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Final Report Resonance Ionization Mass Spectrometry for Post-Detonation Nuclear Forensics

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Final Report Resonance Ionization Mass Spectrometry for Post-Detonation Nuclear Forensics

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Resonance Ionization Mass Spectrometry for Post-Detonation Nuclear Forensics

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ABSTRACT

Isotope ratio measurements of the actinide elements provide essential information for nuclear detonation forensics and proliferation detection. Resonance Ionization Mass Spectrometry (RIMS) is a high-sensitivity, elementally selective, laser-based form of mass spectrometry that offers the potential to determine the isotopic composition of materials without sample preparation. Due to the elementally selective approach of RIMS, basic research questions of atomic spectroscopy and the probability for producing neutral atoms in the gas phase, must be studied element by element. The studies carried out in this work represent basic research into the application and optimization of RIMS to the analysis of post-detonation debris.

1. INTRODUCTION

The purpose of this report is to document the activities and findings of the project "Resonance Ionization Mass Spectrometry for Post-Detonation Nuclear Forensics," conducted during the period September 1, 2012 to June 30, 2019 (with finalization through September 30, 2019). This report describes the overall goals and objectives of the project and provides year-by-year summaries of the activities, results, outcomes, training/professional development opportunities, and efforts to disseminate results. Since these topics have been previously summarized in annual reports, the approach taken in this Final Report is to first provide a summary of the technology (Resonance Ionization Mass Spectrometry, RIMS) and its application to post-detonation nuclear forensics, followed by a description of the overall goals and objectives of the project, and then a concatenation of the year-by-year summaries of the project's activities and results. In the final sections of the report, some summary conclusions and recommendations for future research are presented as well as a summary of students graduated and papers published in association with this project.

2. OVERALL SUMMARY/BACKGROUND OF RIMS TECHNOLOGY

Resonance Ionization Mass Spectrometry (RIMS) is a high-sensitivity, elementally selective, laser-based form of mass spectrometry and offers the potential to determine the isotopic composition of materials without sample preparation. Unlike most other techniques, RIMS is capable of accurate isotopic analysis in the presence of isobaric interferences. For example, U and Pu must be chemically separated prior to conventional mass spectrometric analysis of any post-detonation material to avoid isobaric interferences at mass 238: ^{238}Pu interferes with ^{238}U and vice versa. RIMS uses lasers tuned to specific resonance transitions to discriminate against isobars inside the mass spectrometer, thus eliminating the need to remove them prior to analysis. In theory, RIMS can be applied to virtually any element in the periodic table, but it has only recently been applied to the difficult task of actinide isotopic analysis.

Figure 1 shows a diagram of the RIMS process in which a small amount of material (as little as a few hundred atoms) is desorbed or sputtered from a solid sample as a cloud of neutral atoms; atoms of the element of interest are selectively excited and ionized using lasers tuned to characteristic intermediate (resonant) electronic states unique to that element; and the resulting ionized atoms are accelerated into a mass spectrometer where the isotopes are separately detected. Although RIMS is an established technique in cosmochemistry and environmental analysis, nuclear debris samples present a number of significant challenges requiring additional research and development before RIMS can be used confidently to quantify actinide isotope abundances. Recent experiments have demonstrated the ability of RIMS to measure ^{235}U/^{238}U and ^{234}U/^{238}U ratios to better than 1% precision and accuracy from uranium oxide materials without sample preparation, as well as the ability to discriminate U and Pu from each other in silicate samples containing both elements.

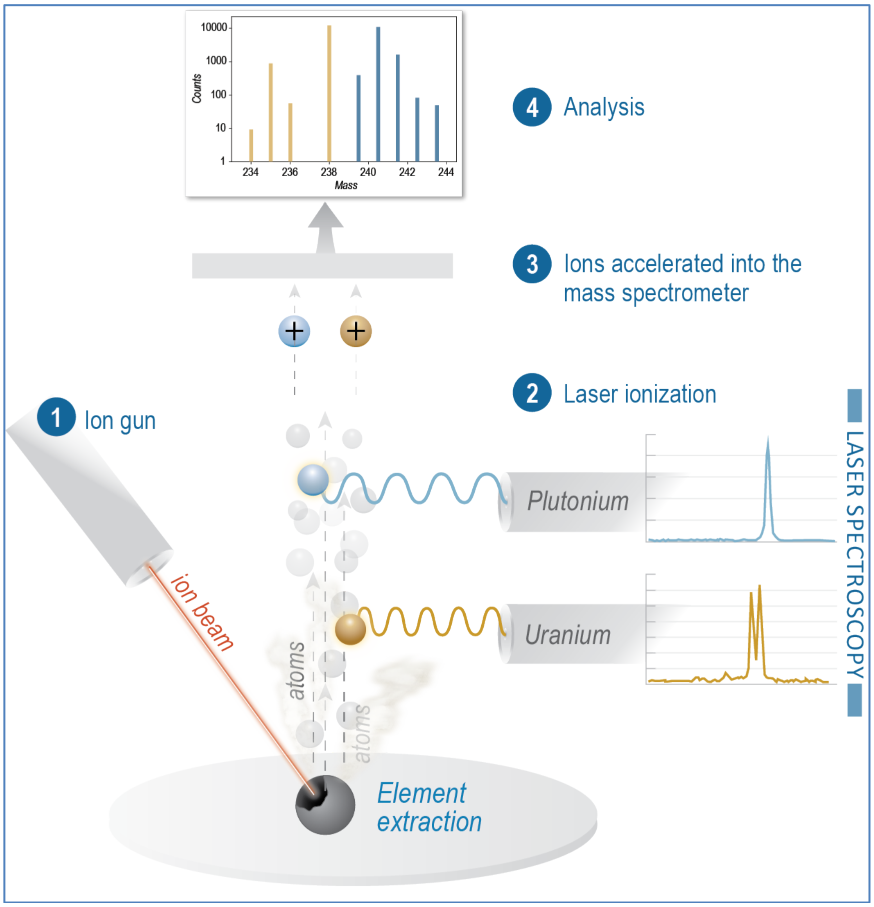


Figure 1. A diagram showing how Resonance Ionization Mass Spectrometry is performed. (1) Solid samples are first atomized using an ion beam or laser, (2) the atomization event is followed by selective ionization using lasers tuned to excite specific elements like uranium or plutonium, (3) after ions of the element of interest are formed they are accelerated into a mass spectrometer for (4) mass analysis.

These recent experiments have also demonstrated the ability to detect U and Pu isotopes in these fallout materials, but at the beginning of this project, the work had not yet been extended to quantifying isotope abundances of these or other actinide elements that may be present. Three fundamental questions must be answered to determine if RIMS can be applied to the forensic analysis of these materials: (1) What fraction of atoms of each element in this glassy material can be vaporized in the form of neutral atoms (as opposed to ions or molecules which degrade the analysis) so that resonance ionization may be applied? (2) What are the relative laser ionization efficiencies of each isotope of the element of interest? and (3) Can the ionization process be controlled by the judicious choice of laser parameters such that rapid, robust isotopic analysis can be routinely performed?

In this project, we conducted several basic research tasks to improve RIMS for the conditions and missions relevant to Post-Detonation Radiological and Nuclear Forensics. The work in this project contributed to the development of this method for rapid isotopic identification and measurement of nuclear material samples, while eliminating the need for time-consuming separation radiochemistry. The project focused on the underlying physics and chemistry of laser photon-solid interactions required to optimize RIMS for the analysis of actinides in post-detonation types of materials.

3. OBJECTIVES OF THE PROJECT AND APPROACH TAKEN

The overall objectives of this project include the following:

- Address fundamental science questions related to the atomic spectroscopy of actinides and the efficiency of the atomization process from silicate matrices.
- Investigate basic issues critical to understanding the sensitivity and accuracy of RIMS for post-detonation materials.

To accomplish these objectives, a stepwise approach based on progressive annual activities was implemented. These steps were influenced by the introduction of the new LLNL LION RIMS system early in the project. This enabled close coordination and a series of activities that included modeling and simulation as well as theoretical analysis and experimental studies. The year-by-year goals of this project, as summarized in the project's annual reports, are the following:

Year 1. The goals for activities in year 1 were the following:

- Prioritize elements to be studied for development by RIMS.
- Procure or prepare high- and low-concentration (silicates) standards containing elements of interest.
- Complete prioritization study of elements relevant to nuclear forensics research.
- Develop improved understanding relative ionization probability of Pu.
- Complete a Laser Science Feasibility Study.

Year 2. The goals for activities in year 2 were the following:

- Continue to improve understanding of relative ionization probability of Pu.
- Develop understanding of the relative ionization probabilities of Am and Cm.
- Procure an alternative laser system proposed by the Laser Science Feasibility Study, and begin initial testing.

Year 3. The goals for activities in year 3 were the following:

- Complete measurements of yields and sensitivities for U and Pu based on prepared standards to determine production of neutral atoms.
- Complete measurements of prepared standards to determine production of neutral atoms
- Develop ionization model to include realistic spatial description of laser power.
- Test alternative laser system for compatibility with RIMS instrumentation.

