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Application of Diode Lasers to the Isotopically Selective Determination of Uranium in Oxides by Optogalvanic Spectroscopy

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Abstract. We have observed isotopically selective diode laser-excited optogalvanic effects in uranium at 778.42 and 776.19 nm. The samples were natural abundance uranium oxide, as well as depleted (0.3% ^{235}U), natural (0.7% ^{235}U) and enriched (9.75% ^{235}U) uranium metal or powders. The measurements were carried out in a demountable-cathode glow discharge cell. Preliminary evaluations of precision for uranium isotopic ratios measured using this technique suggest that it should have broad analytical applications for uranium and other amenable actinides or lanthanides.

INTRODUCTION

Previously, tunable semiconductor diode lasers were used to promote transitions in gaseous lanthanum atoms with isotopic selectivity (1). As a basis for a useful analytical determination, we used a diode laser to achieve isotopically selective excitation of gaseous uranium atoms generated from samples of uranium or uranium oxide by sputtering in a demountable hollow-cathode glow discharge (GD) cell. The excitation process was monitored by optogalvanic spectroscopy (OGS). Uranium has been studied by OGS in commercial hollow-cathode lamps at 778.42 nm (2,3). Isotope detection was achieved in one study using a single frequency CW dye laser (2). Diode lasers were used to observe ^{238}U in another study (3), but no isotopic selectivity was noted. Our work was carried out to evaluate the possibility of developing fieldable instrumentation for the estimation of isotope ratios of uranium containing samples. Instrumentation based on diode laser excitation of a sputtered sample in a GD cell followed by OGS detection should have broad application.

EXPERIMENTAL

The details of the experimental work for these studies are described elsewhere (4) but are summarized here. The demountable-cathode GD cell is shown in Figure 1. It consists of standard vacuum crosses fitted with two windows. The cathode assembly is removable through the top of the cell. The sample cathode was fabricated by pressing uranium powder or a 50-50% mixture of uranium oxide and silver powder into a hollow cylinder that was approximately 5 mm diameter, 2.5 mm long with a 2.4 mm hole in the center. This sample fits into the ring at the base of the cathode. A special die was made for sample preparation; a pressure of 3×10^7

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Pa for five minutes was necessary to form the cathodes. Several uranium samples were used in these studies, natural abundance uranium and U_3O_8 (0.7% ^{235}U), depleted uranium powder (0.3% ^{235}U), and enriched uranium (10% ^{235}U). After loading the cathode into the cell, a discharge was maintained in argon support gas (500 to 900 Pa); the current was held constant in the range of 20 to 50 mA at an applied discharge voltage of 250 to 500V. Sample manipulation was accomplished by movement of the cathode probe assembly from outside the cell. The cell body served as the counter electrode of the discharge.

Figure 1. Demountable hollow cathode glow discharge cell.

The OGS studies were carried out with either of two CW lasers. One was an argon-ion laser-pumped titanium:sapphire (Ti:S) tunable ring laser (Innova-100 argon ion laser and model 899-29 Ti:S ring laser, Coherent Laser Group, Santa Clara, CA). The output power of this system was 1W, but was generally attenuated. The other laser was an AlGaAs semiconductor diode laser (model ML-64110N, Mitsubishi Electric Corp., Tokyo) with a nominal room temperature output of 30 mW at 777 nm. The diode laser was used with commercial control electronics (model LDM-4412 laser

mount, LBT-5910 thermoelectric temperature controller, and LDX-3620 ultra-low noise current source, ILX Lightwave Corporation, Bozeman, MT). The manufacturer's specification states that the temperature is controlled to $\pm 0.005^\circ C$ and the current supply noise is 2 μA or less. Either laser beam was directed through the sample as a focused beam (50 μ dia.) or, more recently, as a pencil of light of 1 mm diameter. The diode laser power at the experimental wavelengths of 778.42 or 776.12 nm was 3 and 8 mW, respectively, with focused power densities of 150 and 400W/cm². As shown in Figure 1, either laser beam was chopped at 1000 Hz with a mechanical chopper (model SR540, Stanford Research Systems, Inc., Sunnyvale, CA).

For OGS measurement, the ac component of the cathode voltage was routed to a digital oscilloscope (model 2246A, Tektronix, Inc., Beaverton, OR) and a lock-in amplifier (model SR510, 1s time constant, Stanford Research Systems, Inc., Sunnyvale, CA). The output of the lock-in was digitized by the Ti:S control computer or, in the case of the diode laser, a separate computer.

RESULTS AND DISCUSSION

We have observed and studied isotopically selective OGS at 778.42 and 776.19 nm with diode laser excitation in samples of uranium in a demountable GD cell. The two excitation processes are described in Table 1 along with other information available for these transitions (5,6).

Table I. Uranium Transitions of Interest

Wavelength (nm)	Transition (cm ⁻¹) Term symbols	Relative Emission Intensity (5)	Isotope Shift (6) (GHz)
778.42	620 → 13463 $5K_5^o - 5K_6$	425	3.0
776.19	7005 → 19885 $3K_6^o - 5M_7$	30	-12.6

In Figure 2, we show OG spectra at 778.42 of uranium in a pellet of U₃O₈-silver. It is noteworthy that the GD process liberates free uranium atoms from an oxide sample. In the lower spectrum, the ²³⁸U is on scale. The upper spectral response was enhanced to show the ²³⁵U hyperfine structure adjacent to the ²³⁸U line. Although this wavelength is diode laser accessible, these spectra were obtained using the Ti:S ring laser. The observed ²³⁸U linewidth was 925 MHz fwhm at the laser power density of 1x10⁵ W/cm². This power density is much higher than that of diode lasers, but similar spectra were also observed at laser power densities on the order of 400 W/cm² by attenuating the Ti:S laser beam.

Figure 2. OG spectrum of uranium in natural abundance U₃O₈ sputtered in a glow discharge.

Note in the upper spectrum of Figure 2 that the hyperfine structure of ²³⁵U can be seen in the base of the ²³⁸U OGS line. The width of the hyperfine structure for ²³⁵U for this transition has not been published, but it can be seen that there is not complete resolution of the two isotopic features.

Examining the second entry in Table I, it is apparent that a much larger isotope shift is available if one can use the 776.19 nm transition as the basis of an OGS process. This excitation represents a transition from the highest-lying metastable state of uranium. The relative emission intensity is weak, but these intensities do not relate directly to OGS. In Figure 3 we compare the diode laser excited OGS spectra at 778.42 and 776.19 nm for an enriched metal uranium sample (10% ²³⁵U). The diode laser power densities at the sample were 150 W/cm²

(3 mW) and 400 W/cm² (8 mW), respectively. There is complete separation of the ²³⁵U hyperfine structure and the ²³⁸U line at 776.19 nm corresponding to the isotope shift (6) given in Table I. The relative intensities of the two OGS spectra cannot be assessed from the figure, but in other studies with the Ti:S laser at essentially constant power over these spectral ranges, the 776 nm OGS spectrum was only five times less intense than the 778 nm spectrum.

Figure 3. OG spectra of enriched (9.75% ²³⁵U) uranium metal at 778.42 and 776.19 nm.

Currently we are carrying out a further evaluation of the 776.19 nm OGS transition. We examined depleted uranium and were able to quantify the minor ²³⁵U isotope at this wavelength. In preliminary measurements of uranium isotope ratios by OGS, we have obtained run-to-run and sample-to-sample precisions of better than $\pm 1\%$ or $\pm 3\%$ relative standard deviation, respectively, at either wavelength.

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