

An Improved Tool for Nuclear Forensics

In the aftermath of an aboveground nuclear explosion, measuring the isotopic compositions of fallout can provide important forensic information, including data pertaining to the production and irradiation histories of key materials. Livermore scientists working with collaborators at Argonne National Laboratory and the University of California at Berkeley have recently demonstrated rapid and high-accuracy isotopic measurements of plutonium and uranium using a laser-based technique known as resonance ionization mass spectrometry (RIMS).

Resonance ionization uses pulsed laser light to first excite an atom or molecule and then remove an electron to create an ion. Although scientists have understood the basic physical principles involved in the process for many years, it was not until the mid-1990s that a method was developed to provide unprecedented analysis of stellar nucleosynthesis processes captured in grains of star dust. Lawrence Livermore researcher Kim Knight, whose background is in cosmochemistry, and colleagues theorized that the RIMS technique could also be applied to study samples derived from nuclear events on Earth.

Postdetonation nuclear forensics is primarily concerned with detecting the presence of uranium (U) and plutonium (Pu) and measuring isotopic ratios, $^{235}\text{U}/^{238}\text{U}$ for example. Conventional mass spectroscopy cannot distinguish between different isotopes of identical mass—in particular, ^{238}U and ^{238}Pu —in the same sample. As a result, the two actinides must be extracted from a forensic sample and separated from each other in a process that can take longer than decision makers would want to wait. The challenge is that postdetonation nuclear forensics demands rapid answers. RIMS uses lasers to separate elements, thus circumventing the lengthy steps of chemical separation and sample preparation. As a result, several actinides can be measured from virtually unprocessed samples in only a few hours.

Calming the Jitters

RIMS works in three stages. First, a focused laser or ion beam desorbs or sputters material from the surface of a sample, forming a cloud of ions, neutral atoms, and molecules. (See the figure on p. 12.) Ions are removed from the cloud using a brief voltage pulse, and the neutral atoms are left behind. Next, a set of wavelength-tunable lasers selectively excites atoms in the cloud, promoting them to an intermediate excited state. A final laser

further excites electrons, knocking them off the atoms and creating ions. Because the laser wavelengths are precisely tuned to match an element's unique intermediate excitation and ionization states, only atoms of the desired element are ionized. Finally, the photons are accelerated in a mass spectrometer to obtain isotopic measurements.

Building lasers for demanding forensics applications has been a significant challenge. Even tiny fluctuations in laser wavelength, power, and bandwidth can introduce errors that affect the reproducibility of results. According to Knight



