



Technical Note

Hybrid interferometric/dispersive atomic spectroscopy of laser-induced uranium plasma

Phyllis K. Morgan^a, Jill R. Scott^b, Igor Jovanovic^{c,*}^a The Pennsylvania State University, University Park, PA 16802, USA^b Idaho National Laboratory, Idaho Falls, ID 83415, USA^c The Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

An established optical emission spectroscopy technique, laser-induced breakdown spectroscopy (LIBS), holds promise for detection and rapid analysis of elements relevant for nuclear safeguards, nonproliferation, and nuclear power, including the measurement of isotope ratios. One such important application of LIBS is the measurement of uranium enrichment ($^{235}\text{U}/^{238}\text{U}$), which requires high spectral resolution (e.g., 25 pm for the 424.4 nm U II line). High-resolution dispersive spectrometers necessary for such measurements are typically bulky and expensive. We demonstrate the use of an alternative measurement approach, which is based on an inexpensive and compact Fabry–Perot etalon integrated with a low to moderate resolution Czerny–Turner spectrometer, to achieve the resolution needed for isotope selectivity of LIBS of uranium in ambient air. Spectral line widths of ~10 pm have been measured at a center wavelength 424.437 nm, clearly discriminating the natural from the highly enriched uranium.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) enables nearly instantaneous material composition analysis with high spatial resolution and essentially no sample preparation. Rapid elemental and isotopic characterization of materials relevant to nuclear safeguards is desirable. LIBS is advantageous in such applications because it is unaffected by ionizing radiation and compatible with measurements at a large standoff. Unlike LIBS, techniques such as X-ray fluorescence spectroscopy can be affected by the presence of gamma radiation [1]. Furthermore, LIBS can be used to measure non-radioactive sources. Filamentation LIBS can be used to conduct measurements over long distances, in situations where laser beam focusing onto a surface can be challenging (e.g., in highly radioactive areas or in facilities with limited access) [2]. Because LIBS directly samples the material surface, it requires the analyte to be accessible within the field of view of the laser source. The potential for use of LIBS for analysis of nuclear fuel composition, waste storage, and reactor process monitoring has been explored for its real-time, *in-situ* capability to verify inventory and characterize nuclear materials, even in harsh environments [3,4,5]. Experiments have been conducted to study the effects of experimental parameters, including laser pulse duration and shape, in order to improve sensitivity and reproducibility in LIBS of nuclear materials [6,7].

One of the challenges when making isotopic measurements by LIBS is the physical broadening of emission peak widths, which can approach or exceed the isotope shift. In a LIBS plasma, Doppler and Stark effect are the predominant mechanisms of peak broadening and are influenced by the gas environment surrounding the plasma [8,9]. Another challenge is of technological nature. Isotope measurements usually require high-resolution spectrometers and temporally gated detectors to resolve the isotope shift. In previous LIBS studies, the isotope shift between ^{235}U and ^{238}U of 25 pm at the 424.437 nm atomic emission line has been measured [15–18]. In the study of uranium by Pietsch *et al.*, a 1 m focal length spectrometer was used with a single channel detector and a boxcar integrator, operating as a monochromator scanning in 1 pm increments. The measurement was made under 2.67 Pa pressure [10]. Smith *et al.* measured the 0.05 nm isotope shift between ^{239}Pu and ^{240}Pu at the 594.5 nm emission line, under a 13.3 kPa helium atmosphere, using a 2 m focal length double-pass spectrometer with an intensified charge-coupled device (ICCD) [11]. LIBS has also been used to study isotopes of uranium and hydrogen, in air at atmospheric pressure, using a 0.55 m focal length Czerny–Turner spectrometer coupled to an ICCD [12]. The individual peaks of the uranium isotopes were not resolved. Instead, partial least squares analysis was successfully applied to predict a range of uranium samples with different enrichments. Cremers *et al.* observed the uranium isotope shift with high-resolution spectrometers [13]. This study was based on a LIBS system with compact, portable laser delivery and light collecting optics coupled to one of two relatively expensive laboratory echelle spectrometers. This LIBS

* Corresponding author.

E-mail address: ijovanovic@psu.edu (I. Jovanovic).

system was able to distinguish the isotopes of uranium, hydrogen, and lithium with careful experimental timing.

Isotope analysis of uranium is also possible by alternative laser ablation sampling analysis such as laser-induced fluorescence [14,15,16] and laser absorption spectrometry [17,18]. For example, Liu *et al.* used laser absorption to measure the $^{235}\text{U}/^{238}\text{U}$ isotope ratio at 682.0768 nm (–12.8 pm isotope shift). A negative value of the isotope shift indicates that the ^{235}U wavelength is greater than that of ^{238}U , and *vice versa* [15]. Smith *et al.* used laser-induced fluorescence to distinguish between the uranium isotopes at 683.2719 nm (16.8 pm shift) [17]. A disadvantage of these approaches is that multiple lasers and detectors are required for probing and analyzing the plasma plume. With a single laser for sampling and analysis and a single detector, LIBS is comparatively simpler.

