

Direct Analysis of Cotton Swipes for Uranium and Plutonium Isotopic Determination by Microextraction-ICP-MS

Veronica C. Bradley, Brian W. Ticknor, Paula Cable-Dunlap, Cole R. Hexel, Benjamin T. Manard
Oak Ridge National Laboratory
Oak Ridge TN, USA

This manuscript has been authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

Abstract

The determination of uranium and plutonium isotopic abundance on environmental samples collected by International Atomic Energy Agency (IAEA) inspectors is vital for the detection of undeclared nuclear activities and material under the international nuclear safeguards regime. Current analytical protocols require time-consuming sample preparation steps prior to subsequent measurement by inorganic mass spectrometry (MS). Recent efforts from this laboratory have focused on developing sample preparation methods for faster analysis, potentially allowing higher sample throughput[1]. Alternative methods including microextraction sampling in conjunction with inductively coupled plasma-mass spectrometry (ICP-MS) have been recently explored. This methodology, microextraction-ICP-MS, was developed such that uranium and plutonium could be extracted from the swipe surface and directed into the ICP-MS for an in-situ measurement, eliminating the need for swipe ashing and digestion. A commercial off-the-shelf microextraction system was customized with an automated movable XY stage that can be programmed to save sampling locations, allowing for automated rapid sampling of swipe surfaces. Additional efforts have focused on the utilization of collision cell technology to the microextraction ICP-MS method. This would eliminate the need for lengthy column chemistry procedures to purify separated uranium and plutonium fractions before analysis. Here, the extracted U/Pu analyte is measured by reacting the uranium ions with CO₂ in the collision cell of an ICP-MS, shifting the uranium to UO⁺, which would not interfere with the plutonium isotopic determination. The developed method utilizing collision cell – ICP-MS technology has demonstrated the ability to measure plutonium isotope ratios in the presence of high uranium concentration on the transient signal from the microextraction system.

Introduction

The International Atomic Energy Agency (IAEA) collects environmental samples at nuclear facilities for the detection of undeclared nuclear materials and activities. These environmental samples are often in the form of 10 × 10 cm cotton swipes. Hundreds of samples are collected each year and sent to the Network of Analytical Laboratories (NWAL) for analysis[2]. The sample analysis is separated into two main processing streams, particle analysis and bulk analysis, which

provide complementary information[3]. The particle analysis generally involves locating individual actinide-containing particles (on the order of micrometers in size) on the swipes then removing and analyzing them with fission track thermal ionization mass spectrometry (FT-TIMS) or large geometry secondary ion mass spectrometry (LG-SIMS). FT-TIMS requires irradiating particles with thermal neutrons to look for particles containing fissile isotopes such as ^{235}U , then transferring the individual particles to TIMS filaments for analysis[4-6]. LG-SIMS utilizes automated particle mapping to quickly scan over a sample with an ion beam, locating regions containing isotopes of interest. These regions are then measured for precise isotope ratios[7-9]. Due to the SIMS ionization method, molecular and hydride ions cause isobaric interferences that can especially affect the measurement of the minor U isotope ratios[10]. Bulk analysis requires ashing and dissolution of a full environmental swipe sample. The U and Pu are then separated and analyzed with multi-collector mass spectrometry for the overall amount of actinides and their average isotope ratio. This analytical protocol is a very labor-intensive and time-consuming process.

The Advion Plate ExpressTM is a commercial-off-the-shelf (COTS) system that is traditionally used for the analysis of thin layer chromatography spots by liquid extraction[11]. More recently it has been applied to the direct sampling of cotton swipes for the analysis of uranium and plutonium isotope ratios by using nitric acid as the extraction solvent, and connecting the system to an inductively coupled plasma mass spectrometer (ICP-MS)[12-14]. Microextraction ICP-MS is a technique that samples a small area of a swipe (2×4 mm) and can take less than a minute per extraction. In the work presented here, the microextraction system has been used to directly sample cotton swipes containing solid uranium particulates, as well as mixtures of U and Pu, to measure the U and Pu isotope ratios at each sampling location.

