analytical chemistry

Article

Cite This: *Anal. Chem.* XXXX, XXX, XXX−XXX

pubs.acs.org/ac

Automated Separation of Uranium and Plutonium from Environmental Swipe Samples for Multiple Collector Inductively Coupled Plasma Mass Spectrometry

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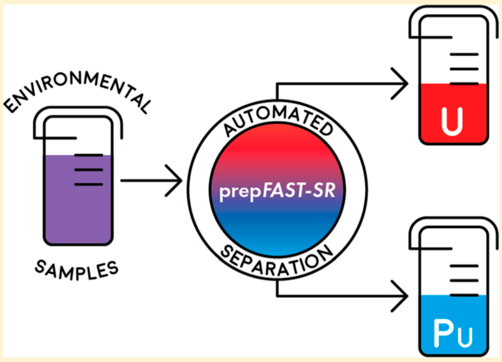
Supporting Information

ABSTRACT: A fully automated method for the separation of low-concentration uranium from plutonium in environmental swipe samples has been developed. The offline chromatography system features renewable 1 mL Eichrom TEVA and UTEVA column generation from bulk resin slurry. Discrete fractions of the separated actinides are delivered into user defined vials for future analysis. Clean room background levels were achieved outside of a cleanroom environment with this method. Purification of uranium and plutonium from various sample matrixes and at various concentrations was successful. Major and minor isotope ratios for both elements were measured via multiple collector inductively coupled plasma mass spectrometry and were in good agreement with certified reference values. Validation of the separation method was conducted on archived environmental samples and agreed with values previously reported using standard column chemistry.



The International Atomic Energy Agency (IAEA) collects environmental samples during inspections of nuclear facilities that are subject to safeguard agreements. These samples are used to verify compliance with declared nuclear activity or detect the presence of undeclared activities.[1] Environmental samples often take the form of swipe samples, where inspectors use clean cotton wipes to swipe surfaces and collect traces of material that may be present. The samples are analyzed by the IAEA's Network of Analytical Laboratories (NWAL) for detection of trace actinide elements by various mass spectrometry techniques. Since its introduction in 1996, environmental sampling has become one of the primary techniques used by the IAEA to detect undeclared material or activities.[2]

Analytical laboratories often study environmental swipes through bulk analysis, in which the entire swipe matrix is digested. Once the digestate is purified, high precision mass spectrometry is used to measure the isotopic composition and content of actinide elements, particularly U and Pu, collected on the swipe. The isotopic composition of a sample may provide information about the source of the material. For example, a perturbation in the $^{235}U/^{238}U$ ratio may indicate U enrichment activities, while the presence of ^{236}U and/or Pu suggests the reprocessing of irradiated material. Typical characteristics of collected field samples are 1 ng to 10 mg of U/swipe and <1 ng of Pu/swipe.[3] The measurement quality goals set forth by the IAEA for the bulk analysis program are $\leq 2\%$ relative expanded uncertainty for the $^{235}U/^{238}U$ and $\leq 20\%$ for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ at >10 ng of U and $\leq 20\%$ for all Pu isotope ratios at >1 pg at a 95% confidence level.[3]

The IAEA depends on the NWAL to support the analysis of environmental samples, with timeliness, efficient sample processing, and accuracy being important considerations for the NWAL laboratories. Due to the sensitivity of the technique for low concentrations of U and Pu, multiple collector mass spectrometry is often employed for this analysis.[4−6] However, these high precision instruments require purified U and Pu fractions, free from interferences such as organics and heavy metals, to ensure the quality of the measurements. Current purification protocols include ashing and dissolving individual swipe samples and then manually loading gravity-driven separation columns—a process that is both time-consuming and thus costly. Additionally, necessary manual manipulation of the sample increases the potential for contamination. From start to finish, the manual purification chemistry takes between 2 and 4 weeks and represents the longest single step in the analysis process. When possible, the separation procedures are also carried out in certified International Organization for Standardization (ISO) cleanroom laboratories with heavily filtered air to reduce airborne contamination.

Separation schemes for U and Pu have been widely studied[7,8] and implemented over the decades since the

Received: May 10, 2018
Accepted: June 29, 2018
Published: June 29, 2018

DOI: 10.1021/acs.analchem.8b02095
Anal. Chem. XXXX, XXX, XXX−XXX

Manhattan Project. Chromatographic techniques including solid phase extraction (SPE)[9−11] and ion exchange (IX) chromatography[12,13] resins have been developed and are used in a wide range of applications. Schemes for the separation of low concentration U and Pu (ng−pg and pg−fg concentrations, respectively) in environmental samples are typically multistep and may be combined with other techniques to ensure adequate purification. The separation chemistry of U and Pu using Eichrom TEVA and UTEVA resins is well-known,[10,11] and Eichrom's Web site details several methodologies.[14] Both SPE and IX chromatography require continuous reagent flow through the columns to remove contaminants and achieve chemical separation of Pu from U. As such, both protocols require considerable hands-on operator time to prepare purified actinide fractions prior to analysis by ICP-MS.

