.004% and 0.008% respectively, for calibrations involving only three and two isotopic standards. It was found that PLS regression is not only immune to both source-flicker and photon-shot noise, but is also effective in differentiating the spectral patterns from the analyte against those from spectral interferences. The influences of spectral interference from single or multiple atomic emission lines were simulated, and new ways to minimize their impacts were formulated and demonstrated. It was found that the wavelength range selected for the computation of the normalization factor should not contain any spectral-interfering peak, and a properly chosen wavelength range increases the tolerance of spectral interference by at least one order of magnitude. With matrix-matched calibration standards, the precisions (expressed as RSDs of the determined ¹³C isotopic abundances) degrade from ~1‰ in the absence of spectral interference, to ~3‰, 10‰ and 20‰ with multiple spectral-interfering peaks that are 10×, 100× and 1000×, respectively, stronger than the molecular bandhead of the analyte. The study concluded that PLS regression is a powerful and indispensable tool for extraction of isotopic information from LAMIS spectra.

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1. Introduction

Laser ablation molecular isotopic spectrometry (LAMIS) is newly developed all-optical technique for isotopic analysis at ambient atmospheric pressure [1–3]. The implementation of LAMIS is similar to the well-known laser induced breakdown spectroscopy (LIBS) technology, in which a laser beam is focused onto the surface of a sample, thereby initiating a plasma above the sample surface. As time evolves, the plasma expands and the dominant species in the plasma shift from ions, to atoms, molecules, and finally fine particles. LIBS measurement involves atomic emission from the ions and neutral-atoms whereas LAMIS

measures the molecular spectra from those radicals that are present when the plasma cools. Because the vibrational and rotational motions of a molecule heavily depend on its reduced mass, which in turn depends on the molecular isotopologue, molecular spectra may exhibit up to two to three orders of magnitude increase in isotopic shifts compared to electronic transitions in atomic spectra [1–3]. Consequently, despite the various line broadening mechanisms operating inside the atmospheric pressure laser-induced plasma, isotopic shifts in molecular spectra are readily measurable with an optical spectrometer of relatively low spectral resolution. In addition, similar to LIBS, the all-optical nature of LAMIS offers the capability of remote analysis in any atmosphere without the need for vacuum equipment. For instance, we recently demonstrated the analysis of zirconium isotopes using a femtosecond laser-induced filament from a sample at a distance of 7.8 m – a technique coined F²-LAMIS (Femtosecond Filament LAMIS) [4].

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Despite the fact that utilizing molecular emission for the determination of isotopic abundance ratio in a sample is a concept with a long history [5,6], it has been relatively recent that isotope ratios were measured through molecular spectra with laser as the excitation source. The first study utilizing the laser induced plasma for isotopic analysis based on molecular spectra was reported by Niki et al. [7] in 1998. Under operation at a reduced pressure of 4 hPa, they demonstrated the marked differences in the BO $A^2\Pi-X^2\Sigma^+$ (0, 2) molecular bands emitted from the two isotopologues, ^{10}BO and ^{11}BO , and reported that the isotopic compositions of the two isotopologues could be measured from their relative peak heights [7]. The claimed detectability was only 5% (i.e., able to detect >5% difference in isotopic abundance) from the natural abundance of boron [7]. In our first demonstration studies of LAMIS under atmospheric pressure, we used a nanosecond-pulsed laser for isotopic analysis of boron [2,3], also utilizing the BO $A^2\Pi-X^2\Sigma^+$ band. The reported precisions, expressed as standard deviations of the percentage compositions of ^{11}B , ranged from 0.9 to 3.7% for a boron-nitride solid sample at natural isotopic abundance. Jovanovic and co-workers [8,9] also performed LAMIS of boron but with a femto-second laser, and reported precisions ~1.9 to 3.0% on the measured isotopic composition. Sarkar et al. [10] advanced the analytical capabilities of LAMIS for boron isotopic analysis through a detailed characterization of the factors limiting the analytical accuracy and precision, and found that a critical factor is the data-pretreatment procedure to remove shot-to-shot spectral variations prior to partial least square (PLS) regression. With several optimization procedures, Sarkar et al. [10] reported an improvement in the precision of determined boron isotopic composition to 2% RSD with a 1000-laser shots measurement. Hydrogen is another element with its isotopic ratio quantitatively determined by LAMIS [11]. Through the measurement and analysis of the OH and OD $A^2\Sigma^+-X^2\Pi$ band, Sarkar et al. [11] reported accuracies from 0.5% to 1.5% and precision from 15% to 18% RSD on the isotopic abundances of deuterium. In all the above examples, the minor isotopes were present at relatively high abundances. The boron figures quoted above were all from boron samples with natural isotopic abundance [2,3,7–10] (the minor isotope, ^{10}B is ~19.9% [12]) whereas the atom percentages of ^2H in the OH/OD LAMIS study [11] ranged from 6% to 97%. There are many isotopes with natural abundances around or less than 1% (e.g., ^{13}C ~1.1%, ^{15}N ~0.4%, ^{18}O ~0.2%, ^{235}U ~0.7% [12]). One objective of the present study is to understand the fundamental limits of analytical accuracy and precision attainable by LAMIS when the minor isotopes are at abundances ~1%.