Materials and Methods

Materials, Reagents, and Sample Preparation

OptimaTM grade nitric acid (HNO_3) diluted by volume with ASTM Type I water ($18.2 \text{ M}\Omega\text{-cm}$) generated from a BarnsteadTM xCAS Plus ultrapure water purification system (Waltham, MA, USA) was used as need. Samples of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, UO_2F_2 , $\text{UO}_2(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ (reagent grade) were obtained from International Bioanalytics (Boca Raton, FL, USA) and used as received. U_3O_8 microparticles were prepared from NBLPO CRM 129a at the Forschungszentrum Julich Institute of Energy and Climate Research (Julich, Germany). Certified reference materials (CRMs) were used to verify isotope ratio measurements and study the performance of the methodology. The CRMs were sourced from the European Commission—Joint Research Center-Geel (JRC-Geel, formerly the Institute for Reference Materials and Measurements (IRMM), in Geel, Belgium) for IRMM 2025 and 2027, and from the New Brunswick Laboratory Program Office for NBLPO CRM 137, 136A, and 144. The isotope ratios of the Pu CRMs were decay corrected to the date of analysis. TX304 10×10 cm cotton swipes were obtained from Texwipe (Kernersville, NC, USA). Individual sampling locations were stamped with a microextraction probe to create a 2×4 mm indentation. These indentations were then loaded with either a $4 \mu\text{L}$ aliquot of a solution containing 0.5 ng Pu g^{-1} and a range between 0 and $50 \mu\text{g U g}^{-1}$, or a solid uranium particle less than $30 \mu\text{m}$ long. Particles were

loaded using an AxisPro micromanipulator fitted with 1 μm W probes. The micromanipulator is shown in figure one.



Figure 1: Axis Pro Micromanipulator

Microextraction-ICP-MS of uranium particulates

An Advion™ Plate Express (Advion, Ithaca, NY, USA) was modified at ORNL to include a automated sampling stage, a camera, and two washing wells (Figure 2). A cotton swipe containing U and / or Pu was placed on the automated stage on top of a teflon square and held in place with a PEEK clamp. Using computer software, the stage was moved so an individual sampling location was directly underneath the microextraction probe. The probe head pressed down on the swipe with 300 N of force, forming a seal on the surface. 5% HNO_3 , pumped at a rate of 0.2 mL min^{-1} with an isocratic pump, was directed through the probe onto the sample where it extracted the actinide content from the cotton. The pressure from the pump forced the solvent back up through a parallel track in the probe head, and through PEEK tubing into a triple quadrupole (TQ) ICP-MS (ThermoScientific iCAP TQ, Bremen, Germany). The nebulizer gas flow was approximately 1 L Ar min^{-1} . The transient signal was integrated with the ICIS peak detection algorithm in the Qtegra™ software. The transient signal was smoothed with a 15-point moving mean function.

A portion of the solid uranium material was dissolved and analyzed with a Thermo Scientific Triton (Bremen, Germany) multiple collector thermal ionization mass spectrometer (MC-TIMS). A total evaporation method, which followed ASTM international designation C1672-17[15], was used for the TIMS analysis. Most of particles used in the study were not isotopic standard reference material, and for these the TIMS isotope ratio value was used as the comparator value for isotope ratios measured with the microextraction-ICP-MS system.

