Real-Time Screening for Uranium Enrichment by Paper Spray Ionization Mass Spectrometry for Field Applications

*John T. Kelly, *Ashlee R. Swindle, *Kyle M. Samperton, KateLyn Smith, Kaitlin Coopersmith, and Patterson R. Nuessle

Savannah River National Laboratory, Aiken, South Carolina 29808, USA

ABSTRACT: A rapid isotope ratio screening technique for uranium enrichment is demonstrated utilizing paper spray ionization (PSI) high resolution mass spectrometry (HRMS). Measurements were conducted using an ambient ionization mass spectrometer coupled to a custom manufactured JEOL PSI attachment apparatus, with de minimus sample preparation requirements. The current method detection limit for individual isotopes (e.g., ^{235}U and ^{238}U) is approximately 50 pg, with subsequent optimization expected to further improve U isotopic sensitivity. The PSI analytical method described herein can support rapid analysis (both in-field and in-lab screening) of isotopes-of-interest, as demonstrated by empirical differentiation of depleted uranium (DU) and low enriched uranium (LEU) analytical aliquots. This analytical workflow holds promise for application to nuclear forensics, international nuclear safeguards, and nonproliferation missions.

INTRODUCTION

The need for rapid, early-phase detection of chemical, biological, radiological, and nuclear (CBRN) agents is ubiquitous and is of the highest importance for protecting first responders and expediting essential analytical results. For example, the military community continues to support method development for detecting threats with significant gaps in reliability and transferability in field-portable detection methods.[1,2] While small molecules can be readily characterized by modern ion mobility spectrometers or quadrupole mass spectrometers,[3,4] radiological threats remain complex in terms of sample preparation and large laboratory equipment requirements.[5-6] Anomalies in uranium isotopic composition and abundance can provide critical information regarding enrichment processes or identification of prohibited uranium products as of recent legislation.[7-9]

After nearly a century of efforts banning the development, production, and stockpiling of nuclear materials, the threat posed by radiological exposure to warfighters is increasingly relevant with the advent of small modular reactors (SMRs).[10,11] International agreements aim to regulate and secure the management of enrichment facilities and accountable nuclear materials, particularly regarding their potential enrichment levels. The advancement of SMRs in military operations have increased risks associated with nuclear material, especially concerning its potential as targets for terrorism or sabotage.[12] Currently, there are several detection methods available for identifying nuclear materials utilizing both in-field and fixed laboratory instrumentation.[6]

There have been major advancements in laboratory analyses to eliminate time-consuming and labor-intensive sample preparation by coupling an automated micro-extraction platform to an inductively coupled plasma mass spectrometer (ICP-MS).[7] Using such methods, reported detection limits of uranium (U) and plutonium (Pu) isotopologues from cotton swipes are as low as 3.6×10^{-16} grams (0.36 fg).[13] Analytical approaches like these have remarkable sensitivity and selectivity and are ideal for safeguards inspections of nuclear facilities; however, this approach requires significant capital equipment, large analytical-grade argon gas cylinders, and highly trained personnel for routine operation and post-processing data.

This work explores the possibility of applying paper spray ionization (PSI) and high-resolution mass spectrometry (HRMS) to screening for uranium enrichment for military operations or treaty compliance. While PSI is widely accepted as a method for chemical identification (e.g., hair, fibers, soil/dust, gunshot residue),[14-20] it is not commonly used for analysis of inorganic species. A notable exception is the pioneering work of Cody and Cane, who performed PSI-MS analysis of inorganics in positive-ion mode using a mixed reference standard (including Ag, Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Mg, Mn, Na, Ni, Pb, Sr, Tl, and Zn).[21]. Implementing a similar system setup, our group previously demonstrated successful uranium detection in less than one minute[23], establishing a foundation for subsequent rapid, quantitative uranium enrichment analyses.

EXPERIMENTAL SECTION

Chemical and Reagents. All chemicals were commercially acquired and used as received. SupraSolv methanol and Fomblin Y were purchased from Sigma Aldrich (MO, USA), Optima Grade nitric acid was purchased from Fisher Scientific (MA, USA), and Gadolinium nitrate from High Purity Standards (SC, USA). Uranium Certified Reference Materials (CRM U005 and CRM U010) were purchased from the New Brunswick Laboratory-Program Office (NBL-PO) as 5-10 mg uranium (U_3O_8 solid form) and then diluted in 2% nitric acid for sample analysis.

