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## Isotope-resolved atomic beam laser spectroscopy of natural uranium

Journal:	<i>Journal of Analytical Atomic Spectrometry</i>
Manuscript ID	JA-COM-07-2018-000242.R1
Article Type:	Communication
Date Submitted by the Author:	28-Aug-2018
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# Journal of Analytical Atomic Spectrometry

## COMMUNICATION

### Isotope-resolved atomic beam laser spectroscopy of natural uranium

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

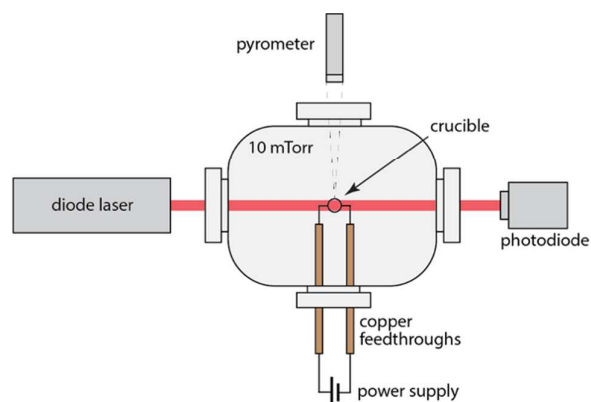
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**We present our results on the development of a technique for conducting laser absorption spectroscopy of uranium in a collimated atomic beam using a compact and potentially fieldable device. A solid natural uranium metal sample is vaporized in a modest vacuum of several mTorr via resistive heating of a tantalum foil micro-crucible. A temperature of over 2000 °C is reached by applying only 200 W of electrical power to the crucible. At this temperature, the vapor pressure of uranium is large enough to generate a stable atomic beam. A diode laser is tuned around the 861.031 nm uranium transition, which allows the observation of absorption bands from both the  $^{238}\text{U}$  and  $^{235}\text{U}$  isotopes. The isotopic composition of uranium Standard Reference Material 960 is obtained from the absorption signal, in excellent agreement with the nominal value. Our approach can be readily applied to the isotopic analysis of other actinides, and it is expected to lead to the development of compact, fieldable instrumentation.**

The rapid analysis of nuclear materials in the field is paramount to applications in nuclear forensics and safeguards for nuclear non-proliferation. Currently, mass spectrometry is the gold standard among the techniques employed in these fields because it provides the most sensitive detection of virtually any atomic or molecular species. Despite possessing extremely high sensitivity, mass spectrometers are too voluminous and heavy for practical field applications, and require time-consuming chemical dissolution and separation steps prior to the analysis of most nuclear materials. Thus, the development of a complementary technique for isotopic analysis of nuclear materials in the field is highly desirable. Such an instrument needs to be compact, capable of rapid deployment in the field, and be able to provide accurate isotopic information about the sample as quickly as possible.

Apart from having a different mass, isotopes of the same atomic element have slightly different electronic energy level structures. These small differences in energies, i.e., the isotope shifts, can be used to uncover the relative amounts of each isotope by high resolution spectroscopic methods. Laser-induced breakdown spectroscopy (LIBS), for example,<sup>1</sup> consists of ablating a small portion of the solid sample with a pulsed laser, which causes the atoms to be heated to temperatures of a few thousand degrees and to be transferred thermally into highly excited states. As these excited species decay into lower energy states, they emit photons characteristic to specific electronic transitions, which are collected and analyzed by a grating-based spectrometer. LIBS can be used to analyze most of the elements present in a sample at once, but, in the case of isotopic analysis, it suffers from some limitations. In particular, to be able to resolve isotope shifts, LIBS must make use of a long-path dispersive spectrometer,<sup>2</sup> adding complexity, and precluding its applicability for field deployment. Instead of detecting light emission from excited species, a variation of LIBS interrogates the ablated species by measuring photon absorption through the plume with a tunable laser, removing the need for a spectrometer. The absorption lines of uranium isotopes at various wavelengths have been observed using this ablation/absorption technique by averaging the absorption signal produced during each nanosecond ablation pulse, and then tuning the absorption laser to reconstruct the absorption spectrum.<sup>3-6</sup> Because laser ablation causes the species to be heated to relatively high temperatures (5,000 – 20,000 °K), significant Doppler broadening is present in the absorption spectrum. In addition, shot-to-shot variations in deposited laser energy, as well as possible inhomogeneities in both the sample and the ablation plume, call into question the reliability of laser ablation absorption spectroscopy to be used for high-precision isotope ratio measurements.