Mechanical systems are being explored to automate the chemistry to reduce personnel involvement. Some of these use fluid-handling techniques such as flow injection (FI), sequential injection (SI), and bead injection (BI) to control solution flow.[15−18] FI primarily automates very simple separation schemes and led to the development of SI, which allows for the control of additional functions such as renewable column generation.[15,19] As a result of these improvements, SI is able to separate more complex samples.[15,17,20] Many FI and SI systems have been described for small scale separation of trace metals and specific radiochemical analysis.[20−23] These custom built, automated systems use hand-packed or prepacked disposable columns to achieve separations.[17,18,21,22] Further advancements in technology led to BI, which scales up FI and SI using larger columns on even more complex separation schemes.[24,25] Unfortunately, these automated platforms are not yet commercially available.

The prep*FAST*-MC from Elemental Scientific Incorporated (ESI) in Omaha, NE, is a commercial-off-the-shelf (COTS) option for automated separations. The system has been used to separate Sr and Ca from basalt and bone ash and Cu from biological material using commercially available columns.[16,26] High throughput was achieved, with 60 samples for Cu isotope analysis conducted on a single ion exchange column.[16] It was suggested that up to 200 samples can be extracted on a single column for Ca and Sr separations.[26] While the reuse of resin material for separations is achievable, IAEA requires the use of fresh resin for each sample. To better meet these demands, ESI has developed the prep*FAST*-SR, capable of renewable column generation.[27] The new prep*FAST*-SR is similar in overall design to the prep*FAST*-MC and includes additional valves for resin control. Recent work has described the fully automated system which reproducibly generates columns with fresh resin for each sample.[27] The single use resin is packed and unpacked mechanically by the prep*FAST*-SR and is ideal for low concentration samples where cross-contamination is a concern. The methods developed here could be applied to the prep*FAST*-MC with more manual interactions.

Here, the use of the new prep*FAST*-SR using TEVA and UTEVA resin is examined to separate U and Pu from environmental swipe samples. After calibrating the elution profiles for the system, simple samples containing low concentrations of U and Pu Certified Reference Material (CRM) standards were separated in 3 M HNO_3 as an initial proof of concept study. The loading capacity of the columns was explored with higher concentration samples. More complex sample matrixes (i.e., cotton swipes, metal contaminants) were used in conjunction with CRMs to evaluate the effect of possible interferences. Finally, archived field samples containing varying concentrations and isotope ratios of U and Pu were successfully separated. The measured isotope ratios were in good agreement with reported values for the major and minor isotope ratios.

■ EXPERIMENTAL SECTION

Reagents and Standards. Optima HNO_3, H_2O_2 (30%), HCl, and HF were purchased from Fisher Scientific. $NaNO_2$ (ACS, 95% min) and $FeSO_4$ Puratronic 99.999% (metals basis) were purchased from Alfa Aesar. Single element standards of Tl, Hg, Ru, Au, Pt, Os, Zr, Bi, Mo, W, Pb, and Th were purchased from High Purity Standards. These reagents were used without further purification. CRMs for U and Pu were purchased from the Joint Research Center of the European Commission [IRMM-183 (U), IRMM-57 (U), IRMM 3100A (U), IRMM-82 (Pu)] or the New Brunswick Laboratory Program Office [NBL-137 (Pu), NBL U010 (U)]. An internal Oak Ridge National Laboratory (ORNL) solution of high-purity ^{244}Pu was used as an isotope dilution spike. Its concentration was determined relative to National Institute of Standards and Technology (NIST) Standard Reference Material 4330C. ASTM type I (18.2 MΩ-cm) water was generated with a ThermoScientific Barnstead GenPure Pro water purification system and was used to prepare all solutions. All labware was acid leached in separate baths of 6 M HCl, 8 M HNO_3, and type I water prior to use.

Instrumentation. The prep*FAST*-SR software and hardware have been previously described.[27−29] While similar to the prep*FAST*-MC in overall design, the prep*FAST*-SR utilizes additional valves and tubing to control resin and gas flow for the automated packing and unpacking of the columns. The prep*FAST*-SR is a low-pressure chromatography system that uses several multiposition valves and a S400V syringe pump to control sample and reagent flow. The fully automated chromatography system operates at low pressures (<100 psi) to separate elements of interest (U and Pu) from the sample matrix and each other. The system generates renewable TEVA and UTEVA columns for single use. The two 1 mL perfluoroalkoxy (PFA) columns are fitted with frits at the exit to allow for reproducible column loading.[27] An overview of the system schematics is shown in Figure S-1.

A high-resolution inductivity coupled plasma mass spectrometer (HR-ICP-MS), the ThermoScientific Element II (Bremen, Germany), was used to characterize the U and Pu elution profiles and to determine trace elements within the purified fractions. The separated aliquots were introduced using a 50 μL/min integrated PFA nebulizer into an ESI Apex Micro. Isotopic ratios were measured with a ThermoScientific Neptune *Plus* (Bremen, Germany) multiple collector inductivity coupled plasma mass spectrometer (MC-ICP-MS) fitted with the Jet interface (NiJet sample, NiX skimmer) for improved pumping capacity. The instrument was equipped with the nuclear detector package and contains an additional L5 Faraday cup, two additional secondary electron multipliers, and two compact discrete dynodes (CDD). A 10^{13} ohm amplifier was installed on the L5 Faraday cup to measure 235-mass with a signal of 0.3 mV or greater. Minor isotope masses and signals below 0.3 mV were measured with a combination of secondary electron multipliers and CDDs. Plutonium isotopes were analyzed using secondary electron multipliers and CCDs only. The detectors were cross-calibrated using isotope pairs with IRMM 3100A prior to each analytical session. Initial column calibration measurement was completed as all Faraday cups with 10^{13} installed on the L1 and H1 cups. Solutions were introduced using a 50 μL/min integrated PFA nebulizer into an ESI Apex Ω desolvator. Isotopic data was blank subtracted, hydride subtracted, and corrected for mass fractionation using NBL U010 reference material.