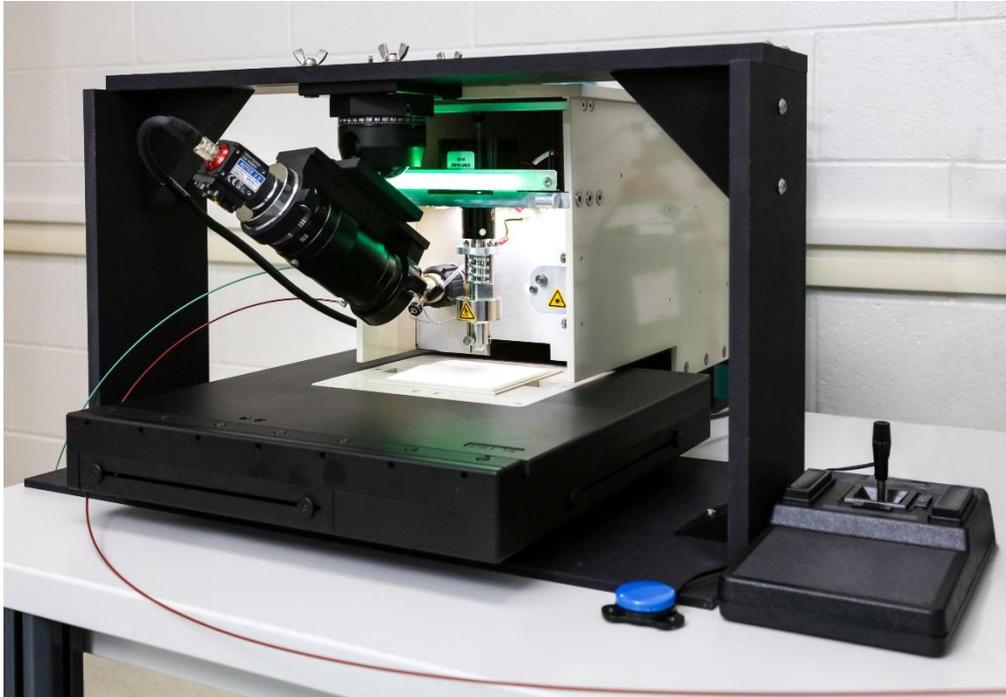


Figure 2: Automated microextraction system

The loaded swipes were imaged with a Hitachi SU3900 scanning electron microscope (SEM, Tokyo, Japan) in variable pressure mode with a backscatter electron detector. SEM images of U_3O_8 particles are shown in figure 3.

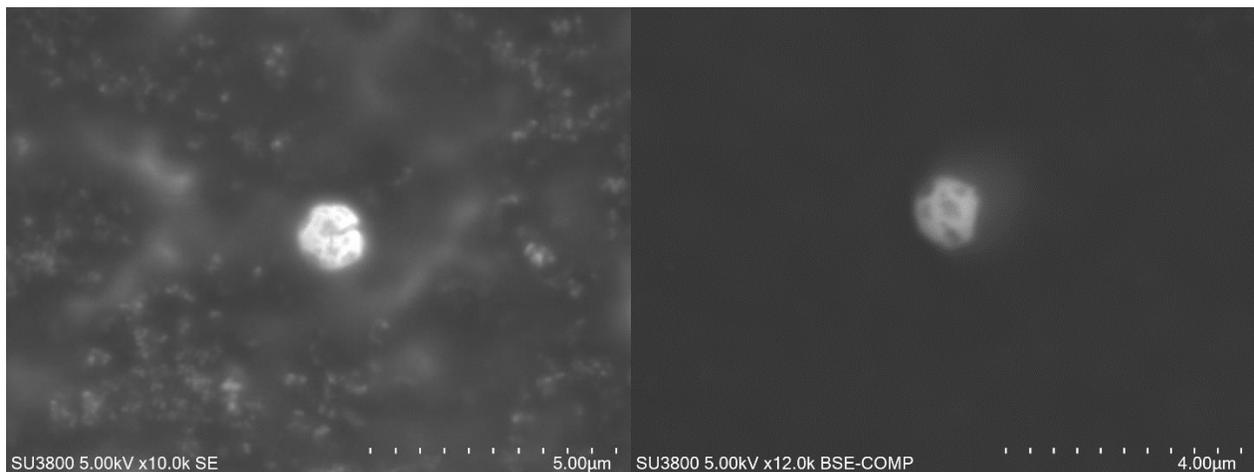


Figure 3: SEM images of U_3O_8 particles on cotton swipes

Microextraction ICP-MS of plutonium and uranium

The ICP-MS was operated in triple quadrupole mode, with CO₂ and He gases flowing through the reaction cell. The reaction gases were optimized to a flow rate of 0.3 mL CO₂ min⁻¹ and 5 mL He min⁻¹. To measure U isotope ratios, the first quadrupole was set to the atomic ion mass, while the third quadrupole was set to the oxide mass. For Pu isotope ratios, both quadrupoles were set to the atomic ion mass. The less abundant isotopes were measured with a 10 ms dwell time, while the more abundant isotopes were measured with a 1 ms dwell time, as shown in Table 1.