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Here, we present a new method for the determination of the isotopic composition of actinide samples by laser absorption spectroscopy. The method consists of generating an atomic beam of the actinide and measuring the absorption of an intersecting laser beam. The ultra-narrow linewidth of the laser is capable of resolving the isotope shifts of most absorption lines. The atomic beam is generated by a recently

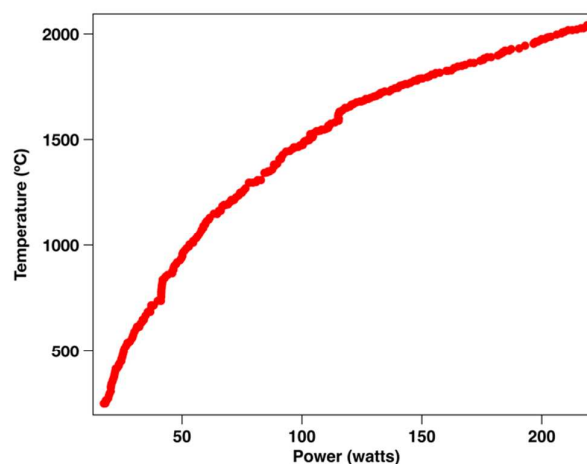
**Fig. 1** Top: schematic diagram of the experimental setup. A tantalum foil micro-crucible is mounted on copper feedthroughs inside a small vacuum chamber. Electrical current is applied to the crucible, which generates an atomic beam of uranium (perpendicular to the page). A tunable diode laser intersects the atomic beam and atomic absorption is detected by a silicon photodiode. Bottom: detail of the tantalum foil micro-crucible mounted on vacuum feedthroughs.

developed resistively-heated tantalum foil micro-crucible capable of reaching temperatures as high as 2600 °C with minimal electrical power requirements, and without the need for active cooling.<sup>7</sup> We demonstrate the determination of isotope ratios in natural uranium samples using this laser absorption spectroscopy method. Fig. 1 describes our experimental setup. A small sample of uranium metal (25 – 50 mg) is placed at the bottom of the tantalum foil micro-crucible. For the present experiments, we analyzed a well-characterized uranium metal standard, namely Standard Reference Material (SRM) 960.<sup>8</sup> The crucible is resistively-heated inside a vacuum chamber up to a temperature of 2200 °C. The vapor escaping the cylindrical crucible forms a collimated atomic beam, which is intersected at right angles by the beam from a tunable external-cavity diode laser (DL-Pro, Toptica Photonics, Germany). The laser light, centered around the 861.031 nm transition of uranium ( $f^3d^5s^2\ ^5L_6 \rightarrow f^2d^2s^2\ ^5K_5$ ,  $0 \rightarrow 11613.977\ \text{cm}^{-1}$ ),<sup>9</sup> undergoes absorption by the atomic beam, which is