High Resolution Mass Spectrometry. Samples were analyzed with a time-of-flight AccuTOF DART 4G mass spectrometer (JEOL, Peabody, MS, USA) in negative-ion mode.[20-23] Mass spectral calibrations were performed using Fomblin Y diluted in methanol before, during, and after sample analyses. The radiofrequency (RF) quadrupole ion guide was set to 800 V, the inlet voltage to -220 V, the ionization voltage to -3000 V, and the detector voltage to -2800 V. For PSI-MS, the spectrometer was equipped with a custom manufactured JEOL paper spray apparatus.[23]

Paper Spray Ionization. Filter paper wedges (JEOL Filter Spray Triangles, P/N JU2016136) were prepared by depositing 8 µL of solvent to the paper, followed by 8 µL of U-bearing standard solution containing 5 ppm internal standard (gadolinium nitrate salt); and dried prior to analysis. The wedges were then mounted into the paper spray apparatus and positioned nominally ~2 mm from the detector orifice. The paper wedges were solvated with a direct dispense of 20 µL of 80:20% methanol:water (by volume) onto the paper substrate for analysis. All samples were run in replicates (ca. 5-10 analyses/sample) to evaluate consistency and reproducibility. The internal standard (gadolinium nitrate) is presented as a series of peaks of the gadolinium tetranitrate anion ($Gd(NO_3)_4^-$), with masses ranging from 402-410 m/z, with 405.87545 m/z the most abundant. The high-resolution accurate mass for ^{235}U and ^{238}U were in the form of uranyl nitrates. Dedicated analyses were performed, with U010 analyzed over two days/sessions (Day 1 and 2), and U005 analyzed over one day/session. Analyses of U010 from the first analytical session were used to calibrate U010 and U005 analyses from the second analytical session.

Data Analysis and Processing. Minimally processed, raw instrument-ouput data files (.cdf formated, centroided) were exported from JEOL msAxel (vers. 1.0.5.2) for offline data analysis. Data processing was performed using R statistical programming environment (vers. 4.4.1), RStudio integrated development environment (IDE), and "ncdf4" package for netCDF file reading. $^{238}U/^{156}Gd$ and $^{235}U/^{238}U$ isotope amount ratios were calculated using the extracted Gd nitrate, ^{235}U- and ^{238}U-bearing uranyl nitrate signal intensities (408, 453 and 456 m/z, respectively). Time-resolved, cycle-by-cycle ion peak heights were used to calculate isotope ratios of interest (e.g.,$^{235}UO_2(NO_3)_3^-/^{238}UO_2(NO_3)_3^- = ^{235}U/^{238}U$). For individual analyses, weighted mean $^{238}U/^{156}Gd$ and $^{235}U/^{238}U$ values and weighted standard errors were calculated. Calibration curves for U concentration and U isotope amount ratio were determined from analysis of CRM U010 (Fig. 1) from one analytical session. These calibrations were used to correct analyses of U005 and U010 measured during the second analytical session (Fig. 2). Individual calibrated analytical results were then used to obtain aggregate weighted means for the U005 and U010 $^{235}U/^{238}U$ isotope ratios.

RESULTS AND DISCUSSION

As shown in Fig. 2, calibrated U005 and U010 PSI analyses reproduce the certified $^{235}U/^{238}U$ of these CRMs within uncertainty. This proof-of-concept study demonstrates the ability of PSI-HRMS to generate accurate isotope amount ratios on relatively ^{235}U-limited compositions (DU and LEU). The applied calibration approach corrects for systematically high-biased, measured $^{235}U/^{238}U$ values. The source of this bias in the measured isotope ratio data has not yet been uniquely identified but may be due to one or a combination sample alignment, background effects, isobaric interferences, and artifacts of the data centroiding algorithm. Regardless, use of our calibration approach largely addresses the observed bias phenomenon and enables generation of accurate and traceable U enrichment data.