Table 1: ICP-TQ-MS settings

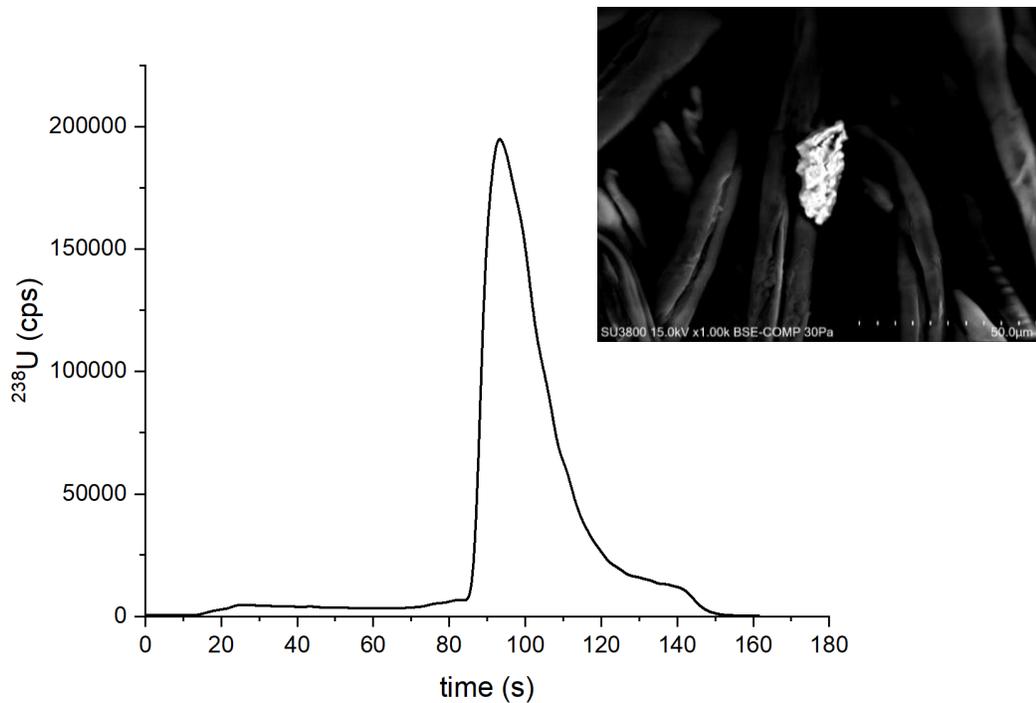
Isotope	Q-1	Q-3	Dwell time (ms)
²³⁴ U	²³⁴ U ⁺	²³⁴ U ¹⁶ O ⁺	10
²³⁵ U	²³⁵ U ⁺	²³⁵ U ¹⁶ O ⁺	1
²³⁶ U	²³⁶ U ⁺	²³⁶ U ¹⁶ O ⁺	10
²³⁸ U	²³⁸ U ⁺	²³⁸ U ¹⁶ O ⁺	1
²³⁸ U	²³⁸ U ⁺	²³⁸ U ⁺	1
²³⁹ Pu	²³⁹ Pu ⁺	²³⁹ Pu ⁺	10
²⁴⁰ Pu	²⁴⁰ Pu ⁺	²⁴⁰ Pu ⁺	10

Five different solutions were prepared containing 0.5 ng NBLPO CRM 137 g⁻¹ with 0, 1, 5, 25 and 50 µg IRMM 2027 g⁻¹ respectively. A 4 µL aliquot of was deposited on a pre-marked location on a cotton swipe. Each solution had 4 replicate sampling locations.