Year 4. The goals for activities in year 4 were the following:

- Integrate alternative laser system into RIMS experiments and test performance compared to existing laser systems.

- Evaluate options for expanded use of commercial off-the-shelf (COTS) continuous wave (CW) lasers and test as appropriate
- Implement understanding of relative ionization probability of Am and Cm and develop ionization approaches for additional elements (i.e., Cs, Ba, Mo, Zr).
- Test methods for improvement of yield of neutral atoms from silicate matrices.

Year 5. The goals for activities in year 5 were the following:

- Demonstrate proof-of-concept measurements by RIMS in post-detonation materials with the LLNL instrument.
- Complete spectroscopic studies of recently discovered simplified ionization schemes for U and Pu.
- Demonstrate measurements of Cs, Ba by RIMS.
- Test methods for improvement of yield of neutral atoms from silicate matrices.

4. YEAR-BY-YEAR SUMMARIES OF WORK ACCOMPLISHED: ACTIVITIES, RESULTS, OUTCOMES, TRAINING/PROFESSIONAL DEVELOPMENT OPPORTUNITIES, AND DISSEMINATION OF RESULTS.

Annual Summary (2013)

- **Major activities (2013)**
  - ⇒ Project startup activities
    - o Completed funding transfers to LLNL
    - o Processed funding transfer to ANL
    - o Retained National Research Council (NRC) post-doc at NPS (Fabio Alves)
    - o Retained PhD student (Brian Kearney)
    - o Completed Thesis Opportunities Seminar at NPS
    - o Completed Physics Colloquium on RIMS at NPS
    - o Completed Project Kickoff meeting at LLNL
    - o Conducted project planning and coordination meetings at NPS and LLNL
  - ⇒ Specific Objectives (2013)
    - o Task 1: Prioritization of elements to be developed for RIMS analysis. Task report prepared.
    - o Task 2: Prepare standards for sensitivity and spectroscopy measurements: Initiated activities under this task.
    - o Task 3: Understanding relative ionization probability of Pu: Initiated activities under this task
    - o Task 4: Laser Science Feasibility Study: Initiated activities under this task.

- **Opportunities for Training and Professional development (2013): Training opportunities included the following:**
  - ⇒ At project initiation, key participants conducted a "Thesis Opportunities Seminar" at NPS to present the background of the RIMS project and to engage potential student

and postdoc participation in the project. Attendees included NPS faculty participants as well as post-docs and students who subsequently participated in the project.
- ⇒ Based on the positive feedback of the "Thesis Opportunities Seminar", a second training development opportunity was conducted at NPS under the auspices of the Department of Physics Colloquium program. This presentation provided broader exposure to the RIMS project for faculty and students at NPS.
- ⇒ A training session on Monte Carlo Modeling (MCNP5) was conducted for project participants at NPS.

- **Results dissemination (2013)**
  - ⇒ Project personnel assembled a project bibliography related to RIMS technology and related project background.
  - ⇒ A Thesis Opportunities Seminar and an NPS Physics Department Colloquium on RIMS were conducted to support dissemination and outreach to the NPS faculty and student communities.

Annual Summary (2014)

- **Major activities (2014)**
  - ⇒ Project management activities (2014)
  - ⇒ Completed funding transfers to LLNL and ANL
  - ⇒ Retained National Research Council (NRC) post-doc at NPS (Fabio Alves)
  - ⇒ Completed Thesis Opportunities Seminar at NPS
  - ⇒ Conducted project planning and coordination meetings at NPS and LLNL
- **Specific Objectives (2014)**
  - ⇒ Task 1: Prioritization of elements to be developed by RIMS: Completed activity to prioritize elements relevant for the development of RIMS. A systematic study of the priority in which elements should be investigated in order to maximize the possible impact on nuclear forensics research was carried out. Candidate elements included U, Th, transuranic elements, and select fission products such as Tc and Eu. This list has been updated to reflect assessments based on potential utility to understanding debris composition as well as the degree of complexity required to develop the RIMS method for the measurement of expected isotope abundances. Factors considered in this study include production of actinides in a fission environment, the existence of available resonance ionization-specific spectroscopic work, as well as practical experimental considerations (sample synthesis for research and activity/safety considerations). The resultant prioritized list of additional elements (beyond U) to be carried forward in this study are, in order of interest, Pu, Am, and Np. If resources and time lines permit, we planned to investigate Th and Eu. Cm was a final choice due to the logistics of creating and handling higher activity, short-lived materials, and the paucity of pre-existing spectroscopic studies.
  - ⇒ Task 2: Prepare standards for sensitivity and spectroscopy measurements: Completed activities under this task. Several test materials, both high-concentration electro-deposited samples and low-concentration (~50ppm Pu) silicate matrices for Pu, were produced and shipped to ANL for experiments. Uranium metal test material was

prepared and shipped to ANL for neutral atom yield experiments. LLNL planned to prepare and or procure other test materials as needed.

⇒ Task 3: Understanding relative ionization probability of Pu: Completed a simulation framework for projection of ionization probabilities of Pu isotopes and integrated laboratory results into the methodology. Special effort was spent this year to ensure that the modeling framework has been developed in a flexible manner to allow rapid development of modeling capabilities for other isotope systems to be developed in future years. Comparison of model predictions and experimental results was at an early stage for Pu.

⇒ Task 4: Laser Science Feasibility Study: The specific objectives for this task were identified as: (a) Study of RIMS laser configurations including dye and solid-state pulsed lasers for time-of-flight mass spectroscopy and CW semiconductor lasers for quadruple mass spectroscopy; (b) Evaluate the possibility of using hybrid schemes where CW semiconductor lasers can be combined with pulsed solid-state lasers to perform the required ionization steps and allow time-of-flight spectroscopy; (c) Identify the isotopes and ionization steps where a CW tunable laser could be tested in the hybrid configuration; (d) Identify the laser performance characteristics (requirements); and (e) Survey the availability of suitable CW lasers with required characteristics for the task, and plan the acquisition and test of the laser device.

- **Significant results (2014):**

⇒ (Tasks 2 and 3) Determined the best ionization wavelength for Pu, which we optimized for non-selective isotopic ionization, rather than previously reported ionization schemes, which used an isotope selective ionization approach.

⇒ (Task 3) Integrated into our modeling framework parameters for doppler broadening of spectral lines, incorporated angular momentum considerations for odd isotopes, enabled select two-photon processes, and multiple ionization pathways. The resulting model has the capability to receive experimental data as input and iterate over different laser or atomic parameters to match this data.

⇒ (Task 3) Measured the saturation behavior of four plutonium isotopes (^{238}Pu, ^{239}Pu, ^{242}Pu, & ^{244}Pu) for use in modeling studies. Measured the wavelength sensitivity of two different transitions used to ionize Pu.

⇒ (Task 4) According to the specific objectives identified above, the following results were obtained: (a) and (b): A study was performed and revealed that hybrid configurations had not been demonstrated yet, however this approach appeared to be an attractive possibility to improve the performance of our current configurations. CW-semiconductor lasers can be used to perform one or two photon excitation steps, while pulsed solid state lasers could be used for the ionization step and provide synchronization for the time-of-flight mass spectroscopy. This could increase selectivity, and simplify tunability and synchronization issues; (c): The research group agreed that the preliminary tests for the laser should be performed using the Uranium RIMS, which is operational at Argonne National Laboratory and/or the mirror system at LLNL. The first and second step ionizations were selected for testing, in this order of priority. Since the ionization steps for Uranium are very close to those of Plutonium, a tunable CW-laser can be used for both. The advantage of testing the system using the existing operational setup is that all other parameters are well controlled and the effects of the new laser can be thoroughly accessed; (d): For this task, the lasers must be very stable over a long period of operation, and finely tunable in the range of both isotopes for each transition step. Our studies indicate that the ideal resolution for tunability should be 0.5 nm; however this requirement could be degraded to a few nanometers to allow the use of a single laser for both elements. The bandwidth can vary from 1 GHz, to excite as many states as possible, down to 50 MHz when high-resolution spectroscopy is desired. The average power of the laser has to be over 1 W to assure the necessary fluence on target after the beam passes all controlling optics. More powerful systems are desired since they allow more control and stability; and (e): A survey of commercially available tunable CW-lasers that comply with the identified requirements was ongoing (see details on plans for the next project period).

- **Training and Professional Development Opportunities (2014)**
  - ⇒ Key participants conducted a series of "Thesis Opportunities Seminars" at NPS to present the background of the RIMS project and to engage potential student and postdoc participation in the project.
  - ⇒ An NPS independent studies course was conducted on the topic of nuclear weapons technology, including nuclear forensics and RIMS technology. Course is PH4860. Student participants included Navy LT Damian Smith and Marine Corps MAJ Matthew Lavallee. Students participated in RIMS briefings and contributed to Task 2 efforts on modeling of ionization potential for Pu.
  - ⇒ Conducted one-on-one meetings between the PI and new NPS MS students to review RIMS technology, work to date, and potential research activities. Three new students have begun MS thesis research related to RIMS; their thesis topics include studying CW semiconductor lasers applicable to the hybrid laser configuration schemes for RIMS; and extension of the ionization modeling/simulation efforts to predict relative ionization probability for new elements.
  - ⇒ An Early Career Research Scientist at LLNL worked closely with NPS graduate students to develop ionization probability model framework for Pu. This involved frequent interactions to share the relevant physics and modeling.

