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Multi-Actinide Isotopic Measurements From A Single Sample By Resonance Ionization Mass Spectrometry

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ABSTRACT

Resonance ionization mass spectrometry (RIMS) is an analytical technique still in its infancy with respect to applications in nuclear forensics. This paper presents our first demonstration measuring both U and Pu isotopes in single samples, and highlights some of the strengths of the method including elemental selectivity. We show data demonstrating the ability to overcome isobaric (same mass) interferences between actinide species, as well as reproducible measurements of both U and Pu isotope ratios on the same sample. Analyzed samples include electrodeposited multi-actinide solutions used for proof-of-concept demonstrations, and low concentration synthetic multi-actinide glasses.

INTRODUCTION

Resonance Ionization Mass Spectrometry (RIMS) uses precisely tuned lasers to selectively excite and ionize atoms of an element of interest, permitting analyses of samples as collected, without complications from isobaric (same mass) interferences. First, atoms are desorbed or sputtered from a sample surface using a focused laser or ion beam. RIMS generates a cloud of ions, molecules and neutral atoms above the sample surface containing all elements originally present in the sample. Ions generated during the desorption process are removed by a brief voltage pulse. Neutral atoms of the element of interest are then selectively excited to an intermediate (resonant) electronic state by laser irradiation tuned to characteristic transitions, unique to that element. This process can be a single step, or can be made even more selective through use of two or more resonant excitation steps. The excited atoms are then photo-ionized from the intermediate electronic state by photons from an additional laser tuned to provide enough energy to place the excited atoms at or over the ionization threshold for that element. Finally, these photo-ions are accelerated into a mass spectrometer, mass analyzed and detected. Chemical separation is not necessary, since all other species are left behind as undetected neutral atoms/molecules.

In the case of Pu, the most common isobaric interferences are ^{238}U (the most common uranium isotope in nature), and ^{241}Am , the daughter product of ^{241}Pu , continually produced in a sample containing the parent. Obtaining accurate U and Pu isotopic data is important to the timely interrogation of materials of nuclear origin. Dissolution, purification and dilution or concentration are necessary prior to attempting most actinide isotopic analyses by mass spectrometry, and are generally the time-limiting step in obtaining isotopic data. RIMS can minimize or even obviate chemical separation and sample preparation steps for actinide isotope analyses in a variety of matrices, providing a rapid, accurate alternative for isotopic analysis. We have already demonstrated direct *in situ* uranium isotope analysis of oxides, metals and silicates by RIMS

[Isselhardt *et al.* 2011; Knight *et al.*, in press], and are pursuing similar work for Pu isotopic analysis by RIMS.

RIMS has been successfully applied to Pu isotope detection in studies by several authors [*e.g.*, Donohue *et al.*, 1984; Eberhardt *et al.*, 1995; Boulyga *et al.*, 1997; Grüning *et al.*, 2004; Ofan *et al.*, 2006]. All studies to date have required considerable sample preparation to obtain useful Pu ion yields, generally involving reduction of the actinide from a highly oxidized form to a more reduced or metallic state. Although multiple authors have reported a detection limit of 10^6 Pu atoms, no data yet exist characterizing the degree to which sample preparation is necessary or advantageous to the end result. In addition, analytical precision and accuracy have not been satisfactorily addressed, in that all applied isotopic studies have consisted of one-time-use methods and measurements, with no work thus far applied towards the rigorous validation of the RIMS method for rapid, precise and accurate measurement of Pu isotopes. We have been working to specifically address the challenges of rapid and accurate Pu isotopic measurements by RIMS using minimal pre-analytical chemistry, through internal LLNL support and support from the National Technical Nuclear Forensics Center. We also demonstrate isotopic detection of multiple actinides within the same sample, including study of both reduced and glassy matrices.