Additionally, laser ablation molecular isotopic spectrometry (LAMIS) was developed to make isotope measurements [19]. Molecular emission spectra can exhibit greater isotope shifts than atomic emission spectra, relaxing the requirements on spectral resolution. For example, the atomic isotope shift for B is 0.002 nm and the observed isotope shift of BO is 0.73 nm [20]. It has also been shown that the use of a non-gated detector can be sufficient for accurate isotope characterization in LAMIS [21,22]. While the resolution requirement may not be as stringent, the signal-to-noise for molecular peaks is often poor and molecular spectra typically require mathematical processing that involve chemometrics. Furthermore, molecular measurements are limited to those elements that combine to form molecular species. Because molecular rotations and vibrations are mass dependent and isotope shifts scale with the reduced mass of the molecular species, heavier atoms exhibit smaller shifts [21]. A molecular isotope shift in LIBS spectra for uranium has not yet been reported.

Effenberger and Scott proposed an alternative method for performing high-resolution LIBS measurements by integrating a low-cost Fabry–Perot (FP) etalon with a 0.5 m focal length Czerny–Turner spectrometer [23]. Instrument performance was demonstrated using the hyperfine doublet of the 313.2 nm mercury emission line, which exhibits a splitting of 29 pm, similar to an isotope shift of uranium. Recently, a method was developed to reconstruct the high-resolution spectrum from a similar hybrid interferometric/dispersive LIBS instrument and showed improvement in spectral resolution and accurate determination of peak ratios compared to conventional pixel-to-wavelength schemes [24].

In this study, we demonstrate for the first time the capability of a hybrid interferometric/dispersive instrument to achieve isotope selectivity in LIBS of uranium. The results of this study could help advance LIBS applications in the field where high-resolution is needed. Compact and cost-effective technologies capable of isotope measurements could benefit nuclear safeguards verification and nonproliferation as well as other high-resolution spectroscopic applications.

2. Experimental

2.1. Samples

The samples used were a natural uranium foil (0.7% of ^{235}U) and a uranium foil highly enriched in ^{235}U to 93%. Both samples were provided by the Penn State University's Breazeale Nuclear Reactor.

2.2. Experimental setup

A diagram of the experimental setup is shown in Fig. 1. The samples were placed in a sealed experimental chamber under atmospheric pressure and mounted to a sample holder at normal incidence to the laser beam. The sealed chamber was used strictly for containment of the ablated uranium. The laser pulse width was 10 ns at a wavelength of 1064 nm generated by a Nd:YAG laser (Spectra Physics). The laser pulses were focused onto the sample through an optical window

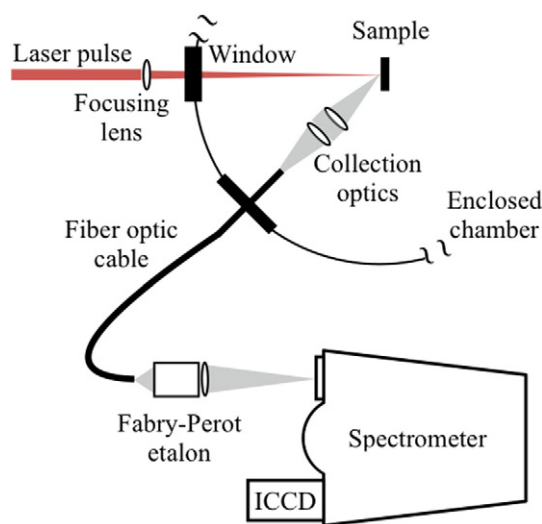


Fig. 1. Schematic diagram of experimental setup, laser beam path (red), and transport of light emitted by the plasma (gray).

using a 300 mm focal length lens. The emission from the plasma was collected and collimated by a 5 cm focal length lens mounted off-axis to the laser beam path. A second lens focused the collimated light into a 400 μm core diameter optical fiber (Ocean Optics), which transported the light to the broadband etalon (custom built by SLS Optics). The FP etalon was aligned to the entrance slit (500 μm width) of the spectrometer. A 25 mm diameter lens with a focal length of 150 mm was used to focus the light transmitted by the etalon onto the entrance slit of the spectrometer (Horiba Jobin Yvon), which had a 550 mm focal length and a 1800 mm^{-1} grating coupled to a 1024 \times 1024 pixel array iStar ICCD (Andor) with 13 μm pixel size. Instrument alignment and spectral calibration was performed using an Hg(Ar) pen lamp (Oriel) acquired with 1 s ICCD exposures for each snapshot (10 snapshots per image), at 24.4% of the maximum detector gain.

2.3. LIBS parameters

For LIBS measurements, the plasma was generated in ambient atmosphere using 30 mJ laser pulses. For conventional LIBS without the FP etalon, spectra were measured using the 0.55 m Czerny–Turner spectrometer with an entrance slit width of 13 μm , ICCD gate width of 1 μs at a delay of 5 μs , and gain set at <1% of the maximum gain. Each spectrum is the average of 5 single-shot spectra. The sample was translated between each spectrum measurement, and cleaning shots were made prior to each measurement to remove oxidized uranium on the sample surface [8]. Because of the lower throughput of the high-resolution hybrid instrument (estimated to be <0.01% for the sampled portion of ring pattern compared to the Czerny–Turner spectrometer alone), each spectrum was collected from 600 laser shots (1 min exposure at a 10 Hz pulse rate). Because of the high repetition rate, the sample was not translated between each pulse during the 1 min exposure. The gate time was set to 10 μs with 5 μs delay, and ICCD gain was set to 97.6% of the maximum gain.

3. Results and discussion

3.1. Spectral reconstruction

The broadband pattern from a FP etalon is composed of superimposed, angularly and spectrally dependent interference fringes that are sampled by the spectrometer entrance slit, separated by the grating, and detected on the pixel array to produce a slice of the fringe pattern (Fig. 2(a)). A spectral reconstruction method was developed to analyze the high-

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