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Determination of actinide isotope ratios using glow discharge optogalvanic spectroscopy

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Abstract

Diode laser-excited optogalvanic spectroscopy (OGS) of a glow discharge has been utilized to measure U-235/U-235+U-238 isotope ratios. This 'optical mass spectrometric' measurement has been demonstrated for a number of samples including uranium oxide, fluoride, and metal. Various diode laser-accessible atomic transitions in the 775–835 nm region have been evaluated; these transitions were chosen by considering OGS sensitivity and isotope shift. Using the 831.84 nm uranium line, for example, it was possible to measure the U-235/U-235+U-238 isotope ratio (0.0026) of depleted uranium samples. A prototypical field instrument to make these measurements has been assembled and demonstrated. A U-236 spectral line was identified in an enriched uranium sample, and an abundance was measured. © 1998 Elsevier Science S.A.

Keywords: Glow discharge; Optogalvanic spectroscopy; Diode lasers; Actinides; Isotope ratio; Uranium

1. Introduction

Measuring isotope ratios is generally a time-consuming analytical procedure that requires expensive, cumbersome laboratory equipment to obtain the best possible precision (±0.1%) and accuracy. Particularly for lanthanides and actinides, there is a need for a rapid, simple mass analysis that might sacrifice some precision and sensitivity for speed. We have exploited the simplicity of diode laser-excited optogalvanic spectroscopy (OGS) of a glow discharge (GD) to develop a simple 'optical mass spectrometer'. This instrument is field portable and can analyze solid samples. For the case of uranium it can measure U-235/U-235+U-238 isotope ratios as low as 0.3% with ±15% RSD precision. For enriched U samples the precision is better, ~±3% RSD. This technique is simple and inexpensive relative to conventional mass spectral analysis, and it provides an isotope screening analysis of lanthanides or actinides with provisions for further analysis of the same sample if warranted.

2. Experimental

The apparatus for carrying out these studies has been described [1,2]. Essentially a solid sample, 150 mg, was mixed with 150 mg of a 50/50 wt.% mixture of powdered Ta and Ag. This mixture was pressed into a tube-shaped cylindrical pellet, 5 mm O.D., 2.5 mm thick, with a 2.4 mm hole in the center. The pressed sample composite was made using either a standard commercial press or a stainless steel cylinder and two opposing 3/4″-16 machine bolts. The prepared sample constituted the cathode in a GD cell; the anode was the cell wall. The discharge was maintained at 600 V in 1050 Pa Ar gas flowing through the cell at 3 cm^3 STP min^{-1}. Light from a tunable semiconductor diode laser, 10–40 mW, was passed through windows in the GD cell and through the center opening in the sample cathode. As the wavelength of the diode laser was tuned across isotope transitions of uranium in the sample plasma, an OGS signal was produced which was proportional to the concentration of that isotope in the discharge. A prototype for a field instrument was developed and will be described in the next section.

3. Results

We have quantitatively investigated this OGS-GD technique for several lanthanides but have concentrated on measuring U-235/U-235+U-238 isotope ratios. There are a number of diode laser-accessible atomic uranium transitions that could be utilized for this GD-OGS technique [3]. One looks for sufficient intensity of the OGS signal and

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Table 1
Relative strengths and isotope shifts of various uranium transitions investigated

Wavelength (nm)	Transition	Relative optogalvanic intensity	Isotope shift[3] (GHz)
835.71	3868–15831 cm^{-1}	0.16	11.6
831.84	4275–16294 cm^{-1}	0.26	10.1
822.31	6249–18406 cm^{-1}	0.19	10.4
791.88	4275–16900 cm^{-1}	0.16	−9.2
790.04	4275–16929 cm^{-1}	0.17	0.6
788.19	6249–18932 cm^{-1}	0.27	9.5
778.42	620–13463 cm^{-1}	1.00	3.0
776.19	7005–19885 cm^{-1}	0.10	−12.6