EXPERIMENTAL SETUP

We utilized 3-color laser schemes for Pu and U ionization (Fig. 1), working to optimize elemental selectivity, enhance background suppression, and minimize detection limits, based on schemes by Grüning *et al.* [2004] and Schumann *et al.* [2005]. Our experiments were done on CHARISMA, a time-of-flight mass spectrometer which is described in detail elsewhere [Savina *et al.*, 2003]. Analytical conditions utilized a 351 nm desorption laser running at 1 kHz with a spot size of $\sim 100 \mu\text{m} \times 150 \mu\text{m}$ for laser desorption. Resonance and ionizing lasers were tunable Ti:Sapphire lasers similar to those described in Isselhardt *et al.* [2011]. Wavelengths outside the 700-1000 nm tuning range of the lasers were generated by extra-cavity frequency doubling in LBO. The total isotope shift across the Pu isotopes ($^{238}\text{Pu} - ^{244}\text{Pu}$) is ~ 12 pm, similar to the total shift for the uranium

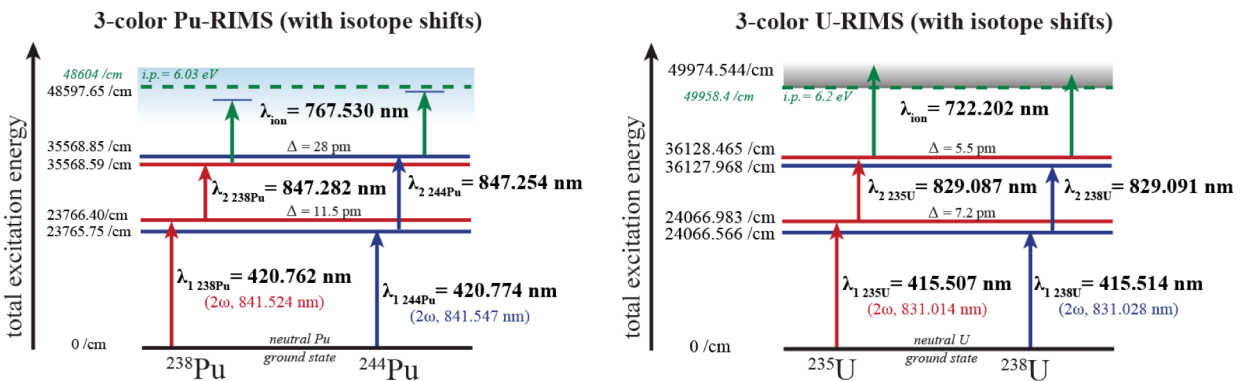


Fig. 1 The 3-step laser excitation schemes for U and Pu. Resonance lasers were tuned to sit at the midpoints of the isotopic resonances of each energy level.

isotopes from ^{233}U to ^{239}U . Isotopic reproducibility is profoundly affected by fluctuations in fundamental laser parameters such as *wavelength*, *power*, and *bandwidth* over the duration of a

given experiment, thus laser bandwidth was broadened to 5-20 pm to dampen sensitivity to isotopic shifts (see [Isselhardt et al., 2011](#)).

Our initial electro-deposited sample (Fig. 2) was prepared from a multi-isotopic Pu-nitrate solution containing ~25% ^{238}Pu , ~25% ^{239}Pu , ~25% ^{242}Pu and ~25% ^{244}Pu , and adventitiously contaminated with enriched (>90% ^{235}U) uranium. The solution was diluted to electro-deposit $\sim 10^{12}$ atoms of Pu and $\sim 10^{13}$ atoms of U onto a titanium stub. Titanium was chosen as the substrate because of the affinity of titanium to getter oxygen, thus helping to optimize the reducing environment for Pu and U. Our second sample was derived from a well-characterized synthetic multi-actinide Ca-Al-Si base glass (RG-UPI) containing ~500 ppm U (^{234}U , ^{235}U , ^{236}U and ^{238}U) and ~50 ppm Pu (^{238}Pu , ^{239}Pu , ^{240}Pu and ^{241}Pu). This glass was fragmented and pressed into soft indium metal for analysis (Fig. 2) to reduce potential charging of the sample, but otherwise unaltered. Neither sample was overcoated.

