

GLOW DISCHARGE SPECTROSCOPY FOR DETERMINATION OF URANIUM ISOTOPE RATIOS*

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ABSTRACT

We have developed a technique for uranium isotope ratio determinations in field settings. Such a technique will be invaluable to inspectors for rapid analyses, where immediate data can help guide a sampling campaign. The method encompasses glow discharge sputtering from pressed sample hollow cathodes, high resolution laser spectroscopy using conveniently tunable diode lasers, and optogalvanic detection. Upon completion of an analysis, most of the sample cathode remains and can be archived as evidence or returned to a laboratory for further examination. Using this technique, we determined the analytical figures of merit (sensitivity, accuracy, linearity, and precision) for $^{235}\text{U}/(^{235}\text{U}+^{238}\text{U})$ isotope ratio measurements for uranium samples with enrichments as low as “depleted” (0.3% ^{235}U). At 10% ^{235}U enrichment and above, the observed precision was $\pm 3\%$; it declined to $\pm 15\%$ for 0.3% samples. Oxide powder samples were amenable to this method, even though the U-O bond is tenacious; glow discharge sputtering was sufficiently energetic to yield gaseous uranium atoms. To optimize the method, different discharge gas conditioning methods were examined to study the corresponding effect on the observed optogalvanic signal strength. A prototype instrument was constructed and will be described. It was tested by analyzing an enriched uranium oxide sample.

Key Words: uranium isotope ratios, diode lasers, optogalvanic spectroscopy

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INTRODUCTION

Recently, there has been a great deal of interest in chemical measurements that can be conducted in field settings. A particular example of this interest has been for isotope ratio determinations, traditionally the province of mass spectrometry in a sophisticated laboratory. For environmental cleanup activities or for decontamination and decommissioning operations, it would be valuable to deploy an on-site technique for rapid, on-site analyses, even if the measurements made were only at modest precision ($\pm 10\%$). The alternative would be sampling, followed by return of samples to an analytical laboratory, analysis, and result reporting. That process can typically consume days to weeks. Rapid turn around results can aid in directing a sampling campaign; if an unusual sample enrichment is discovered, further sampling can be concentrated in the vicinity of the initial sample. For an on-site inspection, access to sufficient sample material for a determination is assumed. Laboratory-based mass spectrometry is very sensitive, amenable to a suite of interesting analytes, and can provide isotope ratios at a precision of $\pm 0.1\%$ or better. Interesting samples discovered by the field technique would be forwarded to a laboratory for more precise analysis.

The method described here encompasses glow discharge sputtering from pressed sample hollow cathodes, high resolution laser spectroscopy using conveniently tunable diode lasers, and optogalvanic detection. Conventional methods for measuring isotope ratios are seldom amenable to field use. They can be difficult and time consuming, involving sample dissolution, filament loading (for thermal ionization mass spectrometry), and ion count logging and interpretation. We have demonstrated a simpler technique, glow discharge optogalvanic spectroscopy^{1,2,3}, for use in instances where only modest accuracy and precision are required. With this method, isotopic abundances are determined using high resolution optical spectroscopy instead of spatial or temporal separation of the masses. Sampling is accomplished without dissolution or any other pretreatment; sample powders are pressed with a conducting binder to form hollow cathodes. These are sputtered in a low-pressure argon dc glow discharge to produce analyte atoms in the gas phase. Only modest vacuum conditions are required, as the operating pressure is approximately 1000 Pa (i.e., a few Torr). The optogalvanic effect is used to quantify the isotopic abundances. As the wavelength of a single longitudinal mode laser is tuned through absorption features of the discharge gas, optical energy is deposited; this results in a change in the ionization equilibrium of the plasma that is detected as a discharge impedance change. The laser beam is modulated using a mechanical chopper, and impedance changes are measured using a lock-in amplifier that processes the ac component of the cathode voltage. Integration of the areas under the resolved spectral signatures of the isotopes yields the abundances. Use of the optogalvanic technique for isotope ratio determinations has been considered in the past by others.^{4,5,6,7,8} The aspect that affords practicality to the method described here is that a semiconductor diode laser was employed as the source. Diode lasers are rugged and their output wavelength is conveniently tuned by varying the device temperature and/or the drive current.

