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Optimization of uranium and plutonium separations using TEVA and UTEVA cartridges for MC-ICP-MS analysis of environmental swipe samples☆

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ABSTRACT

The analysis of environmental swipe samples for ultra-trace uranium (U) and plutonium (Pu) determinations is essential in the nuclear safeguards community. While mass spectrometry techniques for U and Pu detection continually improve, established separation methods are seldom reevaluated. Currently, actinide separations within the forensics community predominantly employ either Eichrom TEVA® or UTEVA® resins. The direct optimization of U and Pu separations utilizing both resins has not been widely reported. Here, several methods were explored with goals of increasing analyte recovery, acquiring cleaner blanks, and improving the separation efficiency of ultra-trace levels of U and Pu from environmental swipe samples. The optimized separation methodology of U and Pu was examined using certified reference materials and archived environmental swipe samples.

1. Introduction

The International Atomic Energy Agency (IAEA) is responsible for verifying compliance with declared nuclear activities and detecting undeclared activities in States that participate in the Treaty on the Non-Proliferation of Nuclear Weapons (NPT) [1]. Under provisions of the NPT, the participating States are obligated to declare stocks of nuclear material, such as uranium (U) and plutonium (Pu), and allow the IAEA to independently verify those declarations through various techniques including environmental sampling and remote monitoring. While environmental sampling techniques are composed of various sample types (e.g., soil, water, biota, and vegetation), cotton swipes taken inside and outside of buildings are the most common. Since implementation of environmental sampling in 1996, swipe sampling has become one of the most heavily utilized methods by the IAEA for verifying the correctness and completeness of declared activities [1,2]. Environmental swipe samples (ESS) have many advantages (e.g., size, portability, and ease of shipment) over other sample media that have been described previously [1].

ESS can be analyzed by different techniques, including particle, bulk and neutron activation analysis through the IAEA's Network of Analytical Laboratories (NWAL). Typically, swipes contain 1.0 – 1.0×10^7 ng U and less than 1 ng Pu per swipe [3]. ESS are commonly examined through bulk analysis, in which the entire swipe is analyzed, as higher Pu detection limits are possible when compared to particle analysis [4]. Measurement quality goals for the relative expanded uncertainty associated with each requested measurement for the bulk analysis program are well defined by the IAEA [3]. To meet these data quality limits, multi-collector-inductively coupled plasma or thermal ionization mass spectrometry (MC-ICP-MS or TIMS) are often used for analysis of U and Pu because of their sensitivity and precision [5–10]. The measurement accuracy needed for this analysis requires purification of the U and Pu fractions to eliminate isobaric and/or molecular interferences (e.g., ^{238}U and ^{238}Pu, or ^{238}UH$^+$ and ^{239}Pu). After complete dissolution of the swipe, the digest is purified by various separation methods unique to each NWAL laboratory prior to analysis. This separation is traditionally achieved through gravity-driven separations with columns of various resins.

Methods for individually separating U and Pu from a complex matrix, have been studied [11,12], and a wide range of applications utilize chromatographic techniques (e.g., solid phase extraction [13–15] and

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ion exchange chromatography [16,17]). The use of Eichrom TEVA and UTEVA resin for the separation of actinides is well known [14,15,18]. While much work has been dedicated to employing these platforms for bulk removal of actinides [19,20] the optimization of the separation methods for low concentrations of U and Pu from ESS using both TEVA and UTEVA resins has not been widely reported [5]. The original work on the Eichrom resins examined the retention of many transition metals [14,15], but did not examine heavy metals (i.e., Pb or Bi) present in some ESS known to cause interferences in a mass spectrometer (e.g., $^{208}Pb^{16}O_2$).

As part of the NWAL, Oak Ridge National Laboratory (ORNL) has standard operating procedures for the separation of individual actinides (U and Pu) from ESS using 2-mL TEVA, UTEVA, and Pre-filter cartridges from Eichrom. Recent studies have suggested that smaller, 1-mL, cartridges might provide lower background levels for U and Pu studies [5]. The 1-mL cartridges (0.35 g) are manufactured by Eichrom to be smaller than 2-mL cartridges (0.70 g). The maximum loading capacities of the 1 mL cartridges are 37 mg of U on UTEVA [14,21] and 30 mg of Pu on TEVA [21]. Eichrom recommends not exceeding 20% of the maximum loading capacity for the resins which is readily achievable with ESS. Often, smaller columns face potential problems with decreased yield based on breakthrough of the analyte as well as the potential for lower resolution during separations. However, in the case of U and Pu, the affinity of the UTEVA and TEVA resins, respectively, is sufficiently high that decreased yields have not been observed within the limits of the resin loading capacity [22]. The smaller cartridge size should reduce the reagent volumes required for separation and improve flow rates leading to decreased separation times [23].