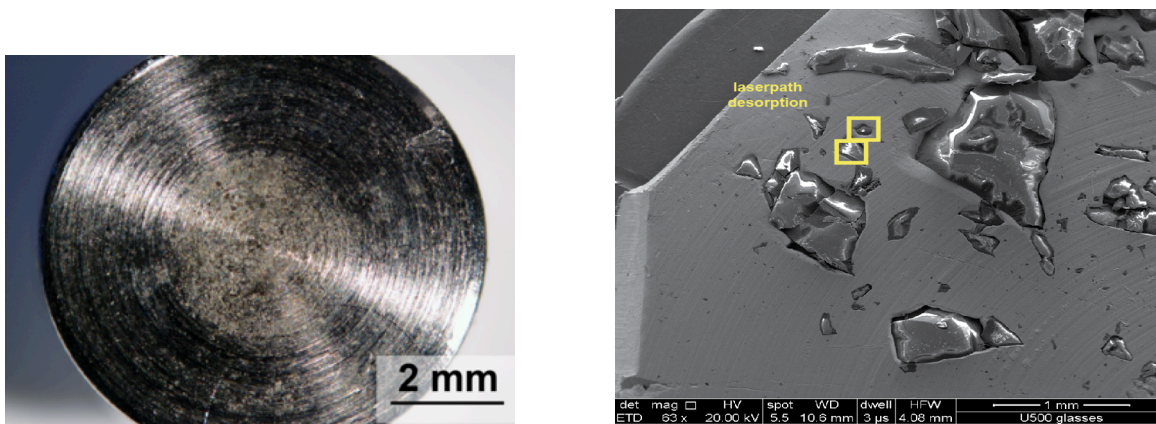


Fig. 2 An optical image of the electrodeposited sample on a titanium stub (left), and a backscattered electron image of the glass shards of RG-UPI pressed into indium (right, yellow areas indicate areas of analysis).

Pu AND U ISOTOPES BY RIMS

Initial experiments using 3-color ionization schemes to analyze the electro-deposited sample yielded excellent results, with selective ionization of all four isotopes of plutonium and four isotopes of uranium, using lasers tuned for Pu and U ionization, respectively (Fig. 3). Moving the laser wavelength 200 pm off of the atomic resonances completely suppressed the atomic Pu signal, and the atomic (but not molecular) U signal.

A closer look at the actinide mass spectrum (Fig. 3) shows a lack of any notable Pu-oxide signal. The minor contamination of enriched U, however, is largely apparent through the presence of $^{235}\text{U}^{16}\text{O}$ and $^{235}\text{U}^{16}\text{O}_2$ in the spectrum when lasers are tuned for Pu ionization. The presence of uranium oxides is a reflection of the tenacity with which uranium exists as an oxide. Some amount of the molecular oxide may dissociate creating a minor background contribution at the uranium atomic masses (234, 235, 236 and 238), but this contribution forms less than 2% of the total atomic uranium signal, and can be quantified and corrected. No significant contributions to the atomic mass regions were observed from either the resonance or the ionization laser alone indicating that multi-photon non-resonant ionization does not contribute to the 3-photon resonant ionization signal.

Additional simple steps, such as overcoating with Ti metal or adjusting laser powers may prove effective at removing the small amount of U observed when working with electrodeposited samples. We intend to explore suppression of this contribution to uranium mass peaks in future experiments.