All results are reported as average ± expanded uncertainty where the coverage factor is $k = 2$ unless otherwise noted. Expanded uncertainties are calculated using methods compliant with the Guide to the Expression of Uncertainty in Measurement unless otherwise stated.[30]

Bulk Sorbent Preparation. Bulk TEVA-resin and UTEVA-resin (50−100 μm particle size) were purchased from Eichrom Industries, LLC. Conditioning of the bulk resin material was adapted from standard Eichrom procedures.[31,32] Slurry preparation was performed according to previously reported methods with 3 M HNO_3 in a 1:5 resin:acid v/v ratio.[27]

General Procedure for Sample Preparation. All samples and reagents were prepared in ISO Class 5 or ISO Class 6 cleanrooms in leached PFA vials. Samples and reagents were then transferred to a standard laboratory and introduced into the prep*FAST*-SR for separation of actinides. Resulting purified actinide aliquots were then submitted for mass spectrometric analysis. Sample solutions for automated column separation were prepared in 3 M HNO_3 contained in leached 15 mL PFA vials (Savillex). Synthetic samples tested included reagent blanks, actinide CRMs, ashed 4 × 4 in.^{2} cotton swipes (previously characterized for U content and isotopics by Pacific Northwest National Laboratory, Texwipe 304, lot: L308AD), and solutions contaminated with metals that may result in molecular interferences in the mass spectrometer. Actinide content was quantified by isotope dilution mass spectroscopy (IDMS) using a gravimetrically prepared in-house ^{244}Pu spike (~2 pg) and/or IRMM-57 (^{233}U, ~2 ng). CRM samples were created from a master stock of IRMM-183 (depleted uranium) and/or NBL-137 (~80% ^{239}Pu), with final concentrations of 1.5−165 ng/g-solution and 0.05−151 pg/g-solution for U and Pu in synthetic samples, respectively.

Simulated swipe samples were prepared by ashing a cotton swipe in a Thermcraft tube furnace equipped with a Eurotherm 2404 temperature controller at 600 °C for two 12 h cycles. The resulting ash residue was digested in 3.6 M HNO_3−2.5 M HF (11 mL) for 48 h at 125 °C followed by 30% H_2O_2 (1 mL) and 4 M HNO_3 (2 mL) for 48 h at 50 °C with dry down steps between reagent additions. Simulated swipe samples contained swipe matrix and U and Pu CRMs in varying concentrations in 3 M HNO_3. Metal contaminated samples were made with a mixed stock solution of single element standards of Tl, Hg, Ru, Au, Pt, Os, Zr, Bi, Mo, W, Pb, and Th in 3 M HNO_3. Once synthetic swipe samples were analyzed, four archived environmental swipe samples were used as a final validation of U and Pu determination by the prep*FAST*-SR system.

The valence state of Pu in all samples and blanks was adjusted to Pu(IV) by adding freshly made $FeSO_4$ (0.2 mL, 1.7 M) and $NaNO_2$ (0.4 mL, 3 M) prior to column separation. After separation, aliquots were dried down for matrix reduction and treated with 8 M HNO_3 and H_2O_2 (30%) to destroy column organics. Final isolated fractions were reconstituted in 2% HNO_3, and isotope ratios were measured by MC-ICP-MS.

Automated Methods. The separations chemistry method is outlined in Table 1 and was adapted from Eichrom analytical procedures.[14,31,32] The columns were packed with fresh resin as previously described.[27] Each sample was then loaded in a user defined volume and flowed sequentially through the combined columns (TEVA, column 1 (C1) to UTEVA, column 2 (C2), Figure S-1). The combined columns were then washed with 3 M HNO_3 to rinse any sample residue through. A change in valve positioning separated the flow between the two columns, and each column was washed with additional 3 M HNO_3. C1 was rinsed with HCl to convert the resin to the chloride form. The U fraction was eluted from C2, followed by the Pu fraction from C1. After elution, the columns were mechanically unpacked and readied for the next sample.[27] The full separation method code and subsequent submethods are provided in the Supporting Information (Tables S-1 and S-2).