In this work, an elution profile for U, Pu, and selected trace metals was made for a single TEVA cartridge and a set of stacked TEVA and UTEVA cartridges (Fig. 1). Evaluation of the elution profile improved the overall characterization of the TEVA and UTEVA resin cartridges to optimize the separation of ultra-trace levels of U and Pu for analysis by MC-ICP-MS. The optimized method was validated by separating certified reference materials (CRMs) IRMM 183, U, and NBL PO CRM 137, Pu. MC-ICP-MS measurements of the purified U and Pu fractions agreed with certificate values for the major and minor ratios. Additional method validation was completed using archived ESS with varying U and Pu content and isotope ratios.

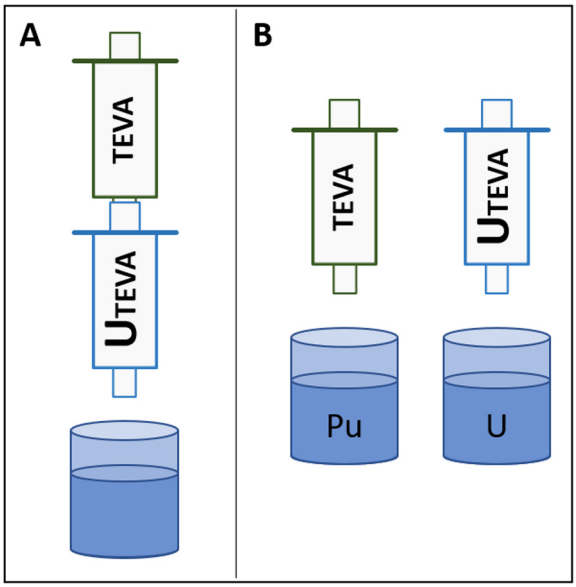

Fig. 1. Diagram of TEVA and UTEVA cartridge arrangements for (A) stacked and (B) individual cartridge use.

2. Materials and methods

2.1. Reagents and Standards

Optima™ grade reagents (HNO_3, H_2O_2 (30%), HCl, and HF) were purchased from Fisher Scientific (Pittsburg, PA, USA); $FeSO_4$ Puratronic® 99.999% (metals basis) and $NaNO_2$ (ACS, 95% min) were purchased from Alfa Aesar (Tewksbury, MA, USA); single element standards of Os, Zr, Bi, Mo, W, Tl, Hg, Ru, Au, Pt, Th, and Pb were purchased from High Purity Standards (Charleston, SC, USA). All reagents and standards were used without further purification. CRMs for U and Pu were purchased from the NBL Program Office (Lemont, IL, USA) [NBL PO CRM 137 (Pu), NBL U010 (U)] or the Joint Research Center of the European Commission (Brussels, Belgium) [IRMM 183 (U), IRMM 57 (U), IRMM 3100 A (U), IRMM 82 (Pu)]. An ORNL high–purity working reference material of ^{244}Pu was used as an enriched isotope spike and the concentration was determined relative to National Institute of Standards and Technology (Gaithersburg, MD, USA) Standard Reference Material 4330 C. A ThermoScientific Barnstead GenPure Pro™ water purification system (Fisher Scientific; Pittsburg, PA, USA) was used to prepare ASTM Type I (18.2 MΩ–cm) water. Labware was acid leached in separate baths of 6 M HCl, 8 M HNO_3, and water prior to use. TEVA and UTEVA cartridges (1 mL and 2 mL, 50–100 μm) and Pre-filter cartridges (2 mL, 100–150 μm) were purchased from Eichrom Industries (Lisle, IL, USA).