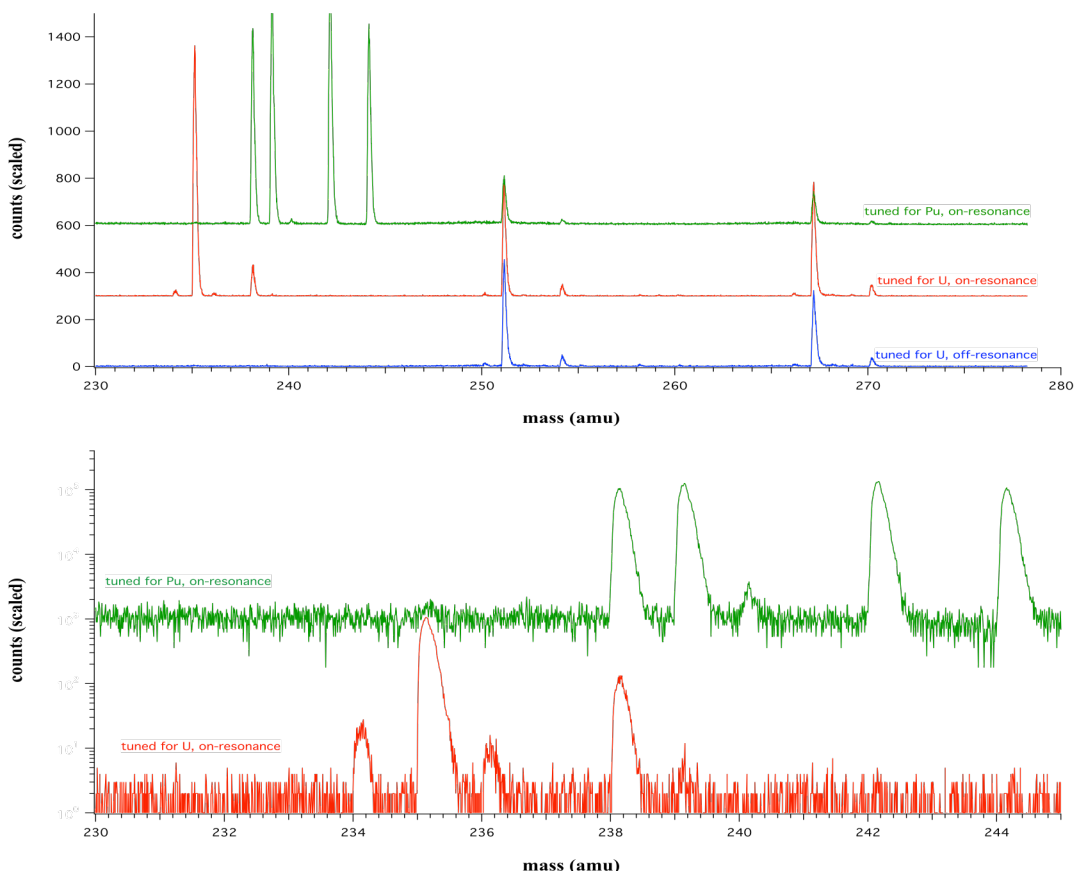


Fig 3 3-color Pu resonant and non-resonant ionization spectra from a titanium stub electrodeposited with a 4-Pu-isotope and enriched U solution. The panel shows (green, top spectrum) the signal when tuned to Pu, the second (red) spectrum shows the signal using lasers tuned to U, and the third (blue) spectrum shows the background, when the first resonance laser is detuned 200 pm. The bottom figure shows the resonant Pu and U signals on a log scale. No significant off-resonance or laser-induced backgrounds were observed. All data are scaled to 25,000 laser shots and are offset arbitrarily in the vertical access for clarity.

Fig. 3 demonstrates the excellent discrimination of isobaric interferences provided by RIMS. Even though the electro-deposited sample contains both U and Pu, an ion signal at the U masses is essentially absent when the lasers are tuned to excite Pu. Similarly, we observe no signal at the Pu masses when the lasers are tuned to excite U. Isotope ratios were measured for all 4 isotopes of Pu and all 4 isotopes of U, some of which are shown in Fig. 4. In both cases the mean squared weighted deviation (MSWD) values of the ensembles is less than one, indicating that the precision of the measurement is statistics-limited; *i.e.*, accumulating more data by counting for longer times, or counting for the same period of time at a higher count rate, would result in higher precision. Uranium measurements represent approximately 25 minutes of data collection, and plutonium

measurements represent approximately 35 minutes of data collection. As a sufficient number of lasers are not available for simultaneous measurement of U and Pu, switching between laser tuning schemes is necessary, and is presently done through a manual optics swap, which takes approximately 2 hours.