reasonable isotope shift in choosing an analytical line. Several transitions that were evaluated are given in Table 1. A typical averaged OGS spectral scan for the uranium transition at 776.2 nm is given in Fig. 1; the sample was depleted uranium metal (0.3% U-235). A generalized calibration plot for various uranium isotope ratio measurements using the 776.2 nm transition is shown in Fig. 2. As can be seen, the technique works equally well for uranium metal, uranium oxide, or uranium fluoride; since it is demonstrated to work for these compounds, it would also be expected to be applicable to any uranium compound of less thermodynamic stability. Note that the precision is obviously poorer as the U-235 content decreases, but the measurement is quite adequate for identifying depleted, natural or enriched uranium. Since ratios of the selected isotope abundances were measured, the method did not require calibration. NIST standards were used to evaluate the technique, but were not necessary for sample determinations. Further, for the data presented in Fig. 2, no correction for laser power variation was necessary. We have not evaluated the technique for other actinides, but it would be expected to be equally applicable to isotope ratio measurements for any f-element sample for which the isotope shift is adequate. In reality it would be applicable to any inorganic sample for which the analyte atom has an accessible optical transition within the range of a tunable laser.

A prototype of a field GD-OGS instrument has been developed specifically for U-235/U-235+U-238 isotope ratio measurements. The details of this instrument are given in a technical report [4]. The configuration of the components of the instrument is shown in Fig. 3. The GD cell is shown in the upper left edge of the layout. It has extended window tubes to minimize sample condensation. For field operation the pressure of the GD cell and the gas flow rate were set by using capillary restrictions. The key to operation of this instrument is wavelength control and scan. The wavelength of an optically isolated diode laser was controlled using a notebook computer. The computer was programmed to scan the diode laser wavelength by changing its drive current in a sawtooth fashion across the isotope shift region of a particular uranium transition.

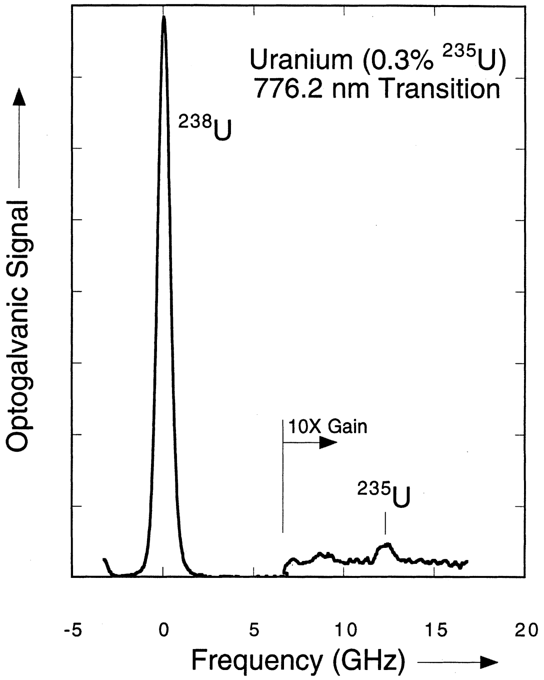

Fig. 1. Average optogalvanic signal for three spectral scans near 776 nm for a depleted (0.3% U-235) uranium metal/silver sample cathode. The detection gain was increased 10-fold at the indicated position.

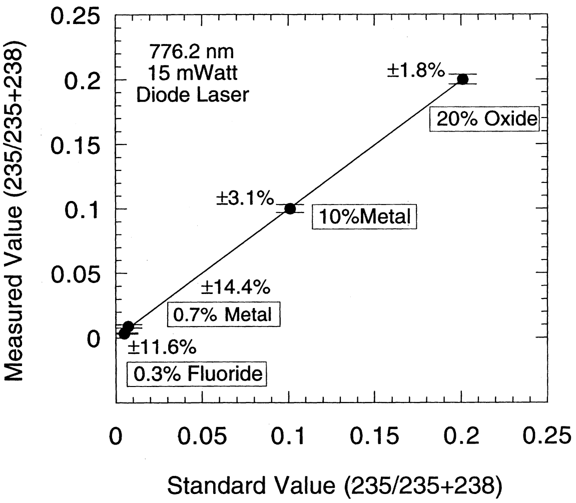

Fig. 2. Measured U-235/U-235+U-238 ratio versus reference value (certified value or thermal ionization mass spectrometric measurement) for several uranium compounds.

