



Isotopic determination of uranium in soil by laser induced breakdown spectroscopy



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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) operated under ambient pressure has been evaluated for isotopic analysis of uranium in real-world samples such as soil, with U concentrations in the single digit percentage levels. The study addresses the requirements for spectral decomposition of ²³⁵U and ²³⁸U atomic emission peaks that are only partially resolved. Although non-linear least-square fitting algorithms are typically able to locate the optimal combination of fitting parameters that best describes the experimental spectrum even when all fitting parameters are treated as free independent variables, the analytical results of such an unconstrained free-parameter approach are ambiguous. In this work, five spectral decomposition algorithms were examined, with different known physical properties (e.g., isotopic splitting, hyperfine structure) of the spectral lines sequentially incorporated into the candidate algorithms as constraints. It was found that incorporation of such spectral-line constraints into the decomposition algorithm is essential for the best isotopic analysis. The isotopic abundance of ²³⁵U was determined from a simple two-component Lorentzian fit on the U II 424.437 nm spectral profile. For six replicate measurements, each with only fifteen laser shots, on a soil sample with U concentration at 1.1% w/w, the determined ²³⁵U isotopic abundance was (64.6 ± 4.8)%, and agreed well with the certified value of 64.4%. Another studied U line – U I 682.691 nm possesses hyperfine structure that is comparatively broad and at a significant fraction as the isotopic shift. Thus, ²³⁵U isotopic analysis with this U I line was performed with spectral decomposition involving individual hyperfine components. For the soil sample with 1.1% w/w U, the determined ²³⁵U isotopic abundance was (60.9 ± 2.0)%, which exhibited a relative bias about 6% from the certified value. The bias was attributed to the spectral resolution of our measurement system – the measured line width for this U I line was larger than its isotopic splitting. Although not the best emission line for isotopic analysis, this U I emission line is sensitive for element analysis with a detection limit of 500 ppm U in the soil matrix; the detection limit for the U II 424.437 nm line was 2000 ppm.

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1. Introduction

The ability to characterize uranium isotopic compositions is vital to many nuclear sub-disciplines (e.g., nuclear industry, nuclear forensics, safeguards, and regulatory agencies) [1–3]. For example, the enrichment level of ²³⁵U provides insight into useful information about the sample, such as its origin (e.g., nuclear weapons, nuclear power or research reactor fuel, natural uranium, or depleted uranium) [2]. An enrichment level for ²³⁵U up to 4.5% generally sets the threshold between peaceful and rogue uses of uranium [4]. Without dispute, mass spectrometry is a powerful method for uranium isotopic analysis. For heavy elements like uranium, the interactions between the electrons and the electric charge distribution of the nucleus [5], which is

isotope specific, shift the electronic energies of the atomic levels, and hence the wavelengths of the atomic emission transitions. Isotopic splitting in atomic emission lines provides a physical basis for isotopic analyses with optical atomic spectrometry, which has been demonstrated through several approaches such as atomic absorption [6–8], atomic emission [4,9–17], atomic fluorescence [1,18,19], and optogalvanic spectroscopy [20,21].

Photon-emission based measurements offer several unique capabilities over MS-based techniques. First, in contrast to most mass spectrometric techniques, no so-called mass bias correction is needed for U isotopic analysis in emission-based methods [15,22]. Second, as photons are clean [23,24], there is no radioactive contamination to the main assembly of the instrument – a crucial issue that cannot be avoided using mass spectrometry [22]. Third, photon-emission based measurements offer the option to perform standoff or remote analysis [25–27].

Since the first demonstration of isotopic analysis of uranium by optical emission spectrometry with an arc discharge as the excitation source [9], many other atomic excitation sources have been developed

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for isotopic analysis of U, including hollow cathode discharge operated at reduced pressure [28,29], inductively coupled plasma–atomic emission spectrometry (ICP–AES) [10–15] conducted at ambient pressure, and laser induced breakdown spectrometry (LIBS) performed either under reduced [16] or at atmospheric pressures [4,17]. Despite the fact that the first work on isotopic analysis of uranium utilizing optical atomic emission was published at least six decades ago, such an analytical task is still challenging with current technology because, even for those isotopes that their isotopic shifts are considered to be substantial, the absolute differences in emission wavelengths are nevertheless small. For instance, U II at 424.437 nm is one of those U lines that is classified as having a large isotope shift, and has been frequently utilized for U isotopic analysis [4,10,12,13,15,16,28–32]; the absolute magnitude in its ^{235}U – ^{238}U isotope shift is only about 25 pm. Although baseline separations for the two isotopic peaks have been reported with ICP–AES operated under atmospheric pressure [11,13–15], the required instrumentation to obtain such spectral resolution is generally demanding. Data analysis, typically involving simple ratioing of the areas under the individual isotopic peaks [11,14,15,17], is rather straightforward if the two isotopic peaks are baseline resolved. Even with only partially resolved isotopic peaks, accurate isotopic analysis is still feasible with advanced data processing techniques, which has been demonstrated with the partial least square (PLS) calibration method [4,10].

Isotopic analysis of uranium by LIBS potentially offers additional advantages, but also with added challenges, over other atomic excitation sources. Samples are directly analyzed with LIBS without the need to perform laborious sample preparation (e.g., matrix separation). The analysis is not only faster, but also results in less radiation dose originating from the sample to laboratory personnel [22]. Moreover, as LIBS can be performed in on-site, in-situ, and standoff fashions, the costs associated with sample collection, transportation, sample preparation, and analysis time are reduced [33]. However, emission-line widths are broadened when LIBS is employed, in particular under atmospheric pressure. The effects from both Doppler and Stark broadening are considerable at atmospheric pressure LIBS [4], and it has been suggested that, with LIBS analysis, the two isotopic spectral profiles can be separated only under reduced pressure conditions [16].