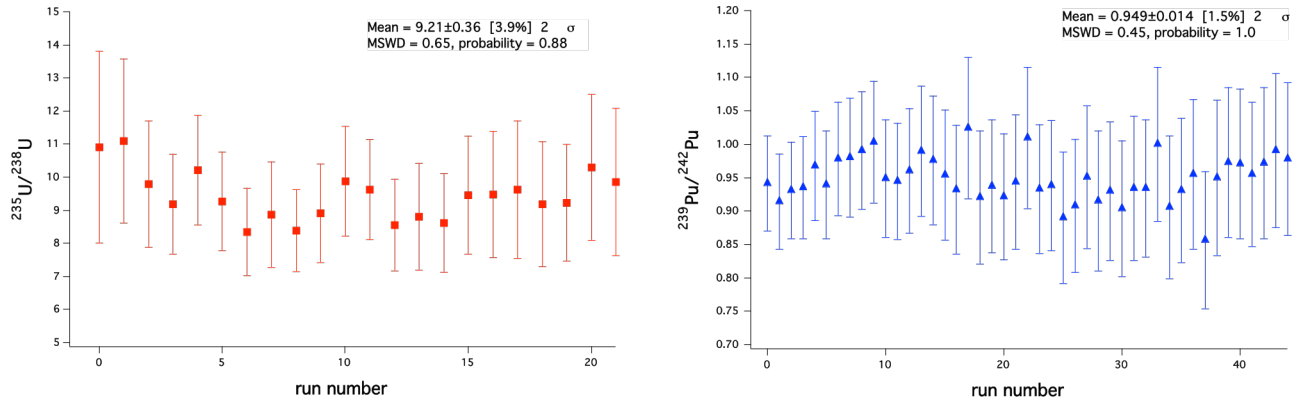


Fig 4 Selected isotope ratios measured from the multi-actinide electrodeposited sample. Each data point represents 25,000 laser shots, and error bars are 2σ . MSWD is ≤ 1 for both measurements, indicating that longer counting time will increase the isotopic precision.

Work with glassy matrices was pursued through experiments on the synthetic RG-UPI glass. Fragments of glass were targeted using the 100 μm x 150 μm desorption laser spot. Ion yields from silicate matrices, while not quantified in this study, appear to be significantly lower than those from reduced matrices such as those of the electro-deposited sample. Both uranium (present at 500 ppm)

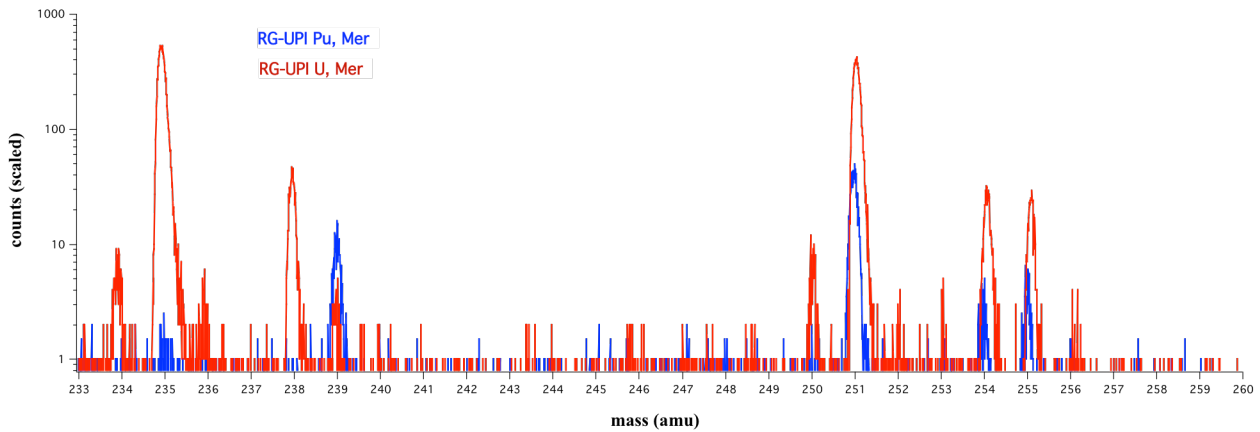


Fig 5 Mass spectra from the synthetic glass RG-UPI (500 ppm U, 50 ppm Pu) with lasers tuned first to U (red), and then to Pu (blue), plotted on a log scale. This synthetic glass yields some ion background, though major isotope signals were generally 10x or greater than background contributions.

and Pu (present at 50 ppm) were resolved. Molecular oxide and dioxide signals were present in both the U and Pu spectra.