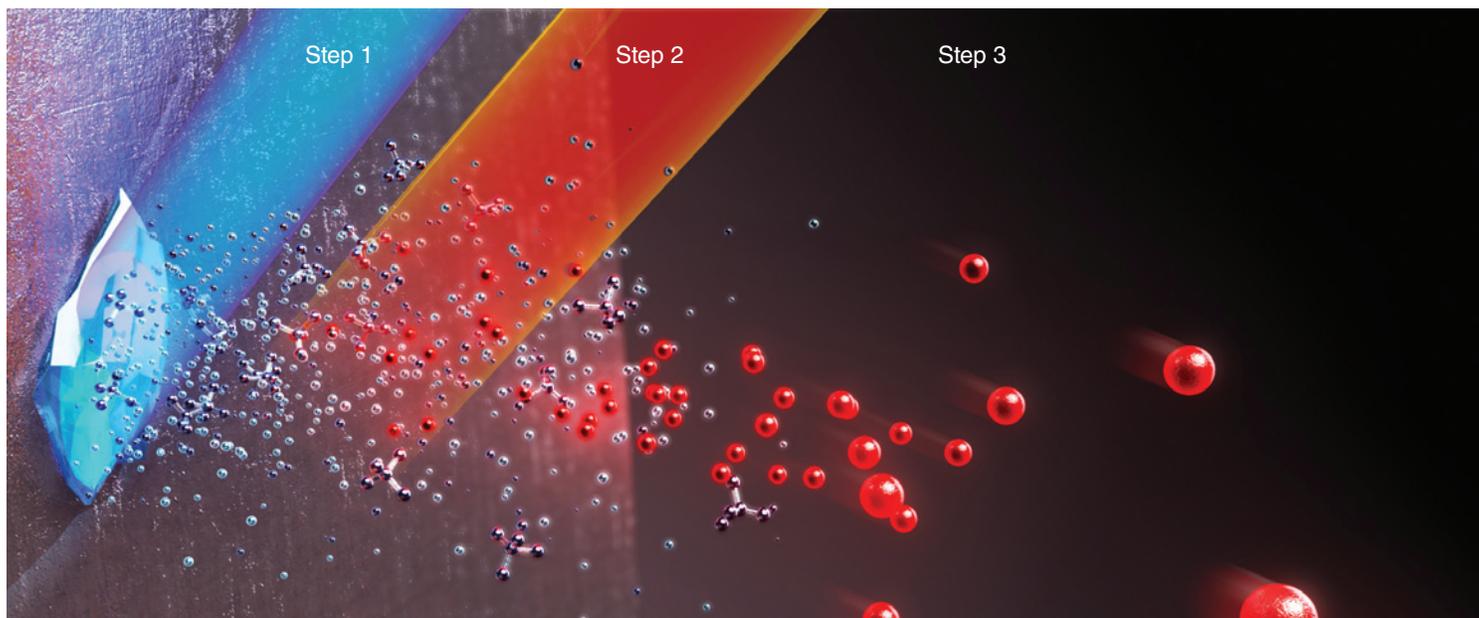
and Argonne collaborator Michael Savina, stabilizing the lasers and reducing jitter has greatly improved the quality of the measurements. By precisely controlling wavelength, pulse timing, power, and pointing stability in the lasers and making adjustments to bandwidth (the spectral range of laser wavelengths present in the laser beam), the team achieved more uniform ionization in experiments and thus better detection and measurement of multiple isotopes.

Speeding Up the Process

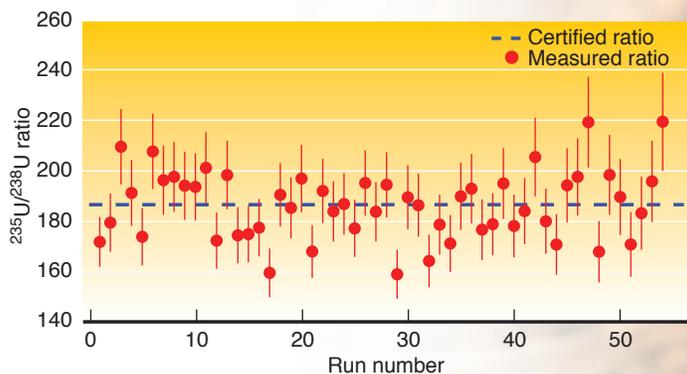
In a breakthrough study, the RIMS team, which includes Livermore postdoctoral researcher Brett Isselhardt, used Argonne's CHARISMA (Chicago-Argonne Resonance Ionization Spectrometer for MicroAnalysis) time-of-flight mass spectrometer—originally designed to study grains of star dust recovered from meteorites—to rapidly assess natural uranium metal and oxide targets. The relative abundances of uranium isotopes (in particular, the $^{235}\text{U}/^{238}\text{U}$ ratio) were measured from solid uranium samples with known isotope ratios. Virtually no sample preparation was required. The idea was to minimize and stabilize laser-induced isotope fractionation, which can be severe.

Variability in the measured isotope ratio means that each isotope has responded differently to the ionization process and can lead to incorrect conclusions. By broadening the laser bandwidth from 1 to 5 picometers (10^{-12} meters) in the first of three resonance lasers, while holding the second and third resonance lasers fixed, the team decreased measurement uncertainty from 10 percent to less than 0.5 percent. The tiny adjustment works because the 5-picometer-wide range of laser wavelengths overlaps the peak energy region needed to excite both ^{235}U and ^{238}U with equal intensity. This study shows that laser bandwidth has an enormous effect on the precision of isotope ratio measurements and demonstrates how to optimize that particular parameter.