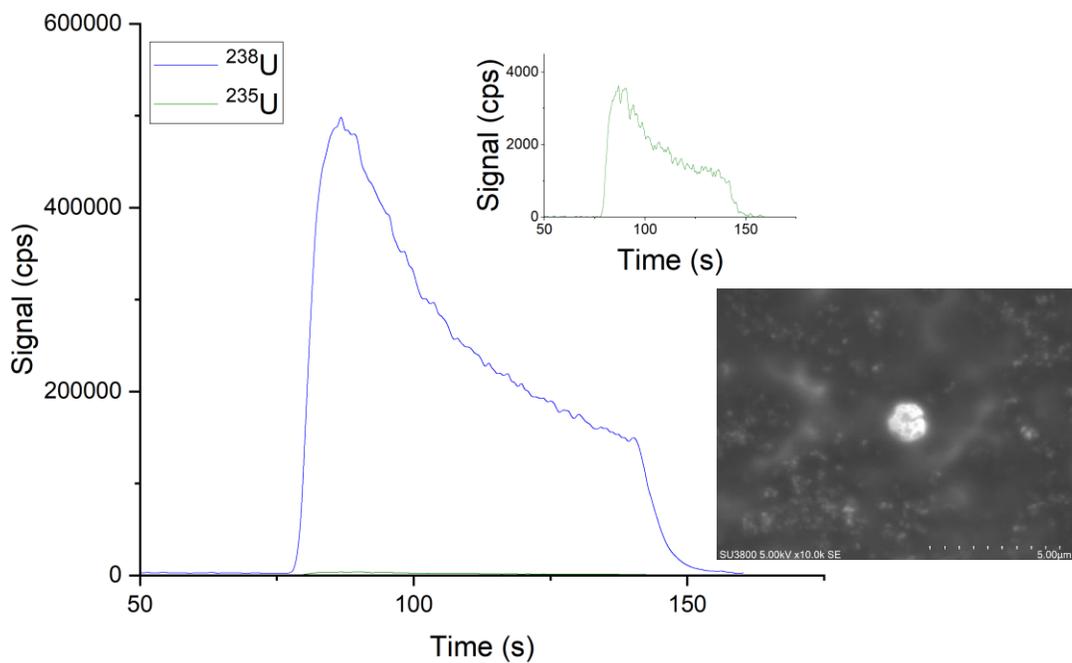
Results and Discussion

Uranium oxide particle extractions

Particulates of 4 uranium compounds, UO₂(NO₃)₂·6H₂O (uranyl nitrate, UN), UO₂F₂ (uranyl fluoride), UO₂(CH₃CO₂)₂·H₂O (uranyl acetate, UAC), and U₃O₈ (triuranium octoxide) were placed on cotton swipes with a micromanipulator. The particulates were extracted in 5% HNO₃ and directed to the ICP-TQ-MS. Figure 4 shows the ²³⁸U transient signal (in counts per second) for two U₃O₈ materials. Figure 4A shows the transient signal for a particle that was stored in ambient conditions for over a year. The transient suggests this particle dissolved more readily in the extraction solvent compared to the transient shown in 4B, which was recently received as a suspension of particles in ethanol from Forschungszentrum Julich, possibly due to structural degradation from exposure to oxygen in the air. The particles from Forschungszentrum Julich were made from NBLPO CRM 129, and therefore have a certified reference material. These particles were loaded onto a swipe by depositing 2 µL of the suspension, which contained approximately 40 particles.



A.



B.

Figure 4: Transient signal from extraction of U_3O_8 particles stored at length in ambient conditions (A) or newly received as a suspension in ethanol (B).

The transient signal was integrated and used to find major and minor uranium isotope ratios. A mass bias correction was applied based on extractions of spots loaded with a uranium sample with known isotope ratios. The mass bias spots were extracted between every three particle extractions. Figure 5 shows the measured $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ for solid uranium particulates of different compounds, UAC, UO_2F_2 , and UN as a ratio to the reference values for those materials from the TIMS analysis, or, in the case of the U_3O_8 particles, as a ratio of the measured to the certified values. Particle sizes ranged from 1 to 30 μm in diameter. The U_3O_8 particles had a measured $^{235}\text{U}/^{238}\text{U}$ ratio of 0.00726 ± 0.00004 , and a $^{234}\text{U}/^{238}\text{U}$ ratio of 0.000058 ± 0.00003 . The certified values for these particles were 0.0072614 ± 0.0000039 and 0.000053 ± 0.00000039 . The % relative difference between the measured and certified value for these particles was -0.043% and 8.7% for the $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$, respectively.