Table 1. Method Description for the Separation of U/Pu with the ESI System with Indications for Flow of Reagent through C1 and C2 Being Sequential (Seq), Separated (Sep), or No Flow (NA)

step	C1	C2	description: reagent (flow rate - mL/min)
1	Sep	Sep	pack TEVA and UTEVA resin columns
2	Seq	Seq	load sample: 3 mL of sample (1)
3	Seq	Seq	wash columns: 10 mL of 3 M HNO_3 (2)
4a	Sep	NA	wash column: 10 mL of 3 M HNO_3 (2)
4b	NA	Sep	wash column: 10 mL of 3 M HNO_3 (2)
5	Sep	NA	convert to chloride: 12 mL of 9 M HCl (2)
6	NA	Sep	elute U: 4 mL of 0.02 M HNO_3−0.005 M HF (1)
7	Sep	NA	elute Pu: 8 mL of 0.1 M HCl−0.06 M HF (1)
8	NA	Sep	unpack UTEVA resin sorbent
9	Sep	NA	unpack TEVA resin sorbent

A system-cleaning method was developed to be used at the discretion of the user to maintain system cleanliness. The method is designed to leach parts and tubing within the prep*FAST*-SR with a solution of 8 M HNO_3−0.1 M HF. The cleaning method was run as a separate method code and was not associated with the sample separation method code. The full method is detailed in the Supporting Information (Tables S-3 and S-4).

Safety Considerations. The radioactive materials used in this work present radiological risks and should be handled accordingly.

■ RESULTS AND DISCUSSION

Automated Separation Method Development. The initial automated method was based on the manual separation of U and Pu using TEVA/UTEVA chemistry conducted at ORNL as part of the IAEA NWAL Bulk Analysis of Environmental Samples program. The use of both TEVA and UTEVA columns provides specificity to separate U and Pu from the bulk matrix. Initially, calibration experiments were done to determine the retention and elution volumes of Pu and U on the prep*FAST*-SR. The total amount of U and Pu recovered from the system and the major U (^{235}U/^{238}U) and Pu (^{240}Pu/^{239}Pu) isotope ratios were examined. As naturally occurring U is found throughout the environment, it was important to select a CRM with isotope ratios significantly different from natural abundance to better determine retention and elution. For this reason, IRMM 183, with a depleted ^{235}U/^{238}U isotope ratio, was chosen. This allows for the differentiation between background U contamination (natural isotopic abundance) and incomplete sample washout or

DOI: 10.1021/acs.analchem.8b02095
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carryover from one sample to the next on the system (depleted isotopic abundance).

Two separate CRM solutions of Pu (2 pg/g, NBL-137) or U (5 ng/g, IRMM-183) were loaded on the columns as described in Table 1. Elution profiles were constructed for the individual columns based on HR-ICP-MS results for the percentage of the total signal found in each 1 mL fraction. The percentage of total recovered signal for Pu and U for two replicates is shown in Figure S-2A and B, respectively. The first calibration of C1 for Pu recovery yielded a 4 mL elution volume with a recovery of 58%. The percent recovery was based on the total recovered signal when compared to a signal for an unprocessed sample. The second Pu run demonstrated a larger elution profile (7 mL) with improved recovery of 85%. The $^{240}Pu/^{239}Pu$ ratio in each fraction was measured to verify the Pu collected was NBL-137. No detectable Pu was observed in other 1 mL fractions. The U was eluted in smaller volumes with near quantitative (>99%) recovery in 4 mL for both replicates. The $^{235}U/^{238}U$ ratio was monitored for the U calibration, and the depleted CRM ratio was observed only during U elution. Results showed natural isotope ratios in all other fractions, suggesting no premature washout or perturbation of isotope ratios in sequential samples occurred.

After the single actinide solutions were used to determine the matrix elution volumes, a mixed CRM solution containing both U and Pu was used to validate the separation of the two elements. The complete calibration elution profile was created by collecting 1 mL aliquots and monitoring for both Pu and U by HR-ICP-MS. Figure 1 shows the combined elution profile, with U eluting first in 3 mL and Pu eluting in 7 mL with 10 mL of separation between the elements. The profiles established final elution volumes for U of 4 mL and Pu of 8 mL. This includes an additional 1 mL at the end of each peak to ensure that all material was collected. The lack of detectable U in the Pu fraction also indicates that adequate washing took place after sample loading. Poor washing would leave U on C1 to elute with the Pu fraction. The absence of either U or Pu in the initial 30 mL shows no loss occurred after sample loading and that the column unpacking and washing methods removed all traces of U and Pu from the column bodies, preventing cross-contamination between samples.

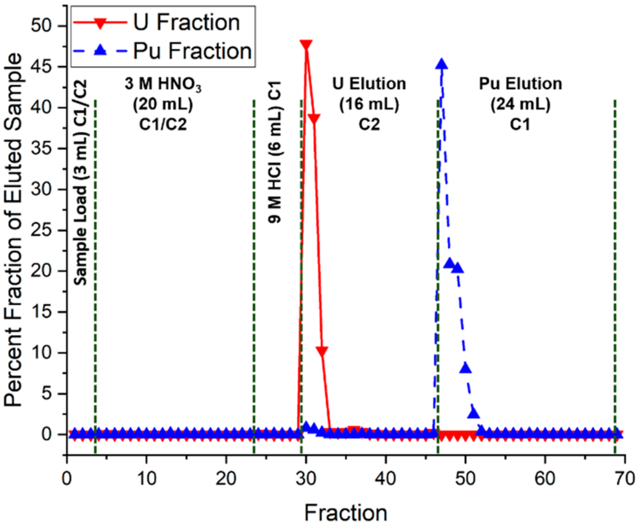

Figure 1. Combined column calibration elution profile for the automated separation of U (red downward facing triangles, solid line) and Pu (blue triangles, dashed line) based on the separation method outlined in Table 1. The percent fraction is calculated by dividing the instrument response rate (counts) in each fraction by the sum of the total counts in all of the fractions.