The effect of including contaminants (e.g., soil) in samples was explored. Different uranium compounds were examined as analytes. To optimize the method, different

discharge gas conditioning methods were examined to study the corresponding effect on the observed optogalvanic signal strength. For such a field method to be of use, the instrumentation must be transportable. A prototype instrument was constructed and is described here. The prototype included a unique monitor to help assure that the diode laser output is indeed at the desired wavelength, a problem for any instrument that incorporates a semiconductor laser. The prototype instrument was tested by analyzing an enriched uranium oxide sample.

EXPERIMENTAL

Prototype instrument description:

A prototype instrument was designed and fabricated. The goal was to create a prototype that would require a minimum of operator training and exhibit a volume of < 0.5 m³ and a weight of < 100 kg. Such an instrument would be van portable. The availability of standard 115 volt AC power has been assumed for this initial prototype. Many of the analytical results reported here were recorded using a laboratory instrument comparable to the prototype, except that a widely-tunable, attenuated (to mimic a diode laser) titanium:sapphire laser was employed for excitation.

A sample press was assembled for pressing sample cathodes in the field. It is similar to those used for preparation of KBr pellets for infrared spectroscopy, except that for this application it was desirable to form hollow cylinders. Because electrically insulating samples may be encountered, sample powders were typically mixed with a silver powder host (50:50 by mass). The resulting sample cathode had a 4.85 mm outer diameter, a 2.38 mm inner diameter, and a 2.54 mm length (depending on the amount of sample loaded).

The discharge cell was assembled from standard copper gasket high vacuum hardware. A vacuum "cube" formed the body of the cell. Three glass windows on flanges were provided for viewing the discharge and for the entering and exiting laser beam; the entrance and exit windows were located on flanged nipples to move the windows further from the cathode and reduce the amount of sputtered material that deposited on them. An additional flange was fitted with a coaxial high voltage sample probe that sealed on an O-ring. The vacuum chamber envelope (at ground potential) served as the discharge anode. Typical operating parameters for the discharge cell were: 1050 Pa argon fill gas flowing at 8 sccm, a 1000 V applied potential (applied through a 50 K Ω ballast resistor), and a 15 mA discharge current. The cell pressure and flow rate were controlled using glass capillary tubes inserted into 1/4" gas lines between the gas bottle regulator and the cell and between the cell and the pump. The capillary lengths and inner diameters were calculated so as to result in the desired flow rate and cell pressure.

For the results derived using the prototype instrument and described here, a commercial, external cavity diode laser (Environmental Optical Sensors, Inc. EOSI, Boulder, CO 80301, model 2001) was employed at 832 nm. The 831.84 nm line corresponds to excitation from the 4275 cm⁻¹ uranium metastable level to the level at 16294 cm⁻¹. Since the isotope shift for this line (10.1 GHz, or 0.023 nm) is large, the 235U signal can be measured unambiguously (without overlap from 238U). The laser

and all the optical components were mounted on an optical breadboard that served as the top of an instrument relay rack.

A critical component for the success of this technique is a device to assure that the measurement wavelength is correct. Diode lasers operate in a single longitudinal mode (< 25 MHz linewidth) and will mode-hop (discontinuously shift output wavelength) by 0.3 to 0.5 nm, depending on the specific laser, unless care is exercised in their operation. These wavelength hops are enormous on the scale set by the spectral line width. Thus, knowledge and control of the precise operating wavelength is critical. A wavelength monitor for scanning the uranium line was developed. Changes in the respective transmission coefficients of two optical components were used: a narrow bandwidth interference filter (for gross wavelength changes, i.e., mode hops) and a tunable Lyot filter (for small wavelength changes).

