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Disclaimer:

Laser-Induced Ionization Efficiency Enhancement on a Filament for Thermal Ionization Mass Spectrometry

The evaluation of trace Uranium and Plutonium isotope ratios for nanogram to femtogram material quantities is a vital tool for nuclear counter-proliferation and safeguard activities. Thermal Ionization Mass Spectrometry (TIMS) is generally accepted as the state of the art technology for highly accurate and ultra-trace measurements of these actinide ratios. However, the very low TIMS ionization yield (typically less than 1%) leaves much room for improvement. Laser induced ionization of molecular species on filaments or desorbed from the filament were conducted approximately 30 years ago. Further research in this area declined due to the low repetition rate duty cycle of the laser. For this study, ionization enhancement was demonstrated when samarium was resonantly ionized using a femtosecond laser; consequently enhancing the resulting mass spectrum signal.

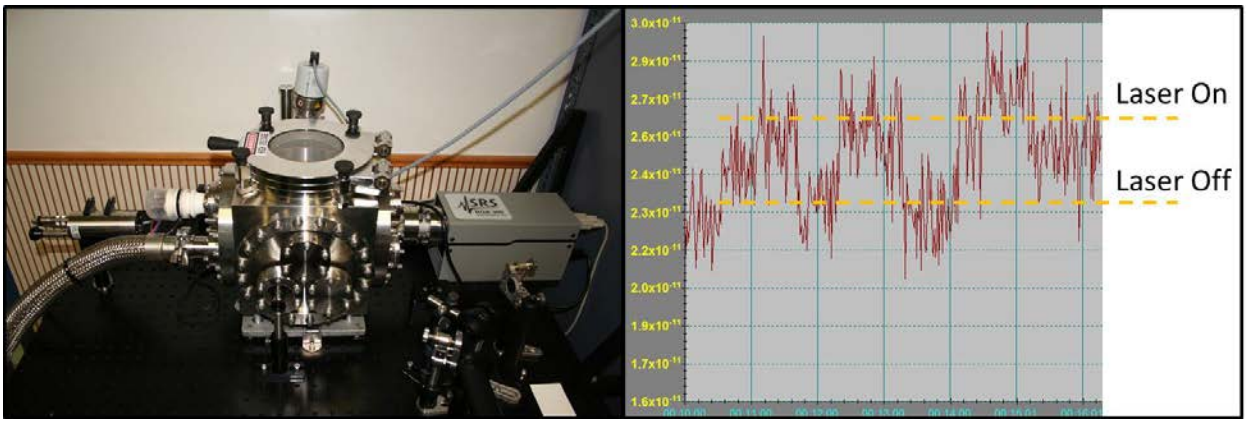

Figure 1: (left) Photograph of vacuum chamber with residual gas analyzer, optical pyrometer, and power supply for TIMS filament and (right) mass spectrum showing ionization enhancement of Sm-152 with and without laser.

Awards and Recognition

None

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature **Date**

Laser-Induced Ionization Efficiency Enhancement on a Filament for Thermal Ionization Mass Spectrometry

Project Team: M. J. Siegfried (Primary), E. Villa-Aleman, G. Hall

Thrust Area: ST3

Project Type: Standard

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The evaluation of trace Uranium and Plutonium isotope ratios for nanogram to femtogram material quantities is a vital tool for nuclear counter-proliferation and safeguard activities. Thermal Ionization Mass Spectrometry (TIMS) is generally accepted as the state of the art technology for highly accurate and ultra-trace measurements of these actinide ratios. However, the very low TIMS ionization yield (typically less than 1%) leaves much room for improvement.

Enhanced ionization of Nd and Sm from a TIMS filament was demonstrated using wavelength resonance with a nanosecond (pulse width) laser operating at 10 Hz when light was directed toward the filament.[1] For this study, femtosecond and picosecond laser capabilities were to be employed to study the dissociation and ionization mechanisms of actinides/lanthanides and measure the enhanced ionization of the metal of interest. Since the underlying chemistry of the actinide/lanthanide carbides produced and dissociated on a TIMS filament is not well understood, the experimental parameters affecting the photodissociation and photoionization with one and two laser beams were to be investigated.

FY2015 Objectives

- Enhance ionization efficiency for thermal ionization mass spectrometry using picosecond and femptosecond lasers
- Demonstrate tunable picosecond lasers can be used to enhance the ionization efficiency of actinides and lanthanides on a heated TIMS filament
- Develop a deeper understanding of the analyte carbide formation, dissociation, and ionization from the heated TIMS filament

Introduction

The measurement of lanthanide and actinide isotope ratios for nanograms to femtograms material quantities is a vital tool for nuclear counter-proliferation and safeguard activities. This is especially true in the evaluation of trace Uranium isotopes such as 232U, 233U, and 236U, as well as Plutonium isotope ratios. Thermal Ionization Mass Spectrometry (TIMS) is generally accepted as the state of the art technology for ultra-low level measurements of these actinide ratios. The standard sample preparation method for low level TIMS analysis consists of loading samples onto anion exchange resin beads and then loading beads onto Rhenium filaments. Currently, the efficiency of a typical TIMS instrument running U or Pu represents the detection of <0.5% of the total number of atoms loaded into the instrument. This fairly poor sample utilization creates significant room for improvement, and new sample ionization methods could generate an order of magnitude or more increase in detection efficiency. This would serve to push down detection limits and allow the measurement of even smaller samples, or alternatively give much higher precision measurements, especially on minor isotope ratios, of sample sizes routinely measured now.