- **Results Dissemination (2014)**
  - ⇒ Thesis Opportunities Seminars on RIMS supported dissemination and outreach to the NPS student communities.
  - ⇒ Special briefings to students on RIMS technology were completed as part of an independent studies course (PH4860) and as introductory interactions for new student researchers.
  - ⇒ Papers were prepared and submitted for conference presentation/publication.

2015 Annual Summary

- **Major Activities (2015)**
  - ⇒ Project management and training activities

- Completed funding transfers to LLNL
- Conducted project planning and coordination meetings at NPS and LLNL

- **Education/Training (2015)**
  - ⇒ Completed Thesis Opportunities Seminar at NPS
  - ⇒ Conducted educational activities at NPS including graduate student courses and undergraduate student internships
  - Two Master's theses on RIMS topics completed during this reporting period
- **Project technical activities (2015)**
  - Delays in construction of LLNL RIMS instrument and unavailability of CHARISMA at ANL for much of this reporting period required a rescheduling of tasks to delay measurements of neutral atom yields until next period.
  - As a consequence, efforts were enhanced on the procurement and initial testing of an alternative laser system for ionization, a CW diode laser.
  - Effort was also focused on improvements our ionization model and our understanding of the relative ionization probability for isotopes of Pu, Am, and Cm.
  - ⇒ See specific objectives and activities (below) for additional details of activities and results
- **Specific Objectives and Activities (2015)**
  - ⇒ Task 1 (Prioritization of elements for development by RIMS).
    - Completed activity to prioritize elements relevant to the development of RIMS during year 1.
  - ⇒ Task 2 (Prepare standards for sensitivity and spectroscopy measurements)
    - Standards for sensitivity and spectroscopy measurements were prepared in preparation for introduction of the new LION RIMS system.
    - Several test materials both high-concentration electro-deposited samples and low-concentration (~50ppm Pu) silicate matrices for Pu were produced and are now available for experiments at LLNL.
    - Uranium metal test material was prepared and used to quantify the useful yield of the LION RIMS system for U atoms from a reduced material.
  - ⇒ Task 3 (Understanding relative ionization probability of Pu):
    - Continued efforts to improve understanding of relative ionization probability of Pu.
    - Completed simulation framework and initial modeling for prediction of ionization probabilities of Pu isotopes.
    - Pu ionization probability as a function of resonance laser irradiance was measured during joint NPS/LLNL experiments, which will be used to accurately define Pu excitation cross sections to be used in detailed Pu ionization modeling.
    - These efforts were the topic of one completed MS student thesis and were continued under another MS student thesis.
    - Comparison of model predictions and experimental results are continuing to be developed for Pu and have been initiated for Am, Cm, and Np.
  - ⇒ Task 4 (Laser Science Feasibility)
    - The specific objectives for this task were identified as:

        - Study of RIMS laser configurations including dye and solid-state pulsed lasers for time-of-flight mass spectroscopy and CW semiconductor lasers for quadrupole mass spectroscopy;
        - Evaluate the possibility of using hybrid schemes where CW semiconductor lasers can be combined with pulsed solid-state lasers to perform the required ionization steps and allow time-of-flight spectroscopy;
        - Identify the isotopes and ionization steps where a CW tunable laser could be tested in the hybrid configuration;
        - Identify the laser performance characteristics (requirements);
        - Survey the availability of suitable CW lasers with required characteristics for the task and plan the acquisition and test of the laser device.
    - Completed follow-on activity to obtain proposed alternative laser system as a result of the promising results of the laser feasibility study
    - Began initial testing.
    - This effort was the topic of a MS student thesis.
- ⇒ Tasks 5 and 7: Measurements of prepared standards to determine production of neutral atoms
    - Although the task 5 activity was originally delayed due to delays in construction of LLNL RIMS instrument, the new LION system was brought into operation during this reporting period;
    - Measurements to determine the overall detection efficiency of the LION instrument were initiated this year.
    - Began initial experiments of the hybrid system with Pu standards following introduction of the CW laser into the second excitation step of the ionization scheme.
- ⇒ Task 6 (Understanding relative ionization probability of additional elements)
    - Developed understanding of the relative ionization probabilities of Am, Cm, and Np.
    - Collected data on the ionization probabilities of Am, Cm and Np.
    - Work was initiated to develop understanding of the relative ionization probabilities of Am and Cm
    - Work was initiated to research the basic atomic data required to predict the relative ionization probabilities of Am, Cm and Np and to integrate the resulting data into the RIMS simulation model.

- **Significant results (2015)**
    - ⇒ (Tasks 2 and 3) As reported previously, determined the best ionization wavelength for Pu, which is different with our approach (non-selective isotopic ionization) than previously reported approaches (selective isotopic ionization) experiments.
    - ⇒ (Task 3) Further improved the integration of doppler broadening of spectral lines, incorporated angular momentum considerations for odd isotopes, enabled select two-photon processes, and multiple ionization pathways into the modeling framework. The resulting model has the capability to compare experimental data to model predictions and test different laser or atomic parameters to best fit the data.

⇒ (Task 3) Measured the saturation behavior of five plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu) of a more realistic isotopic composition for additional use in modeling studies. Measured the wavelength sensitivity of two different transitions used to ionize Pu.

⇒ (Task 4) According to the specific objectives identified above, a novel hybrid configuration was identified as an attractive possibility to increase selectivity using CW-laser to perform one or two photon excitation steps while still using a pulsed laser for the final ionization step to provide synchronization for the time-of-flight mass spectroscopy. This could increase selectivity, and simplify laser system control and synchronization issues. The research group recommended that the preliminary tests for the laser should be performed at LLNL. A laser wavelength required for the second transition in the three photon Pu RIMS scheme was selected for testing. Since the ionization steps for uranium are very close to those of plutonium, tunable CW-lasers can be used for either element. The advantage of testing the system using the operational setup is that all other parameters are well controlled and the effects of the new laser can be thoroughly assessed. The average power of the laser has to be over 1 W to assure the necessary irradiance on target after the beam passes all steering optics. More powerful systems are desired since they allow for more complete excitation and ionization of the neutral atoms. A survey on commercially available tunable CW-lasers that comply with the identified requirements was performed. We selected and procured a laser from Sacher Lasertechnik for experimentation and evaluation for integration possibilities with the LLNL RIMS system. Preliminary tests were performed at NPS and at LLNL.

⇒ (Task 5) Measured the useful yield of the LION instrument for molybdenum and reduced uranium metal to be 25-30%. Figure 2 below shows the results of measurements for detection efficiency where a U metal sample was kept in a reduced state (oxygen poor), to reduce the production of uranium oxide molecules during analyses. The resulting "Detection Efficiency" is determined from the counts detected during analysis divided by the total number of atoms removed from the sample, as calculated from crater volume measurements.

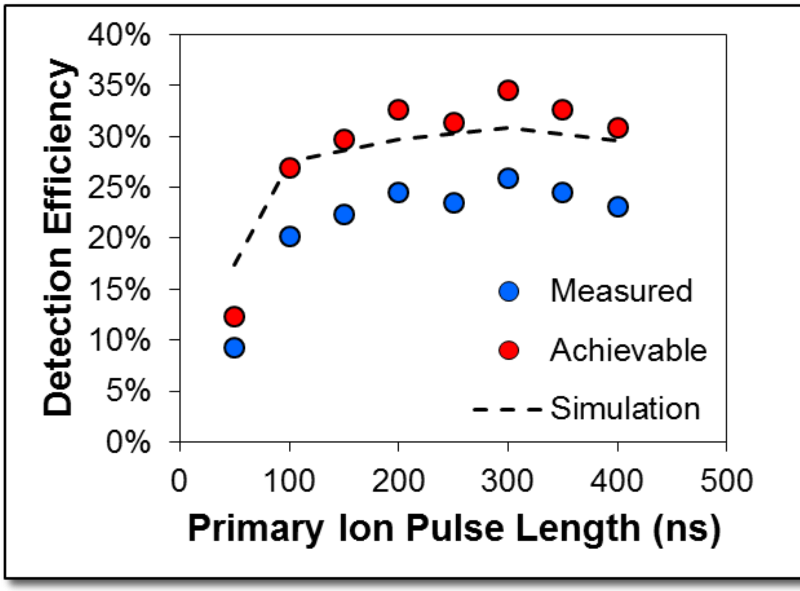


Figure 2. The measured detection efficiency for reduced U metal sample as a function of the pulse length of the primary ion beam (Au^+). This also show the results of electrostatic simulation of ion transport in the LION instrument and a theoretically achievable detection efficiency, if a fourth laser were used to excite U atoms from a low-lying excited state known to be populated during sputtering.