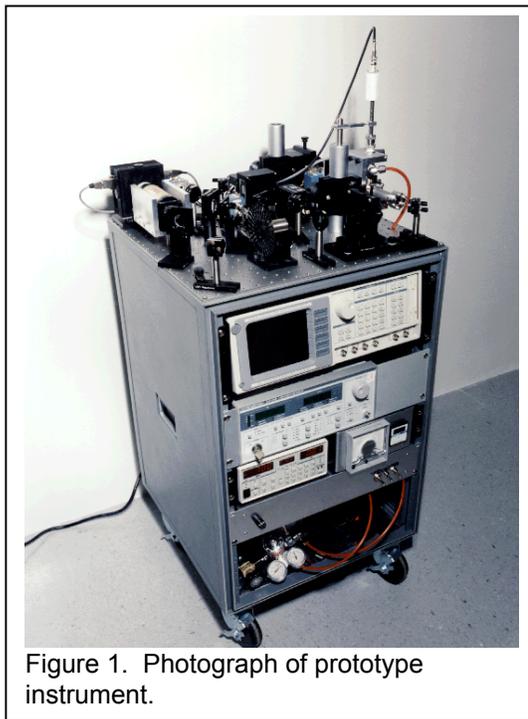


Figure 1. Photograph of prototype instrument.

The ac component of the cathode voltage was monitored as the detection signal. A simple RC network was used to extract that small voltage from the discharge high voltage. A lock-in amplifier (Stanford Research Corp., Sunnyvale, CA 94089, model 850) was used for this signal treatment. A notebook computer controlled the overall measurement via a GPIB 488 interface bus and a digital I/O board. The operating program was developed using Labview© software (National Instruments, Inc., Austin TX 78730).

A photograph of the prototype instrument is shown in Figure 1. The total mass of the prototype is 98 Kg, and the power consumption is 655 Watts.

RESULTS

Uranium spectroscopy:

Several hundred uranium transitions have been identified in the diode laser accessible wavelength range of 670 nm - 1.5 μm . We examined a number of these as possible excitation candidates for isotopic analysis. Several factors entered into the decision to evaluate a particular uranium transition: (a) the transition oscillator strength (emission spectra⁹ were used as a guide), (b) known 235U-238U spectral isotope shifts,¹⁰ (c) whether or not an origin state was metastable relative to the ground state, (d) potential interferences due to nearby spectral lines (e. g., of the argon cell gas), and (e) the availability of commercially-available diode lasers of reasonable output power at the transition wavelength. Two laser wavelengths were identified for 235U/(235U+238U)

quantitation: 776.19 and 831.84 nm. These wavelengths correspond to transitions with modest optogalvanic signal strengths and large spectral isotope shifts (-12.6 and 10.1 GHz, respectively). Discrete diode lasers (for example, from Mitsubishi Electric Corp, Tokyo, Japan, and from Spectra Diode Labs, San Jose CA) were used for measurements at these wavelengths.

Figure 2 illustrates the 776.2 nm uranium line that exhibits an isotope spectral shift sufficiently large for facile determination of isotope ratios. The observed linewidth is Doppler limited and is generally < 1GHz full width at half maximum (FWHM). The sample was depleted uranium metal (0.27% ²³⁵U). The signatures corresponding to ²³⁵U and ²³⁸U are fully resolved. Other uranium lines with smaller isotope shifts (< 1 GHz) are less desirable because of spectral overlap of the isotope features. The spectrum of Figure 2 was recorded using a titanium:sapphire laser with the output attenuated to 30 mW to simulate the robust tunable diode lasers to be employed for field measurements.

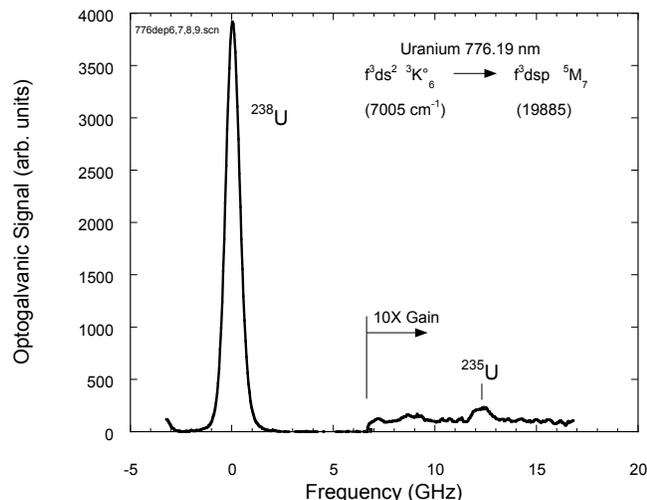


Figure 2. Optogalvanic spectral scan of the uranium 776 nm line for depleted uranium metal.