While signals were sufficient to make precision measurements of uranium isotopes, in this case, only the major isotope of plutonium (^{239}Pu , isotopic abundance ~95%) could be confidently quantified. ^{240}Pu was observed, but requires additional background suppression or increased yield for quantification. While backgrounds were evident at these low U & Pu concentrations, instrument parameters were not optimized for maximum background suppression, and several instrumental options exist to further improve the spectra.

CONCLUSIONS

Rapid measurement of the isotopic composition of multiple elements in a mixed actinide sample without sample preparation lays the foundation for U and Pu isotopic analyses using resonance ionization mass spectrometry. Our experiments have provided several promising results, including the ability to measure a stable multi-isotope Pu signal using a simple electro-deposition sample preparation, and successful detection of both U and Pu from a glassy silicate matrix without any significant sample preparation. Additionally, we have demonstrated that we can easily move between RIMS schemes for two elements in samples of mixed actinides (U and Pu), as well as discriminating against interfering masses (^{238}U and ^{238}Pu). Experimental U and Pu discrimination is excellent, with only a small and independently quantifiable U signal evident when the lasers are tuned to Pu, wholly consistent with an atomic contribution derived from the dissociation of the large uranium oxide and uranium dioxide signals. Resonance ionization continues to demonstrate promise for application to the measurement of actinide isotopes for nuclear forensics.

REFERENCES

- Boulyga, S.F.: Erdmann, N.: Funk, H.: Kievets, M.K.: Lomonosova, E.M.: Mansel, A.: Trautmann, N.: Yaroshevich, O.I.: Zhuk, I.V.; Determination of isotopic composition of plutonium in hot particles of the Chernobyl area. *Radiation Measurements* **28** 349-352, 1997.
- Donohue, D.L.: Smith, D.H.: Young, J.P.: McKown, H.S.: Pritchard, C.A.; Isotopic Analysis of Uranium and Plutonium Mixtures by Resonance Ionization Mass Spectrometry. *Analytical Chemistry* **56** 379-381, 1984.
- Eberhardt, K.: Erdmann, N.: Funk, H.: Herrmann, G.: Köhler, S.: Nähler, A.: Passler, G.: Trautmann, N.: Urban, F.-J.; Chemical Separation of Plutonium from Air Filters and Preparation of Filaments for Resonance Ionization Mass Spectroscopy. *AIP Conference Proceedings* **329** 503-506, 1995.
- Grüning, C.: Huber, G.: Klopp, P.: Kratz, J.V.: Kunz, P.: Passler, G.: Trautmann, N.: Waldek, A.: Wendt, K.; Resonance ionization mass spectrometry for ultratrace analysis of plutonium with a new solid state laser system. *International Journal of Mass Spectrometry* **235** 171-178, 2004.
- Isselhardt, B.H., *et al.*, (2011) Improving Precision in RIMS: The Influence of Bandwidth in Uranium Isotope Ratio Measurements. *Analytical Chemistry* **83**, 2469-2475.
- Knight, K.B., M.R.Savina, B.H.Isselhardt, I.D.Hutcheon, S.G.Prussin, M.J.Pellin, Uranium Resonance Ionization Mass Spectrometry in Natural U-silicate. *Radiochimica Acta*, in press.

- Ofan, A.; Ahmad, I.; Greene, J.P.; Paul, M.; Savina, M.R.; Development of a detection method for ^{244}Pu by Resonance Ionization Mass Spectrometry. *New Astronomy Reviews* **50** 640-643, 2006.
- Savina, M.R., M.J. Pellin, C.E. Tripa, I.V. Veryovkin, W.F. Calaway, A.M. Davis, Analyzing individual presolar grains with CHARISMA. *Geochimica et Cosmochimica Acta*, **67**(17), 3215-3225, 2003.
- Schumann, P.G., Wendt, K.D.A. and Bushaw, B.A., High-resolution triple-resonance autoionization of uranium isotopes. *Spectrochimica Acta B*, **60**, 1402-1411, 2005.

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