Blank Characterization. Process blanks were taken through all steps of the analytical procedure and were analyzed as samples but had no U or Pu added. The purpose of the process blank study was to determine the amount of U or Pu that is inherent to the automated separation method using the prep*FAST*-SR. Negligible Pu background is expected due to the lack of Pu present in the environment.[6,33,34] However, natural U is ubiquitous throughout the environment, even in commonly used labware (e.g., plastics, Teflon, glass, etc.) and ultrapure reagents. Measurable amounts of U will generally be observed in all blanks, even process blanks prepared in cleanrooms.[5,33−35] While steps were taken to reduce the amount of natural U present (i.e., acid-leaching new sample vials, use of ultrapure reagents), some U background remained.

The amount of U and Pu in the process blanks is measured by the addition of enriched isotope spike standards, a method commonly referred to as IDMS.[36] With the addition of a well-characterized IDMS spike, the amount of U and Pu present in a sample can be quantitatively determined by eq 1 following appropriate mass spectrometry analysis.[37] The following notation is used: C = analyte concentration, W = weight, A = atomic weight, a = atomic abundance, R = ratio; the subscripts are defined as s = unspiked sample, t = tracer (spike), m = mixture of spike and sample, i = major isotope in the sample, k = major isotope in the spike; isotopic ratio (R_x) = a_{xi}/a_{xk}.

$$C = \frac{W_t}{W_s}\frac{A_s}{A_t}\frac{a_{kt}}{a_{ks}}\frac{(R_t - R_m)}{(R_m - R_s)} \tag{1}$$

A series of initial process blanks were separated over 3 days, by two different operators, with nine replicate samples each day. The separation of the samples on the prep*FAST*-SR occurred in a standard laboratory without cleanroom infrastructure. No co-elution of the two analytes was observed, as expected on the basis of the calibration profile.

The IDMS results for the automated process blanks and manual chemistry process blanks prepared in cleanroom laboratories over a 4 year period are compared in Figure 2. The manual process blanks were generated in parallel with samples with various actinide concentrations and isotopic compositions. The automated U process blanks had an average ±2σ amount of 0.01503 ± 0.00042 ng of U (n = 26). This compares to an average ±2σ U process blank from the manual chemistry of 0.057 ± 0.088 ng of U (n = 47). These results showed on average the process blanks for the automated chemistry were ∼75% lower than manual separations, with considerably less variation. Several factors likely contribute to the lower blank concentrations observed, including less handling of the samples, completely closed sample lines, and smaller elution volumes.

Process blank values for Pu yielded an average ±2σ of 0.00059 ± 0.00245 pg (n = 27). Figure 3 compares the Pu IDMS results for the automated process blanks and the manual chemistry process blanks. The manual chemistry blanks were processed in cleanrooms over 4 years alongside material with varying concentrations and isotopic compositions. The manual separation showed a larger deviation across separations (0.015 ± 0.055 pg, average ±2σ, n = 47). Overall, the automated

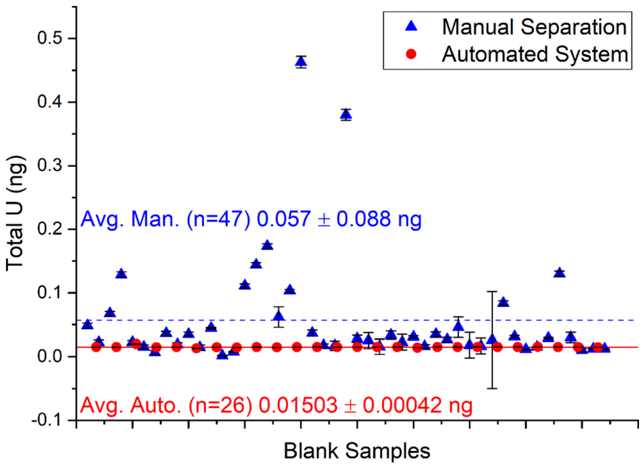

Figure 2. Total U in automated (red circles) and manual (blue triangles) process blanks with 2σ error bars and average lines as determined by IDMS.

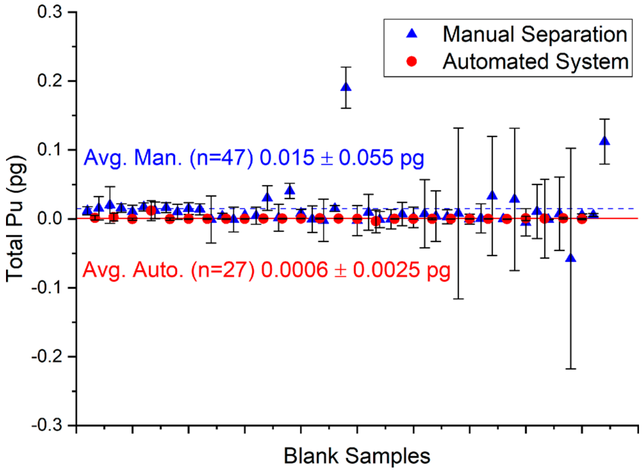

Figure 3. Total Pu in automated (red circles) and manual (blue triangles) process blanks with 2σ error bars and average lines as determined by IDMS.

system provided lower and more consistent blanks, which are primarily attributed to the automation of the separation.