2.2. Inductively coupled plasma - mass spectrometer (ICP-MS)

Trace elements within purified fractions were determined using a high resolution-inductivity coupled plasma-mass spectrometer (HR–ICP–MS), ThermoScientific Element II (Bremen, Germany), as previously described [5]. Isotopic ratios measurements were collected with a ThermoScientific Neptune Plus (Bremen, Germany) multiple collector-inductivity coupled plasma-mass spectrometer (MC–ICP–MS) as previously described [5]. Unless otherwise specified, results are reported as average ± expanded uncertainty with a coverage factor k = 2. Uncertainties were calculated according to the Guide to the Expression of Uncertainty in Measurement unless otherwise noted [24].

2.3. General procedure for sample preparation

Samples and reagents were prepared in an International Organization for Standardization (ISO) Class 6 cleanroom. Samples were prepared in 3 M HNO_3 in perfluoroalkoxy (PFA) vials. Simulated samples included reagent blanks, CRMs, and solutions doped with trace metals were used for method development and validation. Actinide content was quantified by isotope dilution mass spectroscopy (IDMS) using a gravimetrically prepared ^{244}Pu spike and/or IRMM 57. CRM samples were prepared from a master stock of IRMM 183 (depleted U) and/or NBL PO CRM 137 (~80% ^{239}Pu), with final concentrations of 0.3 – 50 ng g^{-1}–soln and 0.1 – 15 pg g^{-1}–soln for U and Pu, respectively. A solution made of single element standards in 3 M HNO_3 with known concentrations (0.01 μg g^{-1}: Tl, Hg, Ru, Au, Pt, and Os; 1.0 μg g^{-1} Zr, Bi, Mo, and W; 5.0 μg g^{-1} Th; 10.0 μg g^{-1} Pb) was used to simulate metal contaminated samples based on previous screen data. Archived ESS with various isotope ratios and amounts of U and Pu were used for method validation. Prior to separation, the valence state of Pu in all samples was adjusted to Pu(IV) as previously described [5]. Briefly, $FeSO_4$ (0.2 mL, 1.7 M) was added to each sample followed by $NaNO_2$ (0.4 mL, 3 M). Samples were degassed for approximately 15 min prior to separation. After separation, fractions were dried down to remove trace HF, treated with 8 M HNO_3 (0.02 mL) and H_2O_2 (0.02 mL, 30%) to dissolve any residues, and dried down again. Final fractions were dissolved in 2% HNO_3 (1.5 mL) and submitted for isotopic analysis by MC–ICP–MS.

Table 1
Separation scheme outline for the traditional ORNL method, the expanded method used for elution profile generation, and the optimized method with volumes and reagents for U and Pu separation.

Step	Description	Traditional vol (mL)*	Expanded vol (mL)	Optimized vol (mL)	Reagent
0*	Pre-filter Precondition	4	N/A	N/A	3 M HNO_3
1	UTEVA Precondition 1	3	10	3	0.01 M HNO_3
2	UTEVA Precondition 2	12	15	5	3 M HNO_3
3	TEVA Precondition	12	15	5	3 M HNO_3
Stack Cartridges TEVA then UTEVA					
4	Load Sample	3	3	3	3 M HNO_3
5	Rinse Sample Vial	3	3	3	3 M HNO_3
6	Wash Stacked Cartridges	15	20	10	3 M HNO_3
Separated Cartridges, store TEVA cartridge upright, UTEVA cartridge attached					
7	Wash UTEVA Cartridge	5	15	5	3 M HNO_3
8	Elute U from UTEVA cartridge	5.5	10	4.5	0.02 M HNO_3-0.005 M HF
Discard UTEVA cartridge, Rinse syringe barrel 3 mL 3 M HNO3, TEVA cartridge attached					
9	Wash TEVA cartridge	5	15	5	3 M HNO_3
10	Wash TEVA cartridge	3	6	3	9 M HCl
11	Elute Pu from TEVA cartridge	N/A	20	10	0.1 M HCl − 0.06 M HF
11*	*Attach Pre-filter cartridge to TEVA cartridge* - Elute Pu from TEVA cartridge	12	N/A	N/A	0.1 M HCl − 0.06 M HF − 0.02 M NH_4I
Total Reagent Volume (mL)		82.5	132	56.5	

Steps 0 * and 11 * are only applicable to the traditional ORNL method.