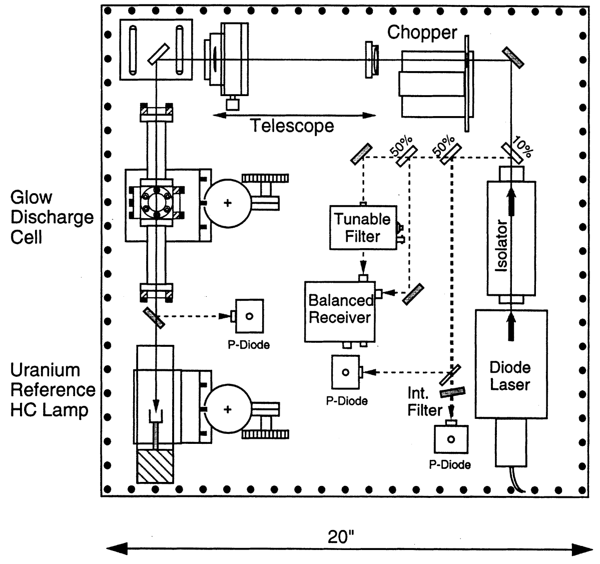

Fig. 3. Configuration of the components for the field prototype GD-OGS instrument for measuring uranium isotope ratios.

Course wavelength information was received from measurement of the transmission through an interference filter; fine wavelength information was determined using a unique wavelength-measuring application (R.W. Shaw, unpublished studies) of a liquid crystal tunable filter combined with a balanced receiver. The resulting spectrum was displayed and stored. The various photodiodes (P-diodes) shown in the figure collect the optical information from the course and fine wavelength monitors to be utilized in the computer diagnostic software. A commercial uranium hollow cathode lamp was also included in the system, to be used as a reference sample for procedural verification. In a demonstration of the prototype instrument, a GD-OGS measurement of a U-200 NIST uranium oxide sample (20.19% U-235) yielded a value of 19% U-235. The uranium transition used for this demonstration was at 831.8 nm.

In other GD-OGS spectral studies of the U-200 sample at 831.8 nm, with our laboratory apparatus, it is of note that we observed a signal from U-236 in enhanced presentations of the spectral range between U-235 and U-238; an example of these spectral results is shown in Fig. 4. This sample of 20% enriched U-235 contains 0.1% U-234 and 0.2% U-236. Based on the U-234 and U-238 isotope shift information for the uranium levels involved in the 831.8 nm transition [3], the signal seen in the figure near −5.7 GHz can be attributed to U-236. Comparing the area measurements of the U-235 and U-236 peaks in this sample, a U-236 abundance of 0.25% is obtained; the NIST certified value for U-236 is 0.2116% for this standard.

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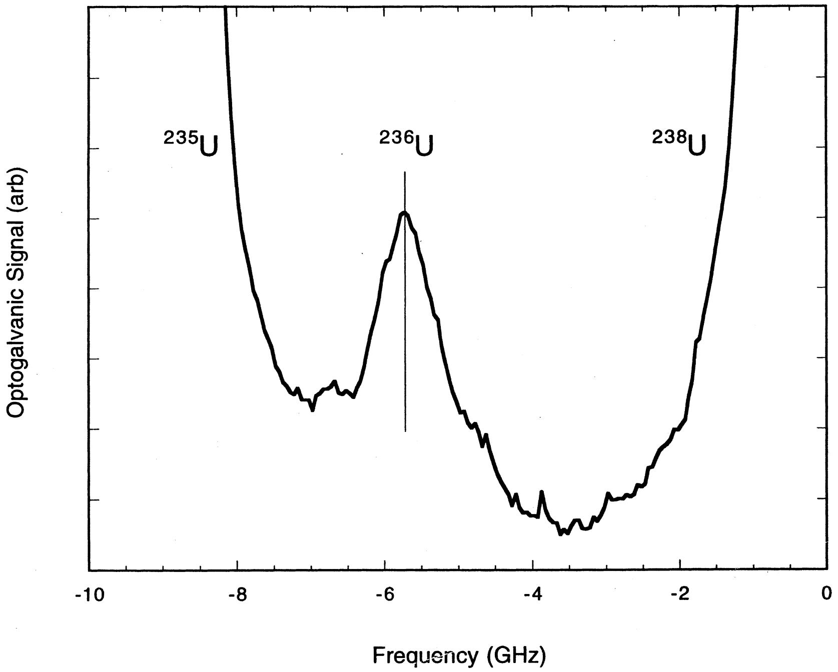

Fig. 4. Enhanced GD-OGS spectrum of an enriched uranium oxide sample (20% U-235) showing signal for 0.2% U-236.

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