The exact chemical processes that take place on a TIMS filament and lead to ionization of the analyte of interest have not been well characterized. Experimental evidence suggests that the actinide metals would vaporize at temperatures much below those at which a TIMS filament is known to operate (>2000 C) and thus be lost as undetectable neutral species. Laser induced ionization of molecular species on filaments or desorbed from the filament were conducted approximately 30 years ago. The laser ionization experiments of Nd and Sm were conducted with a nitrogen pumped dye laser at 1.0 Hz. Further research in this area declined due to the low duty cycle of the nanosecond laser. Femtosecond and picosecond lasers operating at 80 MHz has widened the field for unique experimentation. For this study, femtosecond laser capabilities were employed to study the dissociation and ionization mechanisms of actinides/lanthanides and measure the enhanced ionization of the metal of interest.

The goal of this project is to identify the parameters that could lead to a significant enhancement in the TIMS sample ionization efficiency. The new ultrafast laser capabilities will be employed to study the dissociation and ionization mechanisms of actinides/lanthanides and measure the enhanced ionization of the metal of interest. In order to reduce costs related to work with Pu and U, all experiments in this LDRD will be conducted with Sm.

Approach

A vacuum chamber/pump with several optical ports for laser inputs and optical detectors and a residual gas analyzer was designed and assembled on the side of an optical table. Optical ports will be used for laser inputs and diagnostic sensors. The vacuum system will be equipped with an RGA to measure ion current at masses up to 300 amu. The performance of the vacuum system will be tested with gauging, the performance of the RGA with bare rhenium filaments. The loaded filaments will be made by evaporating elemental analysis Nd and Sm standards onto rhenium. The emission spectra of a rhenium filament with resin/Nd/Sm will be investigated in a vacuum chamber at incremental temperatures up to the ionization temperature while monitoring the ion mass.

Filaments loaded with Nd and Sm will be heated just below the required temperature for thermal ionization. A series of experiments with the laser tuned on and off the resonance ionization of the element of interest will be conducted. Most lanthanides and actinides can be photoionized by a simple two-photon resonance ionization spectroscopy (RIS) process. Nd, with isotopes at 143, 145, 146, 148 and 150 (fission products) and 142 (not fission product) can be resonantly ionized with a laser tuned at 425.8 nm. Sm can be resonantly ionized with the laser tuned at 429.9 nm. Both wavelengths can be accessed with the second harmonic of the ultrafast Ti:Saphire fundamental laser wavelength. The advantage of ultrafast lasers over nanosecond lasers like nitrogen laser is the short duration pulse which can induce multiple harmonic processes efficiently.

A series of experiments will evaluate the use of a laser in the photodissociation of metal carbides on the filament surface. The laser wavelength and power on the filament surface will be changed while monitoring the masses with the RGA. Non-resonant studies will be conducted in the fundamental, 2^{nd} and 3^{rd} harmonics of the laser. Similarly, a series of studies will be conducted the picosecond or femtosecond laser tuned at the resonance wavelength. A filament loaded with Sm and Nd will be evaluated to understand ionization efficiency of one element in the presence of the other.

Results/Discussion

A vacuum chamber capable of heating a TIMS filament, optically measuring filament temperature, and capable of acquiring a mass spectrum of generated ions was designed, built, and assembled adjacent to the side of a laser table. The system was first demonstrated by acquiring a mass spectrum when heating a bare rhenium TIMS filament. Ionization enhancement was demonstrated when samarium was resonantly ionized using a femptosecond laser; consequently enhancing the resulting mass spectrum signal.

FY2015 Accomplishments

- Designed and installed a vacuum chamber capable of heating a TIMS filament, optically measuring filament temperature, and capable of acquiring a mass spectrum of generated ions
- Demonstrated a MS spectrum was obtained when heating a Rhenium Filament
- Demonstrated an ionization enhancement of ~13% when Sm was resonantly ionized using a laser tuned at the resonance ionization wavelength

Future Directions

- Optimize laser settings, filament temperature, and optics for resonance ionization
- Investigate emission spectra of a rhenium filament with Nd/Sm at different temperatures.
- Conduct a series of experiments to evaluate the use of a laser in the photoionization of metal carbides on the filament surface.
- Compare distribution of ions/neutrals of thermal vs. laser induced ionization
- Evaluate targeted/selective photoionization of Nd/Sm

FY 2015 Publications/Presentations

None

References

1. D.L. Donohue, J.P. Young and D.H. Smith, “Determination of Rare-Earth Isotope Ratios by Resonance Ionization Mass Spectrometry”, International Journal of Mass Spectrometry and Ion Physics, 43 (1982) 293-307.

Acronyms

TIMS – Thermal Ionization Mass Spectrometry

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None