Unspiked (or non-IDMS) blank samples were also separated on the automated system along with the synthetic samples. The total amount of U or Pu in unspiked blanks was estimated using eq 2, an estimated conversion factor for cps to V, and the sensitivity of the day for the MC-ICP-MS. Sensitivity of the day was calculated by aspirating 1 ng/g-solution of NBL U010 and determining the instrument response on the center Faraday cup. Estimated amounts of U and Pu present in unspiked blanks were in good agreement with process blank values (~0.022 ng of U and ~0.0005 pg of Pu). Additionally, the ^{235}U/^{238}U isotope ratio was monitored for cross-contamination. Over the course of these studies, U blanks on average exhibited a natural ^{235}U/^{238}U isotope ratio.

$$\sum \text{Isotope Counts (cps)} \times \frac{\text{Sensitivity of the Day}\left(\frac{\text{V}}{\text{ng}\cdot\text{mL}^{-1}}\right)}{6.25\times 10^{7}\left(\frac{\text{cps}}{\text{V}}\right)} \cong \text{Amount of Element}\left(\frac{\text{ng}}{\text{mL}}\right) \tag{2}$$

CRM Separations. To investigate the separation of U and Pu using the ESI prep*FAST*-SR, mixed samples containing both U (IRMM-183) and Pu (NBL-137) were processed sequentially. The automated system was configured to run blanks in between every sample to ensure proper washout and to estimate carryover between samples. The total initial amount of U or Pu present in a sample is detailed in Table 2 for each set of studies.

Table 2. Approximate Amounts of Total U (IRMM-183) and Pu (NBL-137) CRMs in a Sample for Each Set of Experiments

CRM separations	total U (ng)	total Pu (pg)
initial separations	25−30	13−15
swipe matrix	20−25	6
high concentrations	150−165	145−151
low concentrations	1.5	2.8
mid concentrations	50	4.5
Pu recovery	4	0.05
metal interferences	45	2.5

Initial separations included 10 replicate samples and 13 blanks that were collected over 3 days, with different operators performing sample preparation as well as prep*FAST*-SR setup each day. After subsequent dry-down, the ^{235}U/^{238}U isotope ratio was measured by MC-ICP-MS and was accurate to within 0.1% of the certified value (Table S-5). The measured ^{236}U/^{238}U ratio was within 0.3% of the certified ratio. Low signal intensity on the Faraday cups limited the measurement of ^{234}U during initial studies. The Pu samples were within 0.1% of the certified ratio for ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu. The average for the minor ^{241}Pu/^{239}Pu ratio was ~2.5% below the certified value, due to low raw ^{241}Pu counts during measurement. Despite low ^{241}Pu counts, the measured and certified ratios agree statistically.

The analysis of CRM samples derived from loaded swipe samples (Table 2, swipe matrix) showed that there was no matrix effect on the separation of U and Pu. The isotope ratio results for Pu were not perturbed. However, the cotton swipe itself contains an average ±2σ of 2.54 ± 0.04 ng of natural U that mixes with CRM IRMM-183 in the sample. The measured ratios were corrected by subtracting the amount of natural U in the swipe blank from the measured sample results. After correction for the natural U present in the swipe, the results were consistent with the expected certified values. The differences displayed in the results were consistent with the variability observed in the amount of natural U in the swipes.

To determine the operational range of the system, a series of samples with varying ranges of U and Pu were separated. The largest content samples had ~165 ng of U and 151 pg of Pu. Maximum sample amounts were determined by the highest radioactivity that could be handled on the bench without additional safety controls in place. Samples containing high U and low Pu, low U and high Pu, high U and high Pu, low U and low Pu, and mid U and mid Pu were separated on the automated system (Table 2, high, low, and mid concentrations). The results, even at the highest concentration of loadings, showed 99.8% removal of U from the Pu fraction and 99.9% removal of Pu from the U fraction, both of which are critical for a high-quality measurement by MC-ICP-MS and are consistent with the manual column separation.

Carryover of U was not detected in blanks processed immediately following three replicate runs of IRMM-183 at high concentrations (165 ng of U). Sample carryover of ~20 fg of NBL-137 was observed in the blank immediately following three replicate high Pu samples (151 pg of Pu/sample). Results from subsequent blanks analyzed showed no additional Pu, indicating that processing a single blank through the system is adequate to return it to baseline. Carryover was not observed at lower Pu concentrations.

On the basis of estimated U content in separated samples using eq 2, the recovery of U from C2 is near quantitative as expected.[10] Pu recovery can be less consistent, especially at low concentrations (<0.1 pg). Environmental samples for Pu are often in the sub-picogram range, so Pu recovery from the automated system is of importance. To test the recovery of the system for low Pu content in the presence of U, samples were generated that contained 50 fg of Pu and 3 ng of U. After separation, IDMS was used to determine the amount of Pu in the sample. At 50 fg of Pu, recovery is >80%, sufficient for MS analysis and consistent with manual chemistry processing. As the blank values for Pu are sufficiently low on the prep*FAST*-SR, no perturbation of the $^{240}Pu/^{239}Pu$ isotope ratio was observed at this concentration.