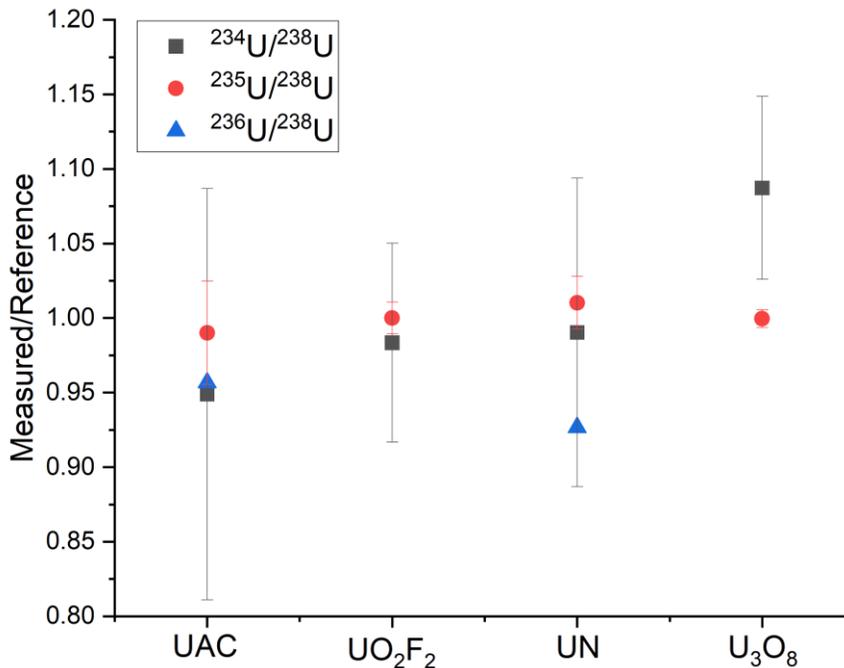


Figure 5: Isotope ratio measurements for different uranium compounds (with $\pm 2\sigma$ uncertainty)

Particle masses were calculated based on an estimation of their surface area taken from SEM images. The calculated masses of extracted particles in this study ranged from 2 ng to 200 ng, and isotope ratio measurements were consistent over all masses. Based on these estimated masses, the detection limit estimated for this method is ~ 50 pg for ^{238}U .

Triple quadrupole ICP-MS

The reaction cell of a ICP-TQ-MS was used to measure Pu isotope ratios in the presence of high amounts of uranium without a column separation prior to analysis, a technique that is

increasingly being studied for Pu measurements in the presence of U[16-21]. Generally, Pu must be separated from U to get accurate measurements at m/z 239 due to peak tailing and hydride formation from the ^{238}U isotope. This is ordinarily accomplished by chromatographic separations, which are time consuming and require a fully dissolved sample and a valence adjustment. In-line chromatography is difficult for Pu because Pu in an HNO_3 matrix is present in many different oxidation states and requires complete reduced to Pu (IV) for a total separation. The method presented here bypasses the valence adjustment and separation by reacting U ions with CO_2 gas in the ICP-TQ-MS reaction cell to form UO^+ . U^+ has a much greater reaction efficiency for oxidizing agents such as CO_2 compared to Pu^+ (0.29 and 0.003, respectively). With a CO_2 flow rate of 0.3 mL min^{-1} it was found that 99.9% of the U^+ was converted to UO^+ , while only 48% of the Pu^+ was converted. This allows for the measurement of Pu isotope ratios as the atomic ion, and the U isotope ratios were measured as molecular ions (UO^+). The measured isotope ratios are shown in Figure 6 for each U concentration (Pu concentration remained constant). The Pu isotope ratios were determined with good accuracy and precision even in the presence of U with $> 100,000\times$ higher abundance.

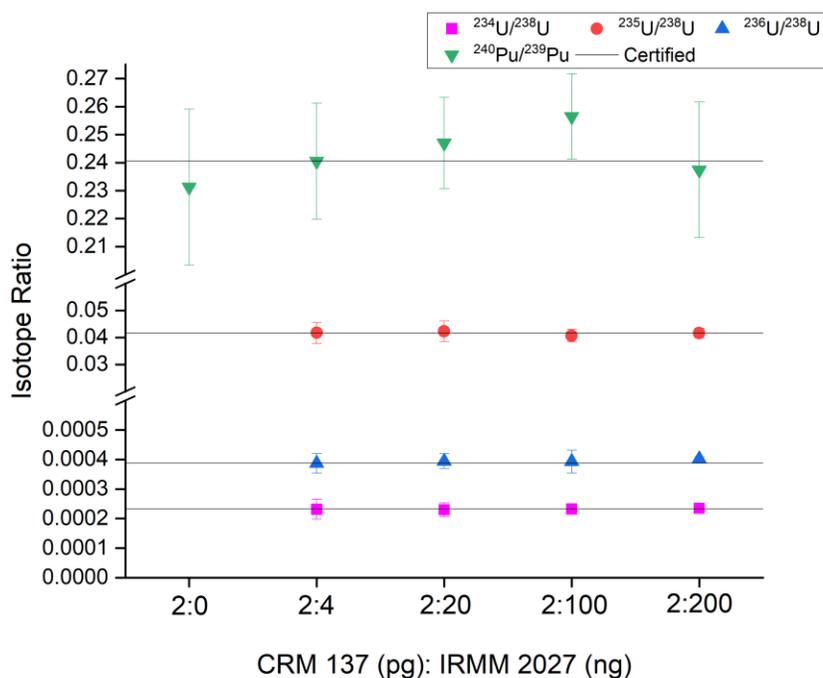


Figure 6: U and Pu isotope ratios with ICP-TQ-MS ($\pm 2\sigma$ uncertainty)