- **Key outcomes or other achievements (2015)**
  - ⇒ Peer-reviewed publication of our ionization model for uranium in the journal of Analytical Atomic Spectrometry (JAAS) entitled, "Rate Equation Model of Laser Induced Bias in Uranium Isotope Ratios Measured by Resonance Ionization Mass Spectrometry".
  - ⇒ Demonstration of a maximum useful yield of the LION mass spectrometer for Mo and reduced U samples of 25-30%, which is an order of magnitude higher than most forms of mass spectrometry. The useful yield for U is reduced from uranium oxide samples; methods to improve this are currently in development.
  - ⇒ Identification of COTS laser systems to explore the potential of simplifying ionization laser systems required to quantify actinide isotopes by RIMS, while reducing costs and improving operability for field use.
  - ⇒ In October of 2015, we performed the first RIMS analysis using the new LLNL LION instrument on a Pu working reference material. Figure 3 below shows measurements made in December 2015 which provide a good example of a mass spectrum obtained from these measurements. The figure presents a histogram of ion counts detected as a function of mass, showing ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu peaks. This sample was also confirmed to have approximately ten times more ^{238}U present than ^{238}Pu, but RIMS was still capable of quantifying the amount of ^{238}Pu, within the statistical uncertainties.

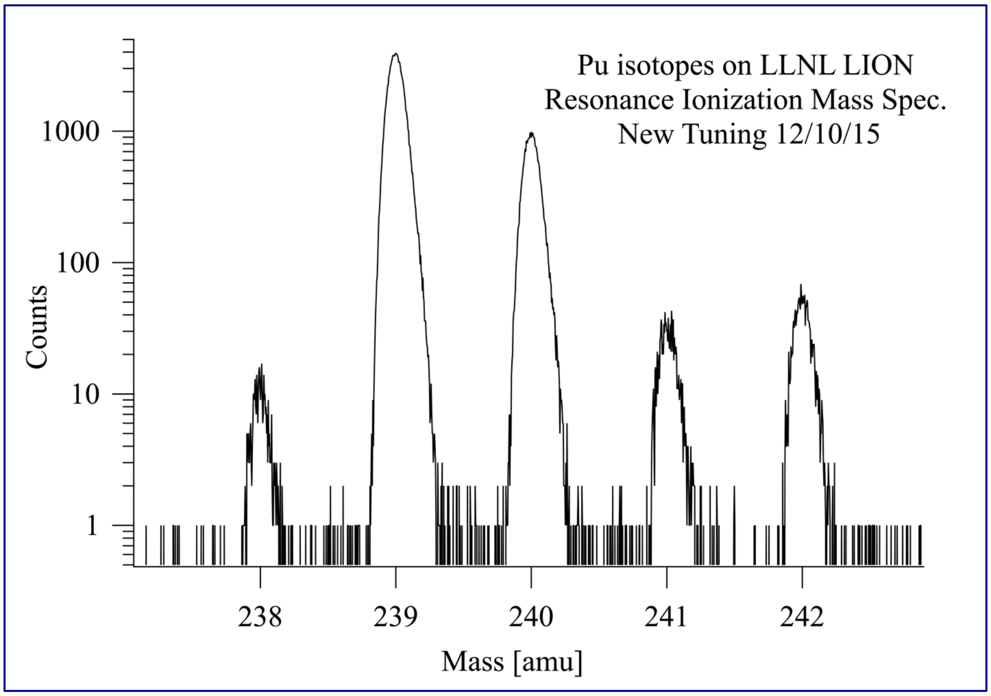


Figure 3. Resonance ionization mass spectrum of Pu sample on new LLNL LION instrument.

⇒ In November 2015 we performed additional RIMS analyses of Pu isotopes on the LLNL LION instrument. Figure 3 below demonstrates the elemental sensitivity to uranium and plutonium isotopes as well as the ability to quantify the off-resonance signal from uranium oxide, which represents the total background in our measurements. (See mass spectrum below). In green is a resonance ionization measurement of a Pu test material, with almost equal ^{238}Pu, ^{239}Pu, ^{242}Pu, and ^{244}Pu. Also shown in blue is a quantitative measurement of the background present in our measurement which can be used to correct our RIMS data to make isotope ratio measurements more accurate; our backgrounds for this measurement were less than 0.5% of our measured results.

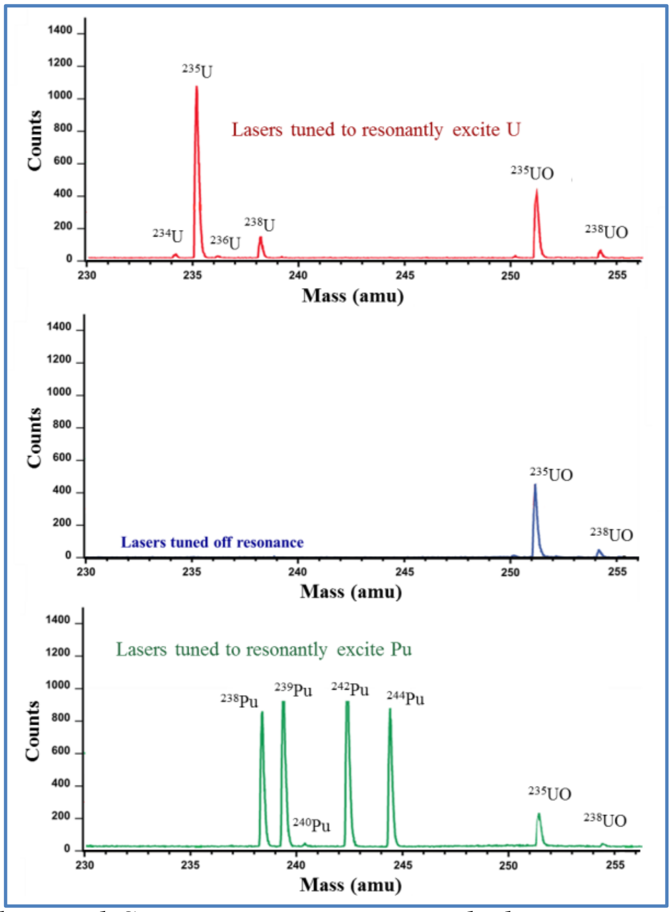


Figure 4: Elemental Sensitivity to uranium and plutonium isotopes in a single sample, simply by changing wavelengths of the excitation lasers and Isolation of the off-resonance signal from uranium oxide measurements.

- **Training opportunities (2015) included the following:**
  - ⇒ Key participants conducted "Thesis Opportunities Seminars" at NPS to present the background of the RIMS project and to engage potential student and postdoc participation in the project.
  - ⇒ Directed Studies courses (PH4993 and 3992, Special Topics in Advanced Physics - Nuclear Weapons Effects) were conducted (Oct-Dec 2015, Jan-Mar 2016 and Apr-Jun 2016) on the topic of nuclear weapons effects, including nuclear forensics and RIMS technology. Student participants were Army MAJ Jacob Capps and Army CPT Drake Brewster.
  - ⇒ An additional regular class (PC4022) on Combat Systems Capabilities was conducted during the period Apr-Jun 2016. A significant portion of this course covered nuclear weapons effects, and the RIMS technology was featured as a key part of the nuclear forensics topic. 14 NPS graduate students participated in this class.
  - ⇒ NPS hosted two USMA and USNA undergraduate summer interns who participated in RIMS related research during this reporting period.

- ⇒ One LLNL scientist and a post-doc each presented work on RIMS at the Radioanalytical and Nuclear Chemistry (RANC) conference in March, 2016.
- ⇒ NPS graduate student Drake Brewster received active technical mentoring of by LLNL post-doc Andrew Kucher and LLNL staff scientist Michael Savina in May/June 2016 on laser testing and operations. Brewster was able to participate in RIMS experiments at LLNL during this process.
- ⇒ Mentorship of Steven Hutchinson by LLNL Co-PI, throughout the year, to further develop model of ionization probability of Pu and additional elements.

- **Results Dissemination (2015)**
  - ⇒ Thesis Opportunities Seminars on RIMS supported dissemination and outreach to the NPS student community.
  - ⇒ Special briefings to students on RIMS technology were completed as part of independent studies courses (PH4993, PH3992 and PC4022) described in the previous section.
  - ⇒ Introductory interactions provided project orientation for new student researchers.
  - ⇒ Papers were prepared, submitted and presented as conference presentations/ publications as described in the previous section.
  - ⇒ Participation by USMA-cadet and USNA midshipman summer interns.

2016 Annual Summary

- **Major Activities (2016)**
  - ⇒ Project management and training activities (2016)
    - o Completed funding transfers to LLNL
    - o Conducted project planning and coordination meetings at NPS and LLNL
  - ⇒ Education/Training (see also next section of report) (2016)
    - o Completed Thesis Opportunities Seminar at NPS
    - o Conducted educational activities at NPS including graduate student courses and undergraduate student internships
    - o Conducted Master's thesis research on RIMS topics with involvement of 4 MS Physics students and two undergraduate interns from USMA and USNA
  - ⇒ Project technical activities (2016)
    - o Completed construction and initiated operations on the LLNL LION RIMS instrument enabling the continuation of measurements of neutral atom yields.
    - o Completed analysis and planning for implementation of alternative hybrid laser system for ionization involving the introduction of a CW diode laser procured and tested in the previous year.
    - o Effort was also focused on improvements the ionization model and our understanding of the relative ionization probability for isotopes of Pu. Addition of Am, and Cm to the modeling capability initiated.
    - o See specific objectives and activities (below) for additional details of activities and results.