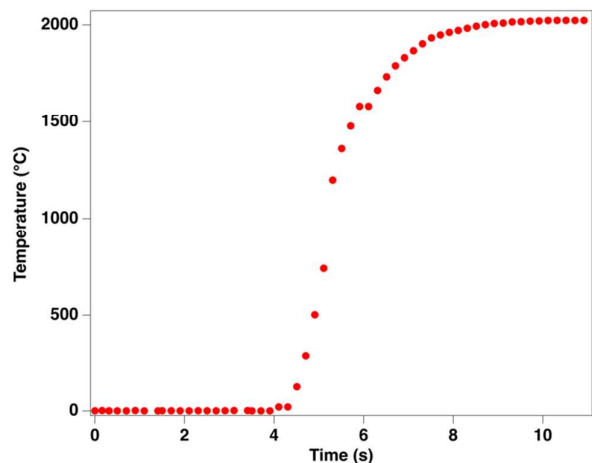
detected by a silicon photodiode. This transition was selected for the present experiments chiefly because of the availability of inexpensive tunable diode lasers that overlap this spectral region, and also because this transition has been previously characterized by other absorption spectroscopy methods.<sup>5,10</sup> The laser beam has a diameter of a few millimeters and its power is relatively low, 5 mW, in order to avoid saturation of the atomic transition.<sup>11</sup> The narrow linewidth of the laser (<300 kHz at 5  $\mu\text{s}$  integration time), combined with a low-divergence atomic beam which reduces transverse Doppler broadening, allows us to easily resolve the 5.1 GHz isotope shift. During the sample analysis, the laser center frequency is rapidly tuned through a range of a few GHz at a scan rate of 5 Hz. External-cavity diode lasers are particularly suitable for this kind of experiment, since they can be rapidly tuned at rates up to 100s of Hz over a frequency span of tens of GHz, as previously demonstrated for Gd atomic beams,<sup>12</sup> for example. A wavelength meter (WS-6, High Finesse, Germany) is used to calibrate the laser frequency. The absorption signal captured by the photodiode is synchronized with the scan rate of the laser and digitized by a data acquisition module (USB-6341, National Instruments, Austin, TX) controlled by LabVIEW.

The crucible is resistively-heated by applying current from a Magna-Power (Flemington, NJ) power supply (5 V, 250 A maximum). Thick gauge wires are connected to vacuum-compatible copper feedthroughs (Kurt J. Lesker, Jefferson Hills, PA), to which the crucible is attached. The crucible temperature is monitored by a fiber-optic two-color pyrometer (iR2C, Omega Engineering, Norwalk, CT) sensitive in the 1,000 – 3,000 °C range. Fig. 2 shows a typical measured crucible temperature vs. applied electrical power. This high efficiency tantalum micro-crucible is capable of reaching 2000 °C with only 200 W of applied electrical power. In order to avoid both cross-contamination between samples and also the long-term effects due to corrosion by molten uranium, crucibles are disposed and replaced after each use, which is possible due to their inexpensive nature.

After loading the uranium metal sample into the crucible



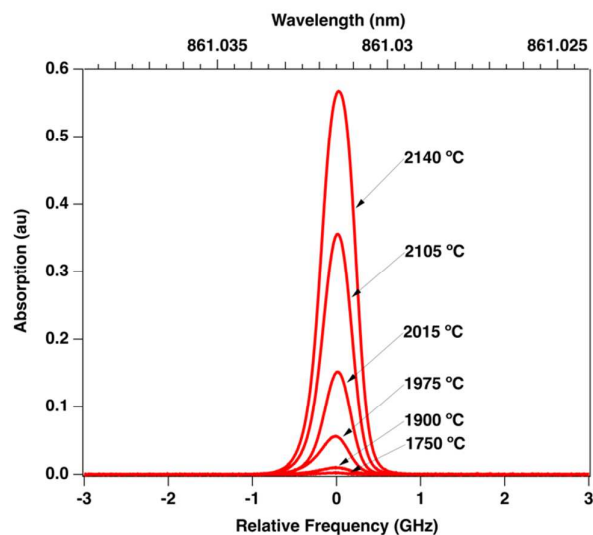
**Fig. 2** Observed crucible temperature versus applied electrical power, as measured with a two-color pyrometer. The total time elapsed when recording this trace was 30 seconds.



the vacuum chamber is evacuated to 10 mTorr by a compact roughing pump. Then, the electrical power is applied in constant current mode. After switching the power supply to a pre-set current value (60-80A), the crucible reaches a temperature of 2000 °C in only 4 seconds (Fig. 3). At the same time that the current is switched on, the data acquisition system starts recording every absorption spectrum through the atomic beam as the laser is tuned across the 861.031 nm transition at a rate of 5 Hz. Fig. 4 shows the evolution of the

**Fig. 3** Rapid increase of the temperature of the crucible as a function of time after switching the power supply to a preset current value.