Conclusions

A microextraction-ICP-TQ-MS method was shown to extract a variety of solid U particulates, including U_3O_8 , a U compound that is important in the fuel cycle, and can be used to measure U and Pu isotope ratios within 10% uncertainty. This method bypasses time-consuming ashing, digestion, and separations currently required for bulk analysis of environmental swipes. The total time required for a single extraction is less than one minute. Major and minor U isotope ratios were successfully measured on a variety of different solid uranium compounds with this method. In particular, the work

presented above demonstrates the first extraction of a uranium oxide CRM with a certified isotope ratio. The microextraction-ICP-MS successfully measured the $^{235}\text{U}/^{238}\text{U}$ ratio of NBLPO 129a to be 0.00726 ± 0.00004 , which has a relative difference from the certified value of -0.04%. The reaction cell U mass-shift allowed for accurate Pu isotope ratio measurements when in the presence of $100,000 \times$ more concentrated U. The $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratios, even with very high amounts of U present, were within 10% of the certified isotope ratio value, which is comparable to solution aspiration ICP-TQ-MS results. The isotope ratio measurements could be further improved by connecting the plate reader to a multiple-collector instrument for simultaneous monitoring of all U and Pu isotopes. The method has shown capable of measuring particles with a mass of 2 ng U. The detection limits were determined to be 50 pg U. This method does not have the spatial resolution to fully replace particle specific analysis methods (the area sampled in a single extraction is $\sim 8 \text{ mm}^2$) but the method has shown sensitivity, accuracy, and precision that could make it a valuable technique for environmental sample analysis.

Acknowledgements

This work was supported by the Department of Energy's National Nuclear Security Administration under contract DE-AC05-000R22725 with UT-Battelle, LLC. Oak Ridge National Laboratory is managed by UT-Battelle for the Department of Energy under contract DE-AC-05-000R22725. The authors would like to acknowledge and thank the U.S. National Nuclear Security Administration (NNSA) Office of Defense Nuclear Nonproliferation Research and Development for funding and supporting this research. The authors would like to acknowledge Tyler Spano (ORNL) for providing and characterizing uranium particulate material. The authors would also like to acknowledge Philip Kegler and Stefan Neumeier from the Forschungszentrum Julich for providing the U_3O_8 particle reference material.

References

- [1] S.C. Metzger, B.W. Ticknor, K.T. Rogers, D.A. Bostick, E.H. McBay, C.R. Hexel, Automated Separation of Uranium and Plutonium from Environmental Swipe Samples for Multiple Collector Inductively Coupled Plasma Mass Spectrometry, *Anal Chem*, 90 (2018) 9441-9448.
- [2] D.L. Donahue, Strengthening IAEA safeguards through environmental sampling and analysis, *J Alloys Compd*, 271-273 (1998) 11-18.
- [3] S.F. Boulyga, J.A. Cunningham, Z. Macsik, J. Hiess, Maxim V. Peńkin, S.J. Walsh, Development, validation and verification of an ICP-MS procedure for a multi-element analysis of uranium ore concentrates, *Journal of Analytical Atomic Spectrometry*, 32 (2017) 2226-2237.
- [4] K.T. Esaka, F. Esaka, J. Inagawa, K. Iguchi, C.-G. Lee, S. Sakurai, K. Watanabe, S. Usuda, Application of Fission Track Technique for the Analysis of Individual Particles Containing Uranium in Safeguard Swipe Samples, *Japanese Journal of Applied Physics*, 43 (2004).
- [5] C.-G. Lee, D. Suzuki, F. Esaka, M. Magara, N. Shinohara, S. Usuda, Selective Detection of Particles Containing Highly Enriched Uranium for Nuclear Safeguards Environmental Samples, *Journal of Nuclear Science and Technology*, 46 (2009) 809-813.
- [6] C.G. Lee, K. Iguchi, J. Inagawa, D. Suzuki, F. Esaka, M. Magara, S. Sakurai, K. Watanabe, S. Usuda, Development in fission track-thermal ionization mass spectrometry for particle analysis of safeguards environmental samples, *J Radioanal Nucl Chem*, 272 (2007) 299-302.