In a subsequent study, the team completed the first in situ analysis of a complex natural uranium silicate (uranium ore) with RIMS using seven experimental configurations. Both two- and three-color laser schemes were assessed along with different methods for dislodging uranium atoms from a sample. To improve precision, the team used an automatic feedback system to track and correct drift in the laser wavelengths and broadened the laser bandwidth to as wide as 10 picometers. Results were achieved in a few hours with precisions of 1 percent for uranium isotope



The difference between resonance ionization mass spectrometry (RIMS) and other mass spectrometric techniques is in the ion-formation process. Step 1: An ion gun removes atoms and molecules from a solid material surface, creating a cloud of atoms and molecules. Step 2: Wavelength-tuned laser light is absorbed by one element, and individual atoms achieve excited states. Step 3: An extraction cone (not shown) collects the ions, which are then accelerated to the mass analyzer. (Artist's rendering by Kwei-Yu Chu.)



RIMS permits accuracies to better than 1 percent while measuring the ratio of uranium-235 (^{235}U) to uranium-238 (^{238}U) over timescales of several hours. Analysis times to collect data, such as these from a highly enriched uranium sample, are less than 4 hours per sample, including preparation time.

compositions measured directly from the uranium silicate after minimal sample preparation.

To measure both uranium and plutonium isotopes in a single material for the first time, the RIMS team prepared samples from a solution of 25 percent each of ^{238}Pu , ^{239}Pu , ^{242}Pu , and ^{244}Pu that also contained ^{235}U and ^{238}U . Sample material was electrodeposited onto a titanium stub to promote reduction. The CHARISMA spectrometer was used with lasers tuned for a three-color excitation and ionization. The challenge was that ^{238}U , which is the most common uranium isotope in nature, creates isobaric (same-mass) interference with plutonium, making the two isotopes difficult to differentiate. By making improvements to the excitation lasers and changing the laser wavelengths between measurements, the team demonstrated excellent discrimination against isobaric interferences. When the lasers were tuned to excite plutonium, the uranium signal was essentially absent, and inversely, the plutonium signal was essentially absent when lasers were tuned to excite uranium. All of the plutonium and uranium isotope ratios were accurately measured.

Inside Desert Glass

The RIMS technique has most recently been demonstrated on fallout debris taken from the Nevada National Security Site. The samples pieces of glass formed during post nuclear tests contained isotopes of both uranium and plutonium. Sample preparation consisted of fragmenting the glassy material and pressing the fragments into soft indium metal to help reduce sample charging. RIMS measurements were again highly successful, detecting both uranium and plutonium at parts-per-million concentrations in

A sample of glass formed in a historic U.S. nuclear weapons test is selected from bulk soils for direct analysis using the RIMS method.

fallout glasses from multiple tests. Rapid detection of the isotopic composition of multiple elements in a single sample with almost no sample preparation lays the foundation for rapid isotopic analyses using RIMS.

The team's research findings demonstrate how RIMS can be adapted to measure different elements in a sample and discriminate against interfering masses. As a result, RIMS holds considerable promise for applications in nuclear forensics. Knight and her colleagues continue to explore ways to improve stability and reproducibility in their measurements. Future studies may include developing techniques to increase the amount of atomic—as opposed to molecular—material in the cloud, suppress molecule ionization, and increase sensitivity to desired elements, improving detection in low-concentration materials.

—Robert Kirvel

Key Words: Chicago-Argonne Resonance Ionization Spectrometer for MicroAnalysis (CHARISMA), fallout debris, nuclear forensics, plutonium isotope, resonance ionization mass spectrometry (RIMS), uranium isotope.

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