- **Specific Objectives and Activities (2016)**
  - ⇒ Task 1 (Prioritization of elements relevant to nuclear forensics research).
    - Completed activity to prioritize elements relevant to application of RIMS to nuclear forensics research during year 1.
  - ⇒ Task 2 (Prepare standards for sensitivity and spectroscopy measurements)
    - Standards for sensitivity and spectroscopy measurements were prepared for use with the new LION RIMS system.
    - Several test materials both high-concentration electro-deposited samples and low-concentration (~50ppm Pu) silicate matrices for Pu were produced and are now available for experiments at LLNL.
    - Uranium metal test material was prepared and used to quantify the useful yield of the LION RIMS system for U atoms from a reduced material.
  - ⇒ Task 3 (Understanding relative ionization probability of Pu):
    - Continued efforts to improve understanding of relative ionization probability of Pu.
    - Completed simulation framework and initial modeling for prediction of ionization probabilities of Pu isotopes.
    - Pu ionization probability as a function of resonance laser irradiance was measured during joint NPS/LLNL experiments, which will be used to accurately define Pu excitation cross sections to be used in detailed Pu ionization modeling.
    - These efforts were the topic of one completed MS student thesis and are continuing under another MS student thesis.
    - Comparison of model predictions and experimental results are continuing to be developed for Pu and were initiated for Am, Cm, and Np.
  - ⇒ Task 4 (Laser Science Feasibility)
    - The specific objectives for this task were identified as:
      - Study of RIMS laser configurations including dye and solid-state pulsed lasers for time-of-flight mass spectroscopy and CW semiconductor lasers for quadrupole mass spectroscopy;
      - Discuss the possibility of using hybrid schemes where CW semiconductor lasers can be combined with pulsed solid-state lasers to perform the required ionization steps and allow time-of-flight spectroscopy;
      - Identify the isotopes and ionization steps where a CW tunable laser could be tested in the hybrid configuration;
      - Identify the laser performance characteristics (requirements);
      - Survey the availability of suitable CW lasers with required characteristics for the task and plan the acquisition and test of the laser device.
    - Completed follow-on activity to obtain proposed alternative laser system as a result of the promising results of the laser feasibility study
    - Began initial testing.
    - This effort was the topic of a MS student thesis.
  - ⇒ Tasks 5 and 7: Measurements of prepared standards to determine production of neutral atoms

- Although the task 5 activity was originally delayed due to delays in construction of LLNL RIMS instrument, the new LION system was completed in the previous reporting period and brought into full operation during this reporting period;
- Measurements to determine the overall detection efficiency of the LION instrument were initiated this year and showed detection efficiency as high as 29±3%.
- Completed measurements of prepared standards to assess the sensitivity of isotope ratio measurements of plutonium as a function of laser irradiance for all three lasers in the excitation scheme.
- Began initial experiments of the hybrid system with Pu standards following introduction of the CW laser into the second excitation step of the ionization scheme.

⇒ Task 6 (Understanding relative ionization probability of additional elements)
- Develop understanding of the relative ionization probabilities of Am, Cm, and Np.
- Collected data on the ionization probabilities of Am, Cm and Np.
- Work has been initiated to develop understanding of the relative ionization probabilities of Am and Cm
- Work has been initiated to research the basic atomic data required to predict the relative ionization probabilities of Am, Cm and Np and to integrate the resulting data into the RIMS simulation model.

- **Significant results (2016)**

⇒ (Task 3) Integrated doppler broadening of spectral lines, incorporated angular momentum considerations for odd isotopes, enabled select two-photon processes, and multiple ionization pathways into the modeling framework. The resulting model has the capability to compare experimental data to model predictions and test different laser or atomic parameters to best fit the data.

⇒ (Task 3) Measured the saturation behavior of five plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu) for use in modeling studies. Measured the wavelength sensitivity of two different transitions used to ionize Pu. These data are being prepared for comparison to modeling results.

⇒ (Task 4) According to the specific objectives identified above, the following results were obtained: A novel hybrid configuration was identified as an attractive possibility to increase selectivity using CW-laser to perform one or two photon excitation steps while still using a pulsed laser for the final ionization step to provide synchronization for the time-of-flight mass spectroscopy. This could increase selectivity, and simplify laser system control and synchronization issues. The research group recommended that the preliminary tests for the laser should be performed at LLNL. A laser wavelength required for the second transition in the three photon Pu RIMS scheme was selected for testing. Since the ionization steps for uranium are very close to those of plutonium, tunable CW-lasers can be used for either element. The advantage of testing the system using the operational setup is that all other parameters are well controlled and the effects of the new laser can be thoroughly assessed. The average power of the laser has to be over 1 W to assure the necessary irradiance on target after the beam passes all steering optics. More powerful systems are desired since they allow for more complete excitation and ionization of the neutral atoms. A survey on commercially available tunable CW-lasers that comply with the identified requirements was performed. We selected and procured a laser from Sacher Lasertechnik for experimentation and evaluation for integration possibilities with the LLNL RIMS system. Preliminary tests were performed at NPS and at LLNL.

⇒ (Task 5) Measured the useful yield of the LION instrument for molybdenum and reduced uranium metal to be 25-30%. The figure below shows the results of measurements for detection efficiency where a U metal sample was kept in a reduced state (oxygen poor), to reduce the production of uranium oxide molecules during analyses. The resulting "Detection Efficiency" is determined from the counts detected during analysis divided by the total number of atoms removed from the sample, as calculated from crater volume measurements.

- **Key outcomes or other achievements (2016)**
  - ⇒ In June 2016, we installed the NPS laser into the LLNL LION system with a configuration to enable rapid switching between the original pulsed laser and the NPS CW laser for the second stage of excitation. Initial measurements indicated issues delivering the necessary number of photons above the sample in the short time available during the other laser pulses (~20ns). These first measurements have provided a preliminary understanding of the challenges inherent on the hybrid system and have enabled new detailed calculations necessary to determine the requirements for pairing pulsed and CW laser systems. These measurements provide the foundation for the anticipated work beginning in the year 4 (first option year) of the project.
  - ⇒ Training opportunities included the following:
    - o Key participants conducted "Thesis Opportunities Seminars" at NPS to present the background of the RIMS project and to engage potential student and postdoc participation in the project.
    - o Directed Studies courses (PH4993 and 3992, Special Topics in Advanced Physics - Nuclear Weapons Effects) were conducted (Oct-Dec 2015, Jan-Mar 2016 and Apr-Jun 2016) on the topic of nuclear weapons effects, including nuclear forensics and RIMS technology. Student participants were Army MAJ Jacob Capps and Army CPT Drake Brewster.
    - o An additional regular class (PC4022) on Combat Systems Capabilities was conducted during the period Apr-Jun 2016. A significant portion of this course covered nuclear weapons effects, and the RIMS technology was features as a key part of the nuclear forensics topic. 14 NPS graduate students participated in this class.
    - o NPS is hosted two USMA and USNA undergraduate summer interns who participated in RIMS related research during this reporting period.
    - o One LLNL scientist and a post-doc each presented work on RIMS at the RANC (Radioanalytical and Nuclear Chemistry) conference in March, 2016.
    - o NPS graduate student Drake Brewster received active technical mentoring of by LLNL post-doc Andrew Kucher and LLNL staff scientist Michael Savina in May/June 2016 on laser testing and operations. Brewster was able to participate in RIMS experiments at LLNL during this process.
    - o Mentorship of Steven Hutchinson by LLNL Co-PI, throughout the year, to further develop model of ionization probability of Pu and additional elements.

- **Results Dissemination (2016)**
  - ⇒ Thesis Opportunities Seminars on RIMS supported dissemination and outreach to the NPS student community.
  - ⇒ Special briefings to students on RIMS technology were completed as part of independent studies courses (PH4993, PH3992 and PC4022) described in the previous section.
  - ⇒ Introductory interactions provided project orientation for new student researchers.
  - ⇒ Papers were prepared, submitted and presented as conference presentations/ publications as described in the previous section.
  - ⇒ Participation by USMA-cadet and USNA midshipman summer interns.

2017 Annual Summary

- ⇒ **Major Activities (2017)**
  - ⇒ Project management and training activities
    - o Completed funding transfers to LLNL
    - o Conducted project planning and coordination meetings at NPS and LLNL
  - ⇒ Education/Training (see also next section of report)
    - o Completed Thesis Opportunities Seminar at NPS
    - o Conducted educational activities at NPS including graduate student courses and undergraduate student internships
    - o Conducted Master's theses research on RIMS topics with involvement of two MS Physics students and three undergraduate interns from USMA and USNA
  - ⇒ Project technical activities
    - o See specific objectives (below) for details of activities and results

- **Specific Objectives and Activities (2017)**
  - ⇒ Task 4 (Laser Science Feasibility)
    - o Integrated CW laser into second Pu ionization stage of LION (i.e., the hybrid PW-CW concept), and conducted initial experiments which did not yield significant ionization of Pu isotopes.
    - o Completed an assessment and analysis of the above measurements to develop a full understanding of the results.
    - o Conducted additional measurements to reconfirm earlier hybrid system results.
    - o This effort was the topic of a MS student thesis.
  - ⇒ Task 6 (Understanding relative ionization probability of elements 2 and 3 on the priority list)
    - o Completed additional efforts to improve the ionization model and our understanding of the relative ionization probability for isotopes of Pu.
    - o Modified the LION system to enable simultaneous measurements of Pu and U isotopes from a single sample. Tested this modification with simultaneous measurements to demonstrate this new capability.