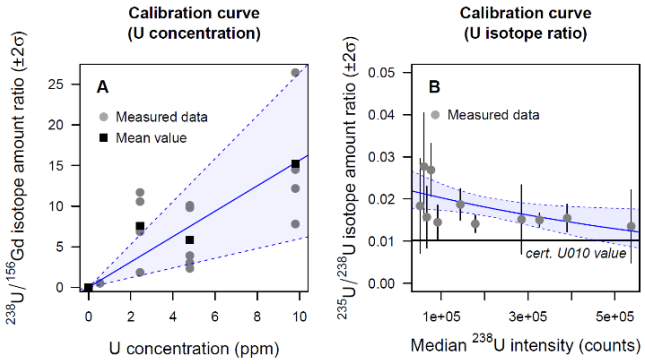

Figure 1. Empirical calibration curves using NBL CRM U010 to obtain A) U concentration and B) U isotope amount ratio ($^{235}U/^{238}U$).

The JEOL paper spray apparatus provides flexibility for precise sample alignment at the instrument orifice for PSI-HRMS measurements. Analyses performed in this study demonstrate the ability to detect and differentiate isotopic enrichment of inorganic uranium species. Figure1 shows a calibration curve for U concentration (Fig.1A) and U isotope amount ratio ($^{235}U/^{238}U$, Fig.1B) using CRM U010. Experiments also demonstrate an empirical isotope detection limit of ca.50 pg per U isotope. Acceptance criteria were established to ensure method accuracy, requiring minimum Gd and U cumulative ion intensities of 10^5 and 10^6 per analysis, respectively.

The isotope ratio for uranium enrichment ($^{235}U/^{238}U$) has been previously demonstrated by extractive electrospray ionization (EESI) as a sensitive and reliable method.[24] While the reported acquisition times for this approach are estimated ~5 minutes, the data presented in this work is up to 100 times faster without the need for collision induced dissociation (CID). The high-resolution accurate mass (HRAM) analysis provides elemental confirmatory identification CID experiments, reducing analysis time. Notably, similar fragments observed in the tandem mass spectra of the $^{238}UO_2(NO_3)_3^-$ anion (456 m/z) and $^{235}UO_2(NO_3)_3^-$ anion (453 m/z) are observed in PSI measurements.

The NO_2 loss channel has been previously explored by infrared ion spectroscopy (IRIS) experimental work the Free Electron Laser for Infrared eXperiments (FELIX) beamline, where there is clear evidence for the oxo-bearing uranyl nitrate over the superoxide by comparing experimental data to computed vibrational spectra. A set of features that correspond a loss of a NO_2 were observed at 410.01122 and 407.00436 that agree with the $^{238}UO_3(NO_3)_2^-$ (410 m/z) and $^{235}UO_3(NO_3)_2^-$ anions. The NO_3 loss has also been observed in PSI experiments at 348.02338 and 345.01652 m/z. Possible dissociation and ion-molecule reaction pathways and products for the $UO_2(NO_3)_3^-$ anion have been previously describe by Van Stipdonk and coworkers.[25] These features provide consistent secondary isotope ratio features for more complicated and complex samples. While in this study we do not quantitatively use these secondary isotope ratio features, future work will assess the utility of these and additional spectral signals to complement the analytical approach presented here.

The purpose of field measurements not only supports international regulations, such as the Nuclear Nonproliferation Treaty (NPT), but could also support missions. Future PSI scope will focus on a SRNL-designed autosampler for radiological sample analysis. This technology will provide the opportunity for routine quality control sample processing.[25] Additionally, future work will investigate characterization of traditional field samples (swipes) and non-traditional media (biota, substrates, etc.), as well as alternative material forms and compositions (^{233}U and UF_6).