uranium absorption signal as the temperature, and hence, the vapor pressure of uranium, increases during this ramping up. The  $^{238}\text{U}$  signal starts to appear at around 1750 °C, and it grows exponentially as a function of the crucible temperature, which results in a 50 times larger signal at 2200 °C than at 1750 °C. Fig. 5 shows the single-scan integrated  $^{238}\text{U}$  signal vs. temperature. As expected, the magnitude of the absorption



signal follows the exponential increase of uranium vapor pressure with temperature. At this point, the crucible temperature is held constant, and several scans are acquired and averaged in order to obtain a precise  $^{235}\text{U}/^{238}\text{U}$  isotope ratio. For this purpose, we simply integrate the areas under the absorption curves of each isotope. Fig. 6 shows the average of 20 scans obtained in 4 seconds at a constant temperature of 2200 °C. This measurement was repeated for 5 different samples of SRM 960, and Table 1 shows the results as a comparison of the average measured isotopic composition values with the SRM 960 mass spectrometry nominal values. Our measurements are in excellent agreement with the standard values, and our precision for the abundance of  $^{235}\text{U}$  is 0.2%.

**Table 1.** Observed vs. nominal isotopic abundances for SRM 960 natural uranium metal.

	$^{238}\text{U}$ (%)	$^{235}\text{U}$ (%)
Present results	99.4±0.3	0.7±0.2
Nominal values	99.27458±0.00039	0.72017±0.00039

Signal to noise ratios (SNR) of 2800 and 20 were obtained for the  $^{238}\text{U}$  and  $^{235}\text{U}$  isotopes, respectively, placing our current sensitivity to detect a single isotope at the 0.1% abundance level. The sensitivity of our technique can be improved further by modifying the geometry of the crucible. The atomic flux ( $F$ ) generated from a cylindrical crucible is proportional to the cylinder cross-section area ( $A$ ) divided by its length ( $L$ ),  $F \sim A/L$ . By increasing the diameter and decreasing the length of the cylinder, the flux and thus the signal strength can be increased up to a limit, dictated by the ability of any given crucible geometry to be heated to the temperatures needed for producing the uranium atomic beam. The losses of applied electrical energy are dominated by blackbody radiation, which is proportional to the crucible surface area. However, our estimates have shown that a crucible design that allows an increase in atomic flux by 10× will only cause a modest increase in surface area, and, therefore, minimally impact the power efficiency. Such a crucible geometry will certainly cause a degradation in atomic beam collimation ( $\sim D/L$ , where  $D$  is the cylinder diameter) and spectral resolution, but this trade-off with spectral resolution may be acceptable for elements and transitions with a large isotopic shift, such as the transition studied here. This trade-off can be avoided altogether if a multichannel approach is used,<sup>7</sup> where each of a series of stacked tubes defines the collimation of the atomic beam.

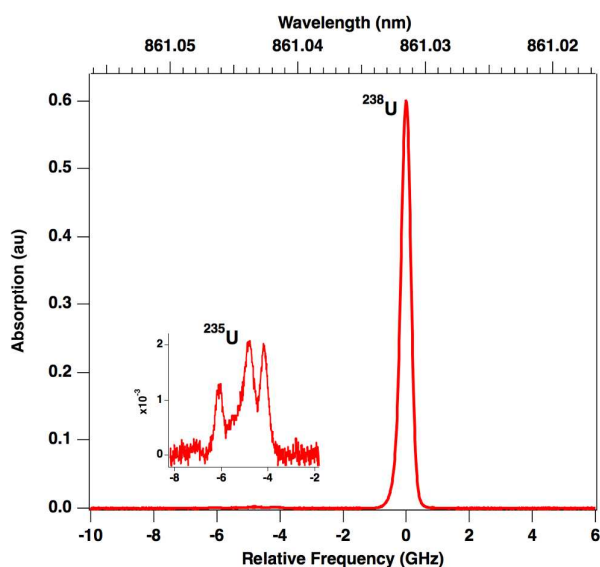


Fig. 6 Absorption spectrum of natural uranium at 2200 °C. The inset shows an expanded view of the  $^{235}\text{U}$  signal.

Fig. 4 Evolution of the absorption signal of the  $^{238}\text{U}$  isotope versus laser frequency at different crucible temperatures. The corresponding wavelength is shown on the top scale.