As spectral line emission is transient and varies with time in LIBS, a gated detector is generally necessary to obtain the optimal measured line width (which is particularly important for isotopic analysis), signal-to-background ratio and emission intensity [17,34]. The choice of a multichannel detector that is able to register emission intensities simultaneously at an array of wavelengths and with temporal gating capability is currently very limited, and most LIBS measurements are performed with an intensified charged coupled device (ICCD). Undesirably, due to electron spreading to adjacent microchannels in the image intensifier tubes [35], the intensifier degrades the attainable spectral resolution [36] and reductions in spectral resolution by factors of 2 to 3 have been reported [37]. Therefore, even though baseline-separated measurements of the ^{235}U and ^{238}U components at U II 424.437 nm with LIBS under atmospheric pressure has been reported [17], both the hardware requirement and the optimization of operating conditions are challenging [17]. In cases when only partially resolved isotopic U peaks are acquired, isotope ratios still can be extracted from the spectra through the use of chemometrics (e.g., PLS), as successfully demonstrated by Doucet et al. [4] with atmospheric pressure LIBS. However, the fact that PLS calibration requires the availability of a series of isotopically enriched standards potentially could be a limitation.

The goal of the present work was to develop an approach for isotopic analysis of uranium with LIBS under atmospheric pressure with relaxed calibration and spectral-resolution requirements. Specifically, the method developed requires no calibration with isotopically enriched standards and the acquired isotopic spectral peaks only need to be partially resolved. Extraction of isotopic information was performed with decomposition of partially resolved spectral peaks. Several spectral decomposition algorithms were examined; different known physical

properties (e.g., isotopic splitting, hyperfine structure) of the spectral lines were successively incorporated into the candidate algorithms as constraints. One main objective of the present study was to understand the effect of treating related fitting variables from the two isotopes as independent or linked variables on the isotopic analysis results. Another objective was to evaluate the analytical capability of LIBS for elemental and isotopic analysis of uranium in an environmental sample matrix. The sample employed in this study was U-doped soil, with U concentrations in the single percentage levels.

2. Experimental

2.1. Sample and sample preparation

Isotopically enriched U_3O_8 powders were blended with soil to give a final U concentration in the single digit percentage level. Certified enriched (63% ^{235}U , CRM U630) U_3O_8 powder was obtained from New Brunswick Laboratory of the U.S. Department of Energy. Neglecting the trace amount of ^{234}U and ^{236}U in CRM U630, the atom fraction of $^{235}\text{U}/(^{235}\text{U} + ^{238}\text{U})$ is 64.37%. The soil matrix that was used in this study was a standard reference material (SRM 2710a) from NIST. This soil SRM is described as Montana I soil and its major (>0.5% w/w) elemental compositions are Si (31.1%), Al (5.95%), Fe (4.32%), K (2.17%), Ca (0.964%), Na (0.894%), Mg (0.734%), and Pb (0.552%). Although a trace amount of U is also present in the soil matrix, the amount is negligible and both the U concentration and its isotopic composition should be defined by the amount of U_3O_8 that was added. The certified mass fraction of U in SRM 2710a is 9.11 mg/kg, and is three orders of magnitude less than the lowest U concentration (1.1% w/w) used in the present study.

Four portions of CRM U630 U_3O_8 powder, with masses 1.3, 3.0, 5.0, and 10.2 mg were weighed and blended with 99, 97, 95, and 90 mg of the SRM 2710a soil matrix, respectively. The concentrations of uranium in the blends were 1.1, 2.5, 4.2 and 8.6% w/w. A blank, which consisted of 100 mg of SRM 2710a, was also prepared. These powdered samples were individually placed into a pellet-pressing die with a diameter of 3 mm, and forces of approximately 6 tons were then applied for 3 min. The prepared U-doped soil sample pellets were about 1 mm thick. The sample pellets were then loaded into a shielded chamber, which contained air at atmospheric pressure, with optical ports for the laser ablation and photon collection.

2.2. LIBS system and measurements

The experimental setup was similar to our previous studies [34,38] and consisted of a Nd:YAG laser, a 1.25 m-focal length Czerny–Turner spectrometer, and an ICCD gated detector. Briefly, the Nd:YAG laser was operated at its fundamental wavelength at 1064 nm with a pulse duration about 5 ns. Laser energy was approximately 40 mJ/pulse. The measured pulse-to-pulse fluctuations in laser power were only 1% RSD. The laser beam was focused onto the soil-pellet sample surface, which was placed inside a sealed chamber, through the designated optical port. The diameter of the laser spot on the sample was approximately 350 μm . Plasma emission was collected orthogonal to the incoming laser-beam direction, through another optical port, with a second fused-silica lens. The laser-induced plasma emission was then directed to the entrance slit of the spectrometer through an optical fiber bundle. The plasma emission was registered by an ICCD detector with typical operating parameters as in other LIBS measurements – a delay time of 1.5 μs and a gate width of 20 μs . Each measurement consisted of an accumulation of emission signals from 15 laser shots on a single fixed spot on the sample, and six replicate measurements were made on each sample.

Two uranium emission lines – U I 682.691 nm and U II 424.437 nm were measured in this study. Herein, the quoted wavelength of an emission line always refers to that emitted from ^{238}U , even during the

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