Uranium isotopic analysis: Figures of merit

Isotope ratio measurements at low enrichment:

The ²³⁵U/(²³⁵U+²³⁸U) isotope ratio was successfully measured for a depleted uranium metal sample, corresponding to the lowest abundance expected for field measurements. The 776.2 nm uranium atomic line was used. Figure 2 shows a scan of the transition for a depleted metal sample. At the position indicated in the figure, the measurement sensitivity was increased ten-fold. The signatures shown that correspond to ²³⁵U and ²³⁸U are distinct and separated. By integrating the signal areas, we found the ²³⁵U/(²³⁵U+²³⁸U) ratio to be 0.0034. A benchmark ratio for this sample measured using thermal ionization mass spectrometry was 0.0027. The use of a more powerful laser diode operating at 831.8 nm resulted in an improved accuracy and precision (3.7% and 7.8% RSD, respectively).

Measurement Accuracy and Precision:

To evaluate the utility of optogalvanic spectroscopy for uranium isotope ratio measurements, four cathodes (fabricated from a ²³⁵U enriched oxide powder, a ²³⁵U enriched metal, a natural metal powder, and a ²³⁵U depleted fluoride powder) were prepared. By choosing four different isotopic compositions and three different uranium compounds, samples were addressed with a wide variety of characteristics.

Figure 3 shows a calibration curve developed from data recorded using the 776.2 nm diode laser. The measured $^{235}\text{U}/(^{235}\text{U}+^{238}\text{U})$ values (peak areas) were plotted versus either the certified values, as in the case of the National Institute of Standards and Technology (NIST) U-200 (nominally 20% enriched in ^{235}U), or versus thermal ionization mass spectrometric values, as measured in the Inorganic Mass Spectrometry Laboratories at the Oak Ridge National Laboratory. Eleven isotope ratio measurements were made for each cathode. Relative standard deviation ($\pm 1 \sigma$) values are shown. The data show a good linear fit with an R value of 0.99986 for a line with slope 1.019 and y-intercept 0.0018. For the four samples analyzed, the percent relative error with respect to the thermal ionization measurements ranged from 2.38% for the nominally 20% enriched ^{235}U sample where the ^{235}U signal-to-noise ratio was > 500 to 1, to greater than 30% error for the natural and depleted samples where the signal-to-noise ratio was < 5 to 1.

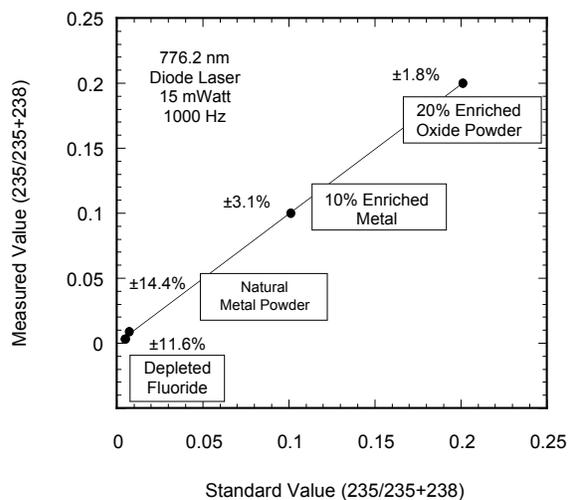


Figure 3. Measured $^{235}\text{U}/(^{235}\text{U}+^{238}\text{U})$ ratio versus reference value for four uranium compounds and enrichments.