The measured-over-certified (M/C) values for the U isotope ratios are displayed in Figure 4 ($^{235}U/^{238}U$), S-3 ($^{234}U/^{238}U$), and S-4 ($^{236}U/^{238}U$). The U data has been corrected for bias on the MC-ICP-MS determined from 3-year average control charts. A small number of samples demonstrated a significant (>3σ) difference between the measured and certified ratio. For the swipe samples, this was attributed to the variability in the amount of natural U present in the swipe combined with the CRM. For other samples, the variability was attributed to poor recovery after sample concentration and preparation for ICP-MS analysis. Pu isotope data plotted in Figures 5 ($^{240}Pu/^{239}Pu$), S-5 ($^{241}Pu/^{239}Pu$), and S-6 ($^{242}Pu/^{239}Pu$) are calculated relative to decay corrected M/C values for NBL-137. The $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ ratios for low concentration samples displayed larger variability due to the small signal associated with the minor isotopes. Individual data points for both U and Pu are plotted; the error bars represent the expanded uncertainty (2σ) on the isotope ratio measurement.

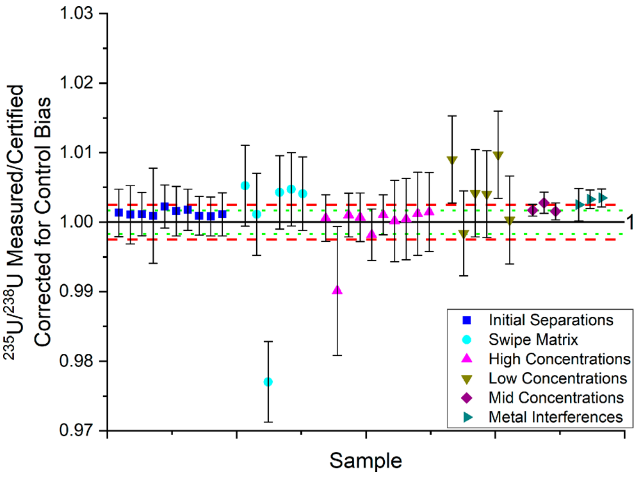

Figure 4. $^{235}U/^{238}U$ M/C isotope ratios compared to instrument controls with 2σ (green, dotted line) and 3σ (red, dashed line) error lines for IRMM-183.

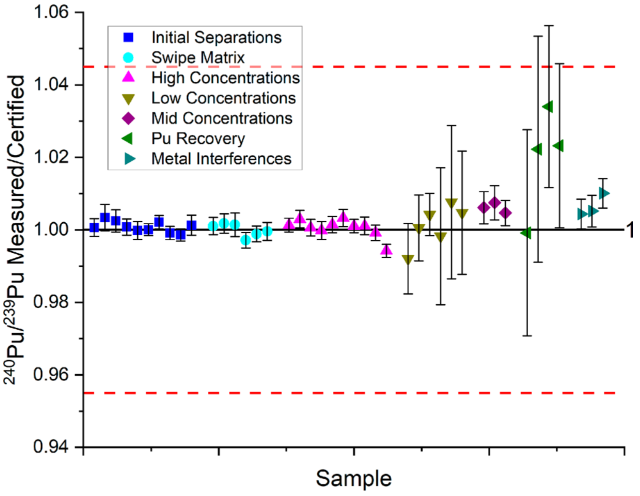

Figure 5. $^{240}Pu/^{239}Pu$ M/C isotope ratios for NBL-137 with 2σ error lines (red, dashed line) for NBL-137 controls.

Metal Interferences Separation. Significant amounts of heavy metals (i.e., Pb or W) are known to create interferences in an ICP-MS plasma, potentially affecting the measurement of U and Pu.[4,38] Additionally, W, Pb, and Th are often present in high quantities in environmental swipe samples due to the nature of the facilities where swipe sampling is conducted. To test the capacity of the prep*FAST*-SR to chemically remove interfering species from the U and Pu, a stock solution was created with 12 elements that could be spiked into samples (Table S-6). Initial separations were verified with blanks spiked with the metals. The separations showed near-quantitative removal of all elements in the U and Pu elution fractions.

Next, CRM and interference solutions were combined and processed. Fractions of the purified U and Pu aliquots were measured by HR-ICP-MS to quantify the removal of the metal contaminants. The remainder of each sample was then submitted for MC-ICP-MS analysis to ensure no perturbation of the U and Pu isotopic ratios occurred. The starting and final concentrations of the contaminant elements in the CRM spiked samples are shown in Table S-7. The results confirm that removal of all species, even at significant quantities, was accomplished by the system for both the U- and Pu-containing fractions. Furthermore, no significant (>3σ) deviations were observed in the major or minor U or Pu isotope ratios, as shown in Figures 4 and 5 (metal interferences).