    - Work has been initiated to develop understanding of the relative ionization probabilities of Am and Cm and integrate the resulting understanding into the RIMS simulation model.
- ⇒ Task 10: Hybrid Laser System Implementation
    - The goal of this task is to move forward with the recommendations of the previous Laser Science Feasibility Study to evaluate a hybrid alternative laser system for the analysis of actinides and fission products, with the ultimate objective of incorporating equipment that could contribute to a more robust, field-deployable RIMS system. Year 4 activities will integrate the previously-obtained commercial off-the-shelf continuous wave laser into the LLNL Lion RIMS apparatus and test the performance of the hybrid system against results obtained for the reference system.
- ⇒ Task 11: Understanding Relative Ionization Probability and Modeling Results Related to the Hybrid Laser System.
    - Activities to update the computational model for analysis of relative ionization probability and to analyze and compare the experimental data resulting from tests of the baseline and hybrid RIMS systems.

- ⇒ **Significant results (2017)**
    - ⇒ Task 5: Completed measurements atomic neutral yields of U based on prepared standards.
        - This includes quantifying useful yields for U from a uranium metal sample including measurements of useful yield from both the oxidized surface layer and the reduced bulk material. These results were published in our recent Analytical Chemistry paper by Savina *et al.* (2017)
        - Complete measurements of yields and sensitivities for U based on prepared standards to determine production of neutral atoms.
    - ⇒ Task 6: Expanded understanding of relative ionization probability to Am and Np based on the existing atomic and molecular spectroscopic data and experimental data on these additional elements.
    - ⇒ Task 10: Hybrid Laser System Implementation and Task 11: Understanding Relative Ionization Probability and Modeling Results Related to the Hybrid Laser System. Tests were completed of the hybrid laser concept in which the second ionization pulsed laser was replaced by a previously procured and tested CW laser. The tests did not result in significant yield of the desired ionization state, and a detailed analysis was completed to fully understand the results and their implications. The results of these tests and the subsequent modeling analysis were presented at the 2017 HEART conference and have been submitted for publication in the JRERE journal. Additional insights summarized in section 4 below.

- ⇒ **Key outcomes or other achievements (2017)**
    - ⇒ Tests of the CW-PW laser-hybrid configuration. Tests were conducted in which the CW laser replaced the pulsed laser for the second excitation step. The beam profile was then shaped to match the approximate size of the pulsed laser it replaced. Since

the CW laser has very narrow bandwidth (~100 kHz), it was set to excite only ^{239}Pu at 847.2774 nm. The observed ionization from the CW laser was negligible compared to a high background ionization rate in this experiment (due to the unavailability of the Ga^{+} ion gun and the limited time window for excitation provided by the first pulsed excitation laser). The results enabled detailed calculations to study how the CW laser can be used to build a significant population in the second excited state prior to the arrival of the final ionization laser beam, see future work.

⇒ Resolution of issues and development of path forward associated with hybrid PW-CW laser implementation. An alternative and more practical path to ionization with commercially available lasers could be a CW/CW system. Such systems have shown utility in detecting trace U isotopes. The effective use of CW lasers in such systems requires a geometry for ionization that significantly increases the time over which atoms interact with the laser beams. This can be accomplished by replacing the laser ablation system with a tube furnace, such that atoms must interact with the CW laser beams over a significant length as they diffuse out of the tube. The useful yield of this system would be considerably less than a pulsed system, but is capable of selectively ionizing single isotopes and has utility in measuring trace isotopes where the major isotope is 10^{5}-10^{6} time more abundant. A two-photon single-color system with a long-lived first excited state would be ideal for the creation of a single CW laser RIMS system. Recent research at LLNL has identified alternative excitation schemes for the current pulsed laser configuration that may also be suitable for CW research. Currently, pulsed lasers provide the only practical means for full laser saturation of multiple isotopic targets in a single pass.

⇒ Simultaneous Pu-U Measurements. We modified the LION system to enable simultaneous measurements of Pu and U isotopes from a single sample. This modification was tested with simultaneous measurements of U and Pu in a spent nuclear fuel sample to demonstrate this new capability. (See Figure 5 below).

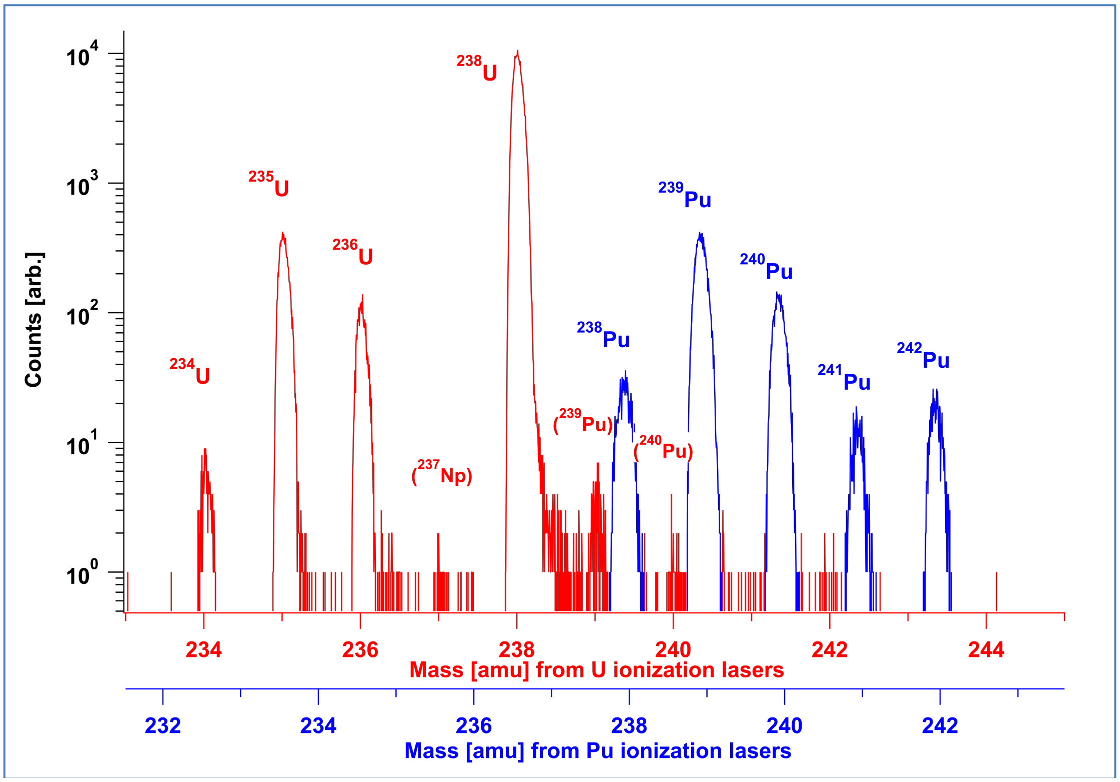
⇒ 

Figure 5. A RIMS mass spectrum of spent nuclear fuel, where U and Pu were quantified at the same time. The lasers for resonantly ionizing Pu have been delayed in time to allow clear separation of the ^{238}U and ^{238}Pu atomic isobars (peaks in parentheses are non-resonantly ionized).

- ⇒ Discovery of a one-color two-photon ionization scheme for uranium. We discovered a one-color two-photon ionization scheme for uranium that is selective and efficient enough to saturate with only a single laser. This greatly simplifies the necessary experimental setup, the automation of laser performance, and cost of future laser procurements. We have also discovered an efficient two-color, two-photon scheme for Pu which still requires some development and testing. This means that both U and Pu could be measured in a single sample by as few as three lasers instead of six.
- ⇒ Argon ion sputtering. We have shown the ability of preferential Ar ion sputtering to improve the neutral atom yield of uranium in uranium oxide matrices by an order of magnitude from 0.2% to greater than 2%,

⇒ **Training opportunities (2017) included the following:**

- ⇒ Key participants conducted "Thesis Opportunities Seminars" at NPS to present the background of the RIMS project and to engage potential student and postdoc participation in the project.
- ⇒ A directed Studies course (PH4993, Special Topics in Advanced Physics - Nuclear Technology) was conducted (Oct-Dec 2016) on the topic of nuclear technology, including nuclear forensics and RIMS technology. Student participant was Army CPT James Bowen.