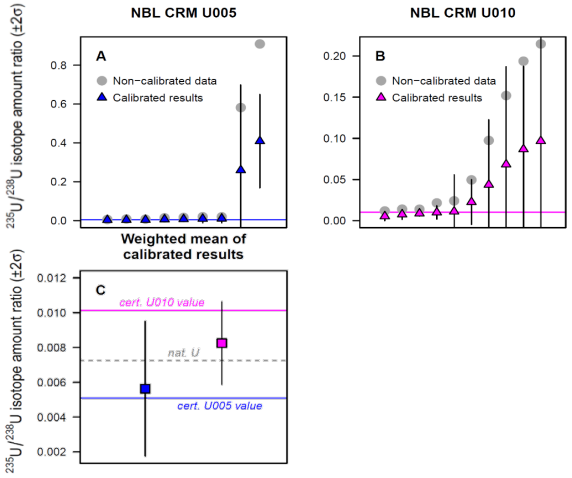

Figure 2. Comparison of non-calibrated (raw) and calibrated $^{235}U/^{238}U$ isotope amount ratios for CRMs U005 (A) and U010 (B). Calibrated results were obtained using the calibration curve in Fig.1B (C) Calibrated $^{235}U/^{238}U$ weighted mean values agree with their certified isotopic compositions; natural U (CRM 129A) certified value also displayed for comparison.

CONCLUSION

This work aims to provide a screening platform for nuclear material assessment and characterization to include isotope enrichment. In comparison to chemical and biological threats, field-portable nuclear and radiological threat detection has been limited to dosimetry and radioactive decay measurements. The detection limits of uranium enrichment as described here is currently 50 pg per U isotope, with detection limits expected to improve with further method development. The PSI technique has been widely adopted across the scientific community for qualitative analysis of chemical and even biological screening, and the data shown here extends towards quantitative radiological signature determination.

Crucially, PSIHRMS is a practical, cost-effective approach to simultaneously determine U enrichment and reduce turnaround times associated with conventional, bulk sample analysis methodologies. While US military laboratories typically screen for uranium and its impact on human health, international nuclear safeguards monitoring requires reliable, defensible, and quantitative results with a ≤2% accuracy for $^{235}U/^{238}U$ at >10 ng U. Our PSI-HRMS provides U detection limits, promising isotope amount ratio precision, and portability to support future on-site detection or screening of radiological samples.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Corresponding Author

* Ashlee R. Swindle, ashlee.swindle@srnl.doe.gov

Author Contributions

All authors have given approval to the final version of the manuscript.
John T. Kelly - analyzed data, prepared figures, and wrote the article.
Ashlee R. Swindle - conceived and designed the experiments, contributed infrastructure and materials, acquired and analyzed data, prepared figures and wrote the article;
Kyle Samperton – developed advanced data processing analyzed data, prepared figures and wrote the article;
Kaitlin Coopersmith - conceived and designed the experiments, acquired and analyzed data, prepared figures and wrote the article;
KateLyn Smith - performed experiments;
Patterson Nuessle – contributed to the conception and experimental designs.

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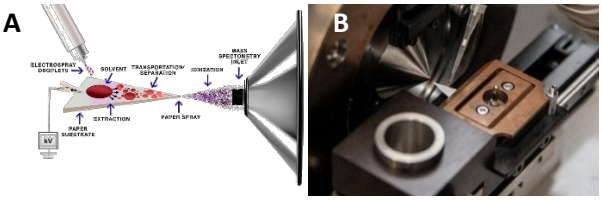

Figure 1. PSI-MS A) conceptual modality and B) JEOL apparatus.

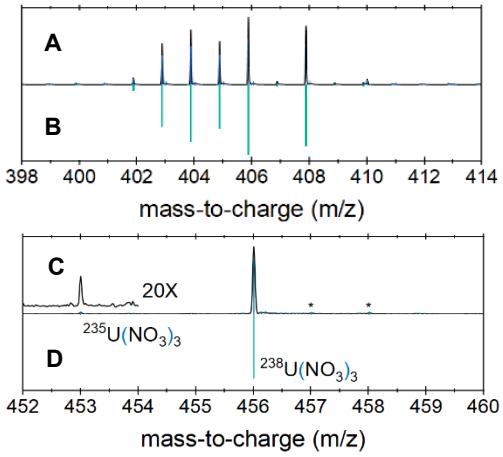

Figure 2. Averaged PSI mass spectra of mixed uranium-gadolinium solutions. A) Measured $Gd(NO_3)_3^-$ spectra, B) Modeled $Gd(NO_3)_3^-$ spectra, C) Measured $UO_2(NO_3)_3^-$ spectra, D) Modeled $UO_2(NO_3)_3^-$