- [7] G. Tamborini, M. Betti, V. Forcina, T. Hiernaut, B. Giovannone, L. Koch, Application of secondary ion mass spectrometry to the identification of single particles of uranium and their isotopic measurement, *spectrochim Acta Part B*, 53 (1998) 1289-1302.
- [8] P. Hedberg, P. Peres, J. Cliff, F. Rabemananjara, S. Littmann, H. Thiele, C. Vincent, N. Albert, Improved particle location and isotopic screening measurements of sub-micron sized particles by secondary ion mass spectrometry, *J. Anal. At. Spectrom.*, 26 (2011) 406-413.
- [9] P. Peres, P.M.L. Hedberg, S. Walton, N. Montgomery, J.B. Cliff, F. Rabemananjara, M. Schuhmacher, Nuclear safeguards applications using LG-SIMS with automated screening capabilities, *Surface and Interface Analysis*, 45 (2013) 561-565.
- [10] F. Esaka, D. Suzuki, T. Yomogida, M. Magara, Application of automated particle screening for effective analysis of individual uranium particles by thermal ionization mass spectrometry, *Anal. Methods*, 8 (2016) 1543-1548.
- [11] H. Luftmann, A simple device for the extraction of TLC spots: direct coupling with an electrospray mass spectrometer, *Anal. Bioanal. Chem.*, 378 (2004) 964-968.
- [12] V.C. Bradley, T.L. Spano, C.V. Thompson, B.W. Ticknor, D.R. Dunlap, S.C. Metzger, C.R. Hexel, B.T. Manard, Analysis of solid uranium particulates on cotton swipes with an automated microextraction-ICP-MS system, *Anal. Methods*, 14 (2022) 4466-4473.
- [13] B.T. Manard, S.C. Metzger, K.T. Rogers, B.W. Ticknor, N.A. Zirakparvar, B.D. Roach, D.A. Bostick, C.R. Hexel, Direct analysis of cotton swipes for plutonium isotope determination by microextraction-ICP-MS, *J. Anal. At. Spectrom.*, 36 (2021) 2202-2209.
- [14] B.T. Manard, K.T. Rogers, B.W. Ticknor, S.C. Metzger, N.A. Zirakparvar, B.D. Roach, D.A. Bostick, C.R. Hexel, Direct Uranium Isotopic Analysis of Swipe Surfaces by Microextraction-ICP-MS, *Anal. Chem.*, 93 (2021) 11133-11139.
- [15] Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer, in: A. International (Ed.) ASTM C1672-17, 2017.
- [16] W. Bu, M. Gu, X. Ding, Y. Ni, X. Shao, X. Liu, C. Yang, S. Hu, Exploring the ability of triple quadrupole inductively coupled plasma mass spectrometry for the determination of Pu isotopes in environmental samples, *J. Anal. At. Spectrom.*, 36 (2021) 2330-2337.
- [17] S. Diez-Fernández, H. Isnard, A. Nonell, C. Bresson, F. Chartier, Radionuclide analysis using collision–reaction cell ICP-MS technology: a review, *J. Anal. At. Spectrom.*, 35 (2020) 2793-2819.
- [18] S. Diez-Fernandez, H. Jaegler, C. Bresson, F. Chartier, O. Evrard, A. Hubert, A. Nonell, F. Pointurier, H. Isnard, A new method for determining (236)U/(238)U isotope ratios in environmental samples by means OF ICP-MS/MS, *Talanta*, 206 (2020) 120221.
- [19] X. Hou, W. Zhang, Y. Wang, Determination of Femtogram-Level Plutonium Isotopes in Environmental and Forensic Samples with High-Level Uranium Using Chemical Separation and ICP-MS/MS Measurement, *Anal. Chem.*, 91 (2019) 11553-11561.
- [20] M. Matsueda, T. Kawakami, K. Koarai, M. Terashima, K. Fujiwara, K. Iijima, M. Furukawa, Y. Takagai, Using CO₂ Reactions to Achieve Mass-spectrometric Discrimination in Simultaneous Plutonium-isotope Speciation with Inductively Coupled Plasma–Tandem Mass Spectrometry, *Chem. Lett.*, 51 (2022) 678-682.
- [21] T. Suzuki, T. Yamamura, C. Abe, K. Konashi, Y. Shikamori, Actinide molecular ion formation in collision/reaction cell of triple quadrupole ICP-MS/MS and its application to quantitative actinide analysis, *J. Radioanal. Nucl. Chem.*, 318 (2018) 221-225.