Archived Environmental Samples. The final method validation was conducted using archived environmental swipe samples analyzed by ORNL from 2014 to 2016. In the present study, samples were analyzed for U and Pu isotopic ratios only, as the analyte concentrations may change over time due to evaporation or loss to vial walls. Typically, only 10−20% of the original sample is archived after processing. The four samples

Table 3. Comparison of Measured vs Reported Values for Major and Minor U Isotopic Ratios and Major Pu Isotopic Ratios with 1σ Errors (N.D. is Nondetectable) for Archived ORNL Environmental Samples

measured/reported	$^{234}U/^{238}U$	1σ	$^{235}U/^{238}U$	1σ	$^{236}U/^{238}U$	1σ	$^{240}Pu/^{239}Pu$	1σ
sample 1	99.88%	0.70%	99.92%	0.95%	99.40%	0.64%	N.D.	N.D.
sample 2	99.48%	1.54%	99.80%	0.65%	N.D.	N.D.	100.7%	2.3%
sample 3	97.04%	1.09%	98.35%	0.81%	96.28%	1.52%	N.D.	N.D.
sample 4-1	100.12%	0.69%	99.95%	0.79%	99.42%	0.94%	100.5%	2.9%
sample 4-2	99.87%	0.57%	100.11%	0.79%	99.65%	0.89%	100.9%	3.6%
sample 4-3	99.95%	0.70%	100.10%	0.79%	99.53%	0.95%	100.2%	4.7%

were chosen to test a variety of isotopic and concentration ranges for both U and Pu. In the original bulk samples, sample 1 had ~30 ng of low-enriched U and ~3 pg of Pu; sample 2 had ~8 ng of natural U and ~10 pg of Pu; sample 3 had 10 ng of low-enriched U and <2.5 fg of Pu; and sample 4 had ~3 μg of depleted U and ~50 pg of Pu. Samples 1−3 archived only ~15% of the original sample, whereas the high U and Pu content in sample 4 meant ~85% was archived. The minor Pu isotope ratios were reported with expanded uncertainty values (k = 2) larger than the measured ratio, indicating the values were not statistically significant and thus they were not used for the validation study.

Table 3 shows the measured over reported values for U and Pu isotopic ratios for archived ORNL environmental samples. MC-ICP-MS results for U isotopics in sample 1 showed very good agreement with the previously reported values. Because of low count rates, the analyzed Pu isotopic results were significantly different than the reported values. This is likely due to the affinity of Pu for PFA vial walls—known to decrease the concentration of Pu solutions over time—and the age of the archived aliquot. To ensure all Pu was in solution in the remaining samples, HF was added to give a final concentration of ~50 mM HF. The samples were heated overnight to help leach the Pu from the vial walls and then dried down to remove the HF from the sample before resuspension in 3 M HNO_3 prior to separation. The major U and Pu isotopic ratios for sample 2 are consistent with previously reported values. The $^{234}U/^{238}U$ isotopic ratio matched the reported value, but the ^{236}U isotope had too few counts to provide an accurate result. Sample 3 had a very low count rate for Pu, as expected on the basis of the sample concentration. The measured $^{235}U/^{238}U$ and $^{234}U/^{238}U$ isotope ratios were within two standard deviations of the reported results, and the measured $^{236}U/^{238}U$ ratio was within three standard deviations of the reported value. Additionally, the measured isotopic quantities were well within IAEA NWAL data quality limits.[3] The high U and Pu concentrations in sample 4 allowed for the separation and analysis to be carried out in triplicate on different days. Table 3 shows isotopic results from MC-ICP-MS analysis of the separated U and Pu fractions, demonstrating excellent agreement with the reported values. The major and minor U isotope ratios show no significant difference from the reported values. The $^{240}Pu/^{239}Pu$ isotopic ratio was also consistent with the previously reported results. The values for all three replicates of sample 4 were within 1σ of the reported values. These results confirm the ability of the system to reproducibly separate actual samples in an automatic, unattended mode of operation.

CONCLUSIONS

The work presented here demonstrates the successful automated separation of U and Pu using renewably generated TEVA and UTEVA columns. The system maintained cleanroom equivalent background concentrations outside of a cleanroom infrastructure, even after several months of use. Purification of CRM actinides was successful and demonstrated no perturbation of U or Pu isotope ratios. The system has been validated for samples with content up to 150 ng of U and 150 pg of Pu. The separation performance and the isotope ratios of purified samples, as demonstrated by analysis of CRMs, were not affected by sample matrixes. Additionally, 98% of metal impurities in U fractions and >99% in Pu fractions were removed during testing. Archived environmental samples agreed with previously reported values. The prep*FAST*-SR system is applicable for the automated separation of U and Pu from environmental samples where unattended overnight operation is beneficial. The flexibility of the prep*FAST*-SR allows for existing procedures needing single use resin to be automated without having to redesign the methods.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.8b02095.

Full automated methods with submethod breakdowns for the separation method and cleaning method; SEM discussion and images of the resin; minor measured/certified (M/C) U and Pu isotope ratios; metal interference concentrations; percent reduction of metal interferences during separation; time savings discussion (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Chris Milojevich for the SEM images and Hwan Kim and Paul Field for their support with the prep*FAST*-SR software. This work is supported by the Safeguards Technology Development Program, International Nuclear Safeguards, Office of Nonproliferation and Arms Control, at the Department of Energy's National Nuclear Security Administration under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Oak Ridge National Laboratory is managed by UT-Battelle for the Department of Energy under Contract DE-AC05-000R22725.

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