Fig. 5 Integrated absorption signal of the  $^{238}\text{U}$  isotope vs. crucible temperature

An important characteristic of the technique presented here is that the atomic beam can be continuously generated for several minutes, and the atomic density and flux remain stable for the duration of the measurement. We estimate that only a few micrograms of sample are consumed in the atomic beam during the duration of each experiment, which makes the technique potentially suitable for the analysis of small nuclear forensics samples. We are in the process of investigating the application of this technique to the analysis of other uranium compounds, since the addition of a reducing agent to the crucible could, in principle, reduce molecular compounds and cause the generation of neutral atomic beams. Furthermore, since uranium metal melts at a temperature much lower than that at which the analysis is conducted (1132 °C vs. 2200 °C), we expect that the sample

will be fully homogenized during the analysis, and, therefore, potential sample homogeneities will not affect the isotope ratio. Sample inhomogeneities can skew the results of other analytical techniques that rely on vaporizing discrete regions of the solid samples, such as LIBS or ablation/absorption methods. In addition, since the laser is scanned across the atomic transition at a rate of 5 Hz, we are able to obtain spectra with a very high SNR by averaging hundreds or thousands of scans acquired in only seconds or minutes. In the case of LIBS or ablation/absorption methods, the measurement can only be made immediately after the generation of each ablated plume, which has a lifetime of the order of micro-seconds. Reconstructing the absorption spectrum requires taking the average of many ablating shots per frequency point. This limits the applicability of the technique for quantitative measurements due to the complexity of plasma-particle interaction processes, which are both space and time dependent.<sup>1</sup>

One of the advantages of optical methods over mass spectrometric techniques for isotopic analysis is that optical methods do not suffer from isobaric interferences, i.e., they are element-specific. Species belonging to different elemental species, but having the same atomic mass (isobars), require either extremely sensitive mass spectrometry techniques or conducting purification steps prior to analysis. On the other hand, spectroscopic methods for quantitative analysis do rely on the ability to cleanly recover the absorption spectrum of each individual species. The technique we have presented here makes use of no chemical processing prior to analysis, leaving open the possibility of spectral interferences. However, the operational conditions of our atomic beam-based spectroscopy eliminate the possibility to have such interferences. First, the energy range over which we tune the laser is extremely narrow, and the overall instrument resolution is extremely high. Any interfering species would have to have an absorption feature exactly corresponding to this energy. Secondly, the crucible itself acts as a physical separation system. Even if a species were found that passed the first criterion, such a species would also need to have a comparable vapor pressure and abundance as uranium in the sample. With a higher vapor pressure, that species would evaporate from the crucible before the spectral acquisition sequence begins. With a lower vapor pressure, an insufficient amount of vapor from the interfering species would be produced. Between these two criteria, we believe that the possibility of finding any species or matrix capable of interfering with the isotope analysis of this system does not exist.

## Conclusions

We have demonstrated isotope-resolved diode laser absorption spectroscopy of a collimated atomic beam of natural uranium. The atomic beam was generated by resistively-heating a tantalum foil micro-crucible using only 200 W of electrical power to reach 2000 °C without any active cooling. After loading the sample into a small vacuum

1 chamber, the isotopic composition of the sample was obtained  
2 in only 4 seconds. The obtained isotopic composition was in  
3 excellent agreement with the nominal standard values. Very  
4 high atomic absorption SNRs were obtained, which allowed  
5 the determination of isotope ratios with a precision of 0.2%.  
6 We expect that the method presented here will lead to the  
7 development of instrumentation capable of deployment to the  
8 field, as required for nuclear forensics and nuclear non-  
9 proliferation applications. In fact, we are currently building a  
10 fieldable instrument based on this technique, which is  
11 estimated to weigh less than 25 kg, occupy a volume of 0.06  
12 m<sup>3</sup>, and require 1000 W of electrical power.

### 13 Conflicts of interest

14 There are no conflicts to declare.

### 15 Acknowledgements

16 We gratefully acknowledge the U.S. Department of  
17 Energy/NNSA Office of Defense Nuclear Nonproliferation  
18 Research and Development for supporting parts of this work.

We also thank Elmer Luján and Katherine Garduño for  
assistance with sample preparation.

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