As many samples contain other co-existing elements besides the element(s) of interest, spectral interferences could potentially limit the accuracy and precision of LAMIS. Brown et al. [13] recently showed that, for isotopic analysis of B using the BO molecular emission in a LaBO_3 sample, La atomic lines strongly overlapped the BO molecular band and thus compromised the analysis. Even for a highly purified sample that contains only the analyte, because atomic emission sometimes overlaps with molecular emission in both the temporal and wavelength domains, the ionic or neutral atomic emission from the analyte itself is a potential source of spectral interference in LAMIS. For instance, in our recent Zr isotopic analysis with LAMIS [14] on a pure zirconium metallic plate, Zr I emission lines overlap with the ZrO band under measurement. As is true with any other analytical technique, the presence of such spectral interferences, without subsequent correction by the analyst, can degrade the analytical performance of LAMIS. In order to further advance the LAMIS technique, it is of prime importance to understand the influence of spectral interference on the analytical accuracy and precision, especially when the minor isotope is present at sub- or single-percentage concentration.

One common approach to extract isotopic abundance information from molecular emission spectra is through multivariate calibration with partial least square (PLS) regression [15,16]. The ideal approach to investigate the precision and accuracy of the LAMIS technique with PLS calibration is through experimental means — such as physically

prepare a set of calibration standards and reference samples with known isotopic abundances, experimentally acquire the spectra with subsequent PLS processing, and compare the predicted results with the reference values. However, such an all-experimental approach is time consuming and it is quite often difficult to precisely control the variable under investigation. For example, as will be discussed in detail later in this paper, one factor that we explored is the effect of the center wavelength of a spectral-interfering line with respect to the positions of the molecular band features (i.e., band head or tail). As it is practically infeasible to prepare a sample with spectral interference at any desirable wavelength, computer simulation is a more viable approach for such a study. In addition, computer simulation allows us to identify the dominant factors influencing the analytical performance of LAMIS, and hence provides valuable guidelines for optimization prior to a measurement.

In this study, computer simulation was employed to estimate the analytical performance of LAMIS with PLS calibration. The focus of this work was to understand the limiting factors for LAMIS when the abundance of the minor isotope is at sub- or single-percentage levels, with emphasis on spectral interference from other co-existing elements in the sample. In addition to understanding how different factors affect the analytical performance of LAMIS, new ways to minimize their impacts were also formulated and demonstrated. The C_2 Swan band ($d^3\Pi_g-a^3\Pi_u$) with $\Delta v = +1$ was selected as the representative system, as the natural abundance of ^{13}C is about 1.1%. Further, the C_2 Swan band is one of the strongest molecular bands present when an organic material is ablated [17,18], and therefore, has been utilized for isotopic analysis of carbon [19–21]. Although the spectra of both the standards and the samples are synthetic in nature, their characteristics (e.g., noise amplitude and distribution, signal strength, and signal-to-background ratio) were all experimentally characterized.

The reported accuracy and precision from computer simulation represent the theoretical limit of the analytical figures of merit of LAMIS. Even though the theoretical limit is likely an optimistic value, such knowledge is still valuable. First, as LAMIS is a new technique for isotopic analysis, the theoretical value serves as a guide on its analytical figures of merit under an idealized situation. Although the required precision for a particular analysis depends on the specific application, many isotopic analyses would require precisions at or better than permit level to match the similar levels of natural variations in isotopic abundance of many elements. If the theoretical limit predicted for a particular molecular isotopic system is very close or short from the requirement, it directly suggests that LAMIS is not a suitable candidate for that particular application. Second, if large gaps are found between experimental analytical figure of merit and the theoretical value predicted under flawless situation, it prompts the researcher to look for, and accordingly remediate, the source of error (e.g., quality of PLS calibration standards, shot-to-shot variations in plasma temperature, possibility of the presence of self-absorption).

2. Experimental

2.1. Sample and experimental setup

The experimental setup was similar to previously described [21]. Briefly, a Nd:YAG laser (Brilliant Eazy, Quantel) operating at 1064 nm, with pulse duration of 5 ns and energy of 115 mJ, was focused onto the sample surface with a fused-silica lens (focal length = 5 cm). The sample was a graphite plate with thickness of 1.3 cm (MFCD00144065, Alfa Aesar). The measured laser spot size on the sample was approximately 2.5 mm. Plasma emission was collected through a 50 mm-diameter lens and imaged with a magnification ratio of 1:1 onto the entrance slit of a Czerny-Turner spectrometer (IsoPlane SCT-320, Princeton Instruments). An intensified charge-coupled device (ICCD) (Princeton Instruments) detector was mounted at the exit focal plane of the spectrometer. The ICCD was operated with a gain

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