Run-to-run, day-to-day and sample-to-sample precision (repeatability) were evaluated using a 776 nm, 30 mW diode laser (400 W/cm^2 at the cathode). The cathode was formed from the NIST U-200 standard. Seventy-seven $^{235}\text{U}/(^{235}\text{U}+^{238}\text{U})$ determinations were made over 7 days with 3 different sample cathodes. Each measurement was the average of eleven $^{235}\text{U}/(^{235}\text{U}+^{238}\text{U})$ ratios. The signals corresponding to ^{235}U and ^{238}U were measured as the area of the peaks, from baseline to baseline, using off-line processing. The run-to-run precision is defined as the percent relative standard deviation at 1σ for $n=11$ measurements of the same cathode. This value ranged from $\pm 1.9\%$ to $\pm 5.5\%$ over five consecutive days. The mean was computed each day and used to determine the day-to-day precision; this was $\pm 2.6\%$ RSD. Sample-to-sample precision was based on measurements from three different cathodes (55 from sample A and eleven measurements each from sample B and C). This value was $\pm 3.5\%$ RSD. The ratios show no trends or biases, varying about a mean of 0.21 and ranging from a high of 0.23 to a low of 0.18.

Discharge conditioning:

A strong dependence of the optogalvanic signal strength on the quality of the discharge was noted. Others have seen a similar effect in mass spectrometric measurements^{11,12,13} and have attributed changes in the discharge character to varying concentrations of water and other gaseous impurities. A number of sources determine the discharge water and oxygen concentrations: a) water in the feed gas, b) vacuum leaks in the chamber, c) outgassing of water from the discharge cell walls, d) adsorbed water on the sample, and e) oxygen atoms sputtered from a metal oxide sample. Tests

of discharge gas conditioning by a number of means were conducted. A gas purification cartridge was inserted into the feed gas supply line. A non-evaporable getter was added to the discharge cell for active removal of components other than argon in the immediate vicinity of the cathode. The boiloff gas from a liquid nitrogen Dewar was used to cool a metal tubing loop in the discharge cell to remove condensable gases.^{14,15} Tantalum metal (a gas phase getter) was incorporated into pressed sample cathodes to sputter along with the analyte atoms. The operational improvements attained via these gas conditioning means translate into enhancements of the accuracy and precision of isotope ratios determined using this method. The sample for these studies was enriched (20% ²³⁵U) uranium oxide (U₃O₈) prepared as a 50:50 weight percent mixture with silver powder and stored in air.

In general, it was observed that the optogalvanic signal increased with time after initiation of the glow discharge, especially if the cell vacuum had been broken to introduce a new sample cathode. Presumably this effect was due to removal of impurities such as water vapor and oxygen with the passage of time. The measurements in this study were conducted using a uranium oxide sample and were expected to be affected by oxygen-containing impurities due to the tenacity of the U-O bond (bond dissociation energy: 182 kcal/mol). The mixture of sputtered products from U₃O₈ is expected to be rich in molecular oxides.

The simple application of a gas purification cartridge (Labclear, Oakland, CA 94601, model Oxiclear DGP-250-R1) made a substantial improvement (40%) in the optogalvanic signal strength over that from a discharge operated with unprocessed argon, nominally 99.9995% pure. Because of the ease of use of this cartridge, it was left in the feed gas line and was present for all of the data presented here.

The primary effect observed upon further conditioning of the discharge gas was an increase of the discharge current (and hence the sputtering), at constant applied voltage. Accompanying that change was a corresponding increase in the analyte optogalvanic signal. The conditioning could be affected by gettering or condensation of gaseous impurities. The former could be accomplished using a heated, non-evaporable getter (SAES Getters, Colorado Springs, CO 80906, model ST172/NP/HITS-L/7.5-7/150C) in the cell or by incorporation of Ta metal in the sample cathode. Tantalum forms a strong oxide bond and was explored as possible vapor phase getter by employing it as a portion of the metallic host when forming sample cathodes. When Ta sputters into the vapor, it can potentially scavenge free oxygen. The non-evaporable getter yielded a six-fold improvement in signal strength, relative to that for a newly-initiated discharge. Gettering by gaseous Ta atoms yielded a two-fold stronger optogalvanic signal than did gettering by the non-evaporable device; however, it was slower. The most effective conditioning technique was cooling using liquid nitrogen (17-fold signal improvement), but this method introduced experimental complications.