- ⇒ Additional directed Studies courses (PH4992, Special Topics in Advanced Physics - Nuclear Particle Scattering and PH4994, Special Topics in Advanced Physics - Nuclear Technology) were conducted (Jan-Mar 2017 and Apr-Jun 2017) on the topics of nuclear measurements and experimentation, including nuclear forensics and RIMS technology. Student participant was Navy ENS Jacob Glessman.
- ⇒ Conducted one-on-one meetings between the PI and new NPS MS students to review RIMS technology, work to date, and potential research activities. One student (LT Steve Hutchinson) completed his MS thesis research related to RIMS; his thesis topic involved extension of the ionization modeling/simulation efforts to predict relative ionization probability for new elements. LT Hutchinson presented thesis seminars to NPS students and faculty on June 12, 2016.
- ⇒ One student (CPT Drake Brewster) participated in the HEART Conference annual meeting in Denver, CO and presented his work on RIMS. CPT Brewster has also submitted a paper based on the findings presented at this conference for consideration by the journal JRERE.
- ⇒ NPS hosted USMA-cadet and USNA-midshipmen summer interns during this period. These interns were briefed on and participated in RIMS project activities. An additional USMA cadet is scheduled to begin his internship in June and will be involved in the project activities.
- ⇒ An annual course on weapons technology was conducted by PI Professor Craig Smith in May 2017 with a 3-week module on nuclear technology. The subjects of nuclear forensics and RIMS technology were integrated into this course which included an invited guest lecture by co-PI Dr. Brett Isselhardt from LLNL.
- ⇒ CPT Drake Brewster participated in the Project on Nuclear Issues (PONI) Summer Conference held at LLNL in June 2017, where he completed discussions with emerging nuclear experts and included a scenario-based discussion relating to a hypothetical nuclear terrorism event. CPT Brewster plans to present his work at a PONI conference that has been scheduled for the coming year.

⇒ **Results Dissemination (2017)**

- ⇒ Thesis Opportunities Seminars on RIMS supported dissemination and outreach to the NPS student community.
- ⇒ Special briefings to students on RIMS technology were completed as part of independent studies courses (PH4992, 4993 and 4994) described in the previous section.
- ⇒ Introductory interactions provided project orientation for new student researchers.
- ⇒ Papers were prepared, submitted and presented as conference presentations/ publications as described in the previous section.
- ⇒ Participation by USMA-cadet and USNA midshipman summer interns.
- ⇒ Incorporation of nuclear forensics and RIMS technology into Weapons Technology course at NPS
- ⇒ Development of RIMS methods at LLNL were briefed to DTRA personnel on two separate occasions.

⇒ Participation in the Project on Nuclear Issues (PONI) Summer Conference held at LLNL in June 2017.

2018 Annual Summary

⇒ **Major Activities (2018)**
- ⇒ Project management and training activities
  - o Completed funding transfers to LLNL
  - o Conducted project planning and coordination meetings at NPS and LLNL
- ⇒ Education/Training (see also next section of report)
  - o Completed Thesis Opportunities Seminar at NPS
  - o Conducted educational activities at NPS including graduate student courses and undergraduate student internships
  - o Conducted Master's thesis research on RIMS topics with involvement of one MS Physics student
- ⇒ Project technical activities
  - o See specific objectives (below) for details of activities and results

⇒ **Specific Objectives and Activities (2018)**
- ⇒ Task 6: Demonstrate measurements of Cs, Ba by RIMS.
- ⇒ Task 8: Test methods for improvement of yield of neutral atoms from silicate matrices.
- ⇒ Task 9: Demonstrate proof-of-concept measurements by RIMS in post-detonation materials with the LLNL instrument.
- ⇒ Task 10: Complete spectroscopic studies of recently discovered simplified ionization schemes for U and Pu.
- ⇒ Task 11: Test the CW-Pulsed laser hybrid configuration.

⇒ **Significant results (2018)**
- ⇒ The COTS CW laser did not pass a feasibility test as a viable replacement for a Ti:Sapph pulsed laser in the LION instrument. This null result is directly related to the pulsed nature of the overall LION instrument. While the CW laser provides well over 1 Watt as measured on an average-power meter, LION operates at a 1 kHz repetition rate where the laser pulses are approximately 20 ns each. This means that the power delivered to the LION target chamber by the CW laser is utilized only for 20 micro-seconds. That is why the power as measured by an average-power meter was not an adequate measure of the laser power delivered to the sample being tested. This experiment led to an in-depth understanding of the parameters required in future laser systems.
- ⇒ New one- and two-color uranium resonance ionization scheme were tested and are shown in Figure 6. The schemes were successfully driven to near saturation by the current Ti:Sapph lasers. The two-color system also showed the ability to access a low-lying populated state of uranium. Accessing this low-lying population increased the precision of future uranium measurements by accessing an additional 37% of the atomized uranium. Previously, the uranium occupying the low-lying energy states was not resonantly ionized or counted in measurements.

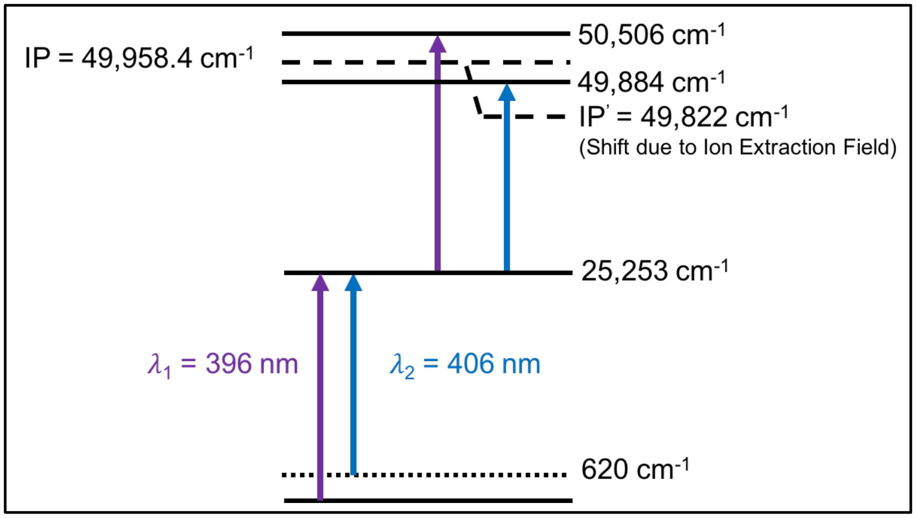


Figure 6. One and two-color uranium laser resonance ionization schemes shown with the utilized excited state and ionization levels with associated energy in wavelength. The 396 nm scheme populates a possible autoionizing (AI) state above the Ionization Potential (IP). The 406 nm scheme populates a possible Rydberg state below the IP. The Rydberg state is ionized by the shift in the IP caused by the ion extraction field.

⇒ Two historic fallout samples were used for demonstration, and uranium isotopes were measured in both samples. The two samples showed different signal-to-noise responses. The accuracy of the measurements is difficult to assess based on the observed variability present in these types of samples, but measurements from at least one sample were consistent with trends observed in previous work. The difference in the observed uranium signal is most likely due to differences in chemical composition and uranium concentration in the two samples.

⇒ Carbon coating and carbon implantation were used to measure the increased efficiency of laser ablation and surface oxidation reduction due to carbon treatments of the surface of two low level uranium bearing fallout glasses. Carbon coating was found to increase the laser's ability to transfer energy to the sample surface and increased the laser ablation efficiency. After transitioning to carbon implantation using methane ions, an increase by a factor of two in the signal-to-noise ratio was achieved (see Figure 7).

⇒ This year the LLNL LION instrument also demonstrated the ability to accurately quantify isotope ratios of cesium (including ^{133}Cs, ^{135}Cs, and ^{137}Cs) and barium (including ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, and ^{138}Ba) in complex matrices containing isobaric interferences for these isotopes. We have not yet attempted to make these measurements in historic silicate fallout samples. Work is continuing to demonstrate additional isotope ratios of interest.

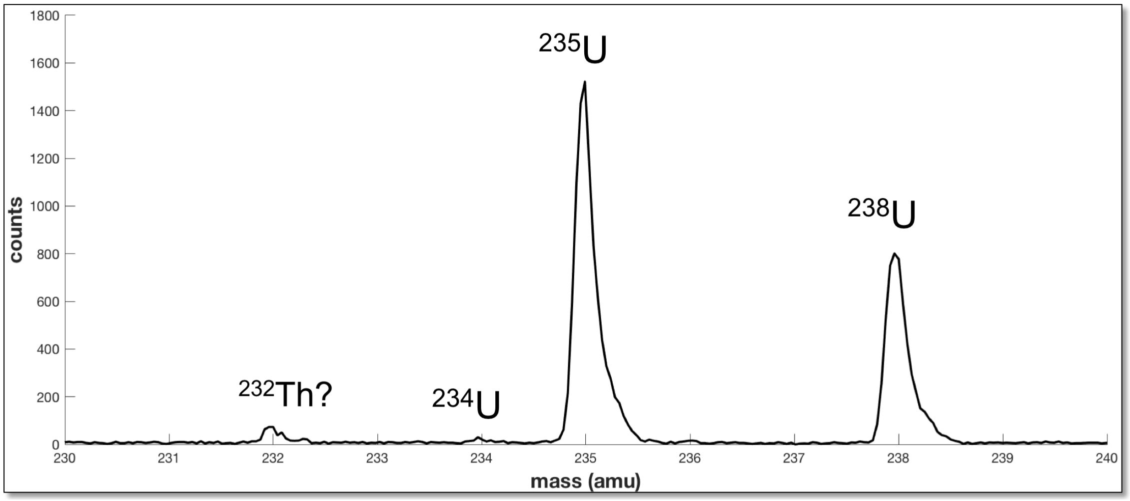


Figure 7. Mass spectrum of the atomic uranium region of a historic fallout sample after carbon coating the surface.

⇒ Key outcomes or other achievements (2018):

⇒ The results of the simplified uranium spectroscopy have been drafted into a journal article (referenced below) which has been submitted and is currently under review at the journal *Analytical Chemistry*. The article highlights the potential for very high efficiency measurements for ideal samples by RIMS and some of the preferential sputtering work we have done with noble gases to demonstrate higher efficiency measurements on more practical UO_2 type samples.

⇒ Several of the key results of this project are further detailed in the master's thesis of Drake Brewster, titled, "Actinide Isotope Ratios Measured by Resonance Ionization Mass Spectrometry: Optimization of Ionization Schemes and Demonstration Using Nuclear Fallout", submitted in December 2017 and referenced below.

⇒ Additionally, the journal article identified below entitled "*A Feasibility Study for the Use of a Continuous Wave Laser for Resonance Ionization Mass Spectrometry Using Laser Ionization of Neutrals at Lawrence Livermore National Laboratory"* provides details related to the evaluation of the use of a continuous wave laser in a hybrid RIMS configuration.

⇒ *Brewster, D. "Actinide Isotope Ratios Measured by Resonance Ionization Mass Spectrometry: Optimization of Ionization Schemes and Demonstration Using Nuclear Fallout," MS Thesis, Naval Postgraduate School, Monterey, CA,* http://hdl.handle.net/10945/56870*, December 2017*

⇒ *Savina, Michael; Trappitsch, Reto; Kucher, Andrew; Isselhardt, Brett, "A New Resonance Ionization Mass Spectrometry Scheme for Improved Uranium Analysis,"* ***Analytical Chemistry,*** *Submitted and under peer review, 2018.*

⇒ *D.E. Brewster, C.F. Smith, B.H. Isselhardt, M.R. Savina, R. Trappitsch, and A. Kucher, "A Feasibility Study for the Use of a Continuous Wave Laser for Resonance Ionization Mass Spectrometry Using Laser Ionization of Neutrals at Lawrence Livermore National Laboratory,"* ***Journal of Radiation Effects Research and Engineering****, Vol. 36, Issue 1, p48, 2018.*

⇒ **Training opportunities included the following (2018)**

- ⇒ Key participants conducted "Thesis Opportunities Seminars" at NPS to present the background of the RIMS project and to engage potential student and postdoc participation in the project.
- ⇒ A directed Studies course (PH4994, Special Topics in Advanced Physics) was conducted (June – July 2017) on the topic of nuclear technology, including nuclear forensics and RIMS technology. Student participant was Ensign Jacob Glesmann, USN.
- ⇒ Additional courses (PH3855, Nuclear Physics and PC4022, Combat Systems Technology – Nuclear Technology) were conducted (April – June 2018) on the topics of nuclear technology, measurements and experimentation, including nuclear forensics and RIMS technology. A total of 15 military officer graduate students participated in these courses.
- ⇒ One student (CPT Drake Brewster, USA) completed his MS thesis on RIMS technology and was awarded the Outstanding Thesis designation and the Johns Hopkins University Applied Physics Laboratory Award for outstanding research upon his graduation in December 2017.
- ⇒ NPS hosted 2 USMA-cadet summer interns during the period May-June 2018. These interns were briefed on RIMS and toured the RIMS facilities at LLNL
- ⇒ CPT Drake Brewster participated in the Project on Nuclear Issues (PONI) Conference held at Barksdale AFB on October 11, 2017, where he presented an invited presentation entitled "Nuclear Forensics and Decision Making: Early Timeline Solutions and Understanding."

▪ **Results Dissemination (2018)**

- ⇒ Thesis Opportunities Seminars on RIMS supported dissemination and outreach to the NPS student community.
- ⇒ Special briefings to students on RIMS technology were completed as part of directed study (PH4994) and regular courses (PH3855 and PC4022) described in the previous section.
- ⇒ Papers were prepared, submitted and presented as conference presentations and peer reviewed publications including the HEART-17 and MARC-XI conferences, the Journal of Radiation Effects Research and Engineering (JRERE) and the Journal of Analytical Chemistry. These are detailed in the Metrics section of this report.
- ⇒ Participation by USMA-cadet summer interns.
- ⇒ Incorporation of nuclear forensics and RIMS technology into Weapons Technology and Nuclear Physics courses at NPS.
- ⇒ Development of RIMS methods at LLNL were briefed to DTRA personnel and faculty/students at USMA.
- ⇒ Participation in the Project on Nuclear Issues (PONI) Conference held at Barksdale AFB in October 2017.

4.0 SUMMARY, CONCLUSIONS & RECOMMENDATIONS FOR FUTURE RESEARCH

Resonance Ionization Mass Spectrometry is a promising approach for obtaining isotope ratio measurements in nuclear materials without the need for prior chemical dissolution or separation chemistry. This technique has the ability to provide information on material composition and/or irradiation history in a matter of hours after sample receipt. Over the five-year course of this project and in partnership with other projects (funded by LLNL LDRD, DTRA, DHS NTNFC, and NA-22) analysis of isotope ratios in mixed actinide samples by RIMS has progressed from a promising concept (TRL 2) to a demonstrated capability using a prototype laboratory instrument (TRL 5/6). While research and development will still be required to mature RIMS methods for specific applications, this project has (1) laid the foundation of new ionization methods for the actinides and other elements of interest (see Figure 8 below for table of elements), (2) demonstrated new atomization methods for maximizing measurement efficiency by RIMS including analysis of uranium in a silicate matrix, (3) explored a wide range of laser parameters useful for performing RIMS using simplified ionization schemes.

The basic research performed by scientists and students under this project have helped outline the value of applying RIMS to rapid and reliable measurement of actinides and other elements in post-detonation materials. This project has outlined an approach to using RIMS for the practical analysis of nuclear materials, research should continue to be conducted towards integration and commercialization of some of the key components now that the requirements for the laser systems are well understood and can be simplified to require only a few specific wavelengths. There is also still a broad space to explore for obtaining the maximum amount of information from a single sample, including optimizing which elements will be measured and exploring the use of matrix matched standards for determining the relative abundance of elements within a sample. As only a handful of RIMS instruments currently exist, there is a need to further develop software and other components to improve the practical use of these instruments that have to-date been custom built and lack the commercial support that other mass spectrometry methods have benefited from.

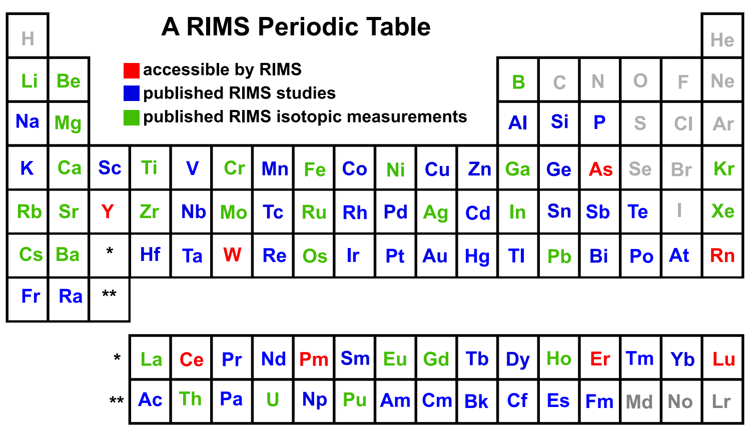


Figure 8. Periodic table of the elements color coded by RIMS accessibility. (Green) Demonstrated isotope ratio measurements by RIMS, (Blue) known RIMS schemes, but no reported isotope ratio measurements, (Red) Elements with atomic structure that allow RIMS measurements but have not yet been reported in the literature, (Gray) RIMS cannot be applied. (Adapted from book chapter by Savina and Trappitsch, in press, 2019)

5.0 STUDENTS GRADUATED

ENS Daniel Watts (6/13/2013)
LT Damian Smith (6/20/2014)
LT Craig Lensegrav
LCDR Sunny Lau
MAJ Philip Rusiecki
MAJ Seth Womac
MAJ Jacob Capps
CPT Drake Brewster
LT Steve Hutchinson

6.0 REFERENCES – PAPERS PUBLISHED AND PRESENTATIONS

- C. Smith and B. Isselhardt, "Resonance Ionization Mass Spectrometry for Post Detonation Nuclear Forensics," NPS Thesis Opportunities Seminar, Naval Postgraduate School, 01/10/2013.
- B. Isselhardt, "Resonance Ionization Mass Spectrometry for Post Detonation Nuclear Forensics," NPS Department of Physics Colloquium, Naval Postgraduate School, 2013.
- C. Smith and G. Karunasiri, "Resonance Ionization Mass Spectrometry (RIMS) for Post Detonation Nuclear Forensics," NPS Thesis Opportunities Seminar, Naval Postgraduate School, 8/29/2013.
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