Sample Matrix Effects:

For field measurements, a uranium sample composition may be molecular, i.e., not pure metal. This factor has a bearing on our technique, in that any portion of a molecular

sample that sputters as a small molecule that is not subsequently dissociated by the discharge will not be detected. For example, if UO is sputtered from a uranium oxide sample, there will not necessarily be an optogalvanic response at a uranium atomic line wavelength. Several stoichiometric uranium compounds were examined to determine the generality of this observation. To detect all of the small molecules that may possibly sputter, mass spectrometry, instead of optogalvanic detection, was selected to monitor the glow discharge. The compounds that have been examined include: uranium metal (probably unintentionally overcoated with an oxide layer), U_3O_8 , UF_4 , UO_2Cl_2 , and $U(SO_4)_2$. The uranium ion yield from silver hosts did not seem to be greatly affected by the choice of uranium starting compound.

The effect on the optogalvanic isotope analysis method of adding contaminants to the uranium sample was examined by recording optogalvanic spectra for samples to which soil had been added. It was expected from the above results concerning discharge gas purity that extraneous sample matrix components would degrade the measurement performance because they could only add unknown and uncontrolled species to the discharge environment. Samples containing 1:1:1:1 by weight U_3O_8 :soil:silver:tantalum were prepared and examined. The uranium oxide incorporated was enriched in ^{235}U to 3%. The soil used was a NIST standard reference material (dried Buffalo river sediment, SFM No. 2704). The optogalvanic signal recorded for these samples was approximately 5- to 10-fold weaker, relative to a comparable $U_3O_8/Ag/Ta$ sample. The precision observed for the isotope ratio measurement was $\pm 15\%$, as dictated by the lower signal-to-noise ratio. That precision is comparable to the precision observed for measurement of depleted uranium samples. Thus, components added to the sample (and eventually to the discharge) by addition of soil do indeed degrade the measurement.

Prototype Instrument Performance:

The prototype instrument was used to determine a uranium isotope ratio. The sample cathode was enriched uranium oxide (20% ^{235}U) in a silver/tantalum binder. An external cavity diode laser was employed, operating at the 831.8 nm uranium line. A single scan of the spectrum was recorded under computer control, along with signals from the wavelength monitor (light transmission through the interference filter and through the tunable filter that had been set for the uranium wavelength). The ^{238}U and ^{235}U spectral features are clearly discernible. Using the integrated areas under these features, the $^{235}U/(^{235}U+^{238}U)$ ratio calculated was 19.0%, in excellent agreement (5.0% error) with the true value. No multiple-scan signal averaging was required to obtain this ratio. For a set of three consecutive scans, the measured precision was $\pm 10\%$. These results demonstrate the viability of this technique.

SUMMARY

We have developed a technique and instrument for uranium isotope ratio determinations in field settings. Such a technique will be invaluable to investigators for rapid analyses during on-site inspections. The method encompasses glow discharge sputtering from pressed sample hollow cathodes, high resolution laser spectroscopy

using conveniently tunable diode lasers, and optogalvanic detection. Upon completion of an analysis, most of the sample cathode remains and can be archived as evidence or returned to a laboratory for further examination.

Using this technique, we determined the analytical figures of merit for $^{235}\text{U}/(^{235}\text{U}+^{238}\text{U})$ isotope ratio measurements for uranium samples with enrichments as low as “depleted” (0.3% ^{235}U). At 10% enrichment and above, the observed precision was $\pm 3\%$; it declined to $\pm 15\%$ for 0.3% ^{235}U samples. Oxide powder samples were amenable to this method. The effects of various discharge gas conditioning methods were studied.

A prototype instrument was constructed. A non-evaporable getter was incorporated into the prototype instrument to optimize its performance. The prototype instrument was tested by analyzing an enriched uranium oxide sample. Research currently underway will extend the capability of this method to measurements of uranium hexafluoride. A gas phase optogalvanic cell is under development, where UF_6 will be introduced into an argon discharge where molecular disruption will yield uranium atoms for analysis.

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