2.4. Separations method

The TEVA and UTEVA cartridges were individually preconditioned as described in Table 1. The TEVA cartridge was stacked on top of the UTEVA cartridge (Fig. 1A). The sample (3 mL) was loaded through both cartridges. Quantitative transfer of the sample was achieved with three vial rinses (1 mL each) ensuring that the sample was completely loaded on the cartridge. The stacked cartridges were then washed and unstacked (Fig. 1B). The individual UTEVA and TEVA cartridge were then washed separately prior to U or Pu elution. The volumes for the traditional ORNL method, the expanded method used for the generation of the elution profile graph, and the optimized method are listed in Table 1. The volumes for the traditional ORNL method were used as guidelines for the elution profile generation. Analysis of the elution profile aliquots by HR-ICP-MS was completed after a 1:10 dilution of the aliquots with 2% HNO_3.

3. Results and discussion

3.1. Optimization of TEVA separation parameters

Conventional protocols for the Eichrom TEVA resin utilize redox chemistry to ensure the highest uptake of Pu(IV) on the TEVA resin [15,25]. Plutonium can then be readily eluted from the TEVA resin via reduction to Pu(III) [16,17,26]. Standard ORNL chemistry achieved this reduction using ammonium iodide in a 0.1 M HCl-0.06 M HF-0.02 M NH_4I solution. Due to the decomposition of NH_4I when hydrated, the eluent must be prepared daily. Additionally, a considerable amount of residue remains after dry downs and must be destroyed by several additions of 8 M HNO_3 and H_2O_2 (30%) prior to introduction into an ICP-MS. The reducing agent is not a requirement to elute the Pu from the TEVA resin. The affinity of the TEVA resin for Pu(IV) decreases with decreasing acid concentration [5,15,25,27,28]. To produce cleaner samples, the recovery of Pu from the TEVA cartridge with low acid solutions containing various amounts of NH_4I as the reducing agent was examined. Percent recovery was calculated by comparing the intensities of a processed and unprocessed ^{244}Pu spike.

The highest recoveries were consistently observed with reduced NH_4I concentrations, as seen in Table 2. At ultra-trace concentrations (< 2 pg Pu) no significant difference in recovery was observed between solutions containing no NH_4I and 0.001 M NH_4I; however, recovery with 0.02 M NH_4I was significantly lower (< 30%). This suggests that low levels of Pu can be more readily removed from the TEVA resin with low acid concentration without the use of a reducing agent. As a result, 0.1 M HCl-0.06 M HF was used throughout the remainder of the studies for the elution of Pu from the TEVA resin. Additionally, removal of the reducing agent from the solution enables reagents to be prepared in advance and eliminates the post-column ammonium iodate residue.

The volume of 3 M HNO_3 necessary to remove all U (IRMM 183) from an individual TEVA cartridge (Fig. 1B) after the initial sample load was examined. The known low affinity of U for the TEVA resin [15] enabled > 93% of the U to be eluted during the initial sample load (3 mL) and vial washes (3 mL) as shown in Fig. 2. Near quantitative recovery of U based on total counts was observed after an additional 5 mL of 3 M HNO_3 was used to wash the cartridge. The $^{235}U/^{238}U$ ratio was monitored to determine when the sample had been fully eluted from the TEVA cartridge. A depleted major ratio matching that of CRM IRMM 183 was observed through 7 mL of 3 M HNO_3 washing and a gradual increase to natural isotopic abundance present in 3 M HNO_3, occurred after 10 mL of washing (16 mL total volume). This suggests that after quantitative sample loading, the TEVA cartridge should be washed with an additional 10 mL of 3 M HNO_3 to ensure that all U has been eluted off the TEVA cartridge. The 10 mL wash ensures all the U is removed from the TEVA cartridge and loaded on the UTEVA cartridge when using the TEVA/UTEVA stacked cartridge configuration (Fig. 1A).

3.2. Cartridge elution profile

Preconditioning of the cartridges prior to sample loading is needed to remove all air bubbles from the cartridge bed. Effective removal of air gaps is achieved between 5 and 10 free cartridge volumes (3.3–6.6 mL) and should be done with the first mobile phase to be used [23]. No detectable analytes were observed during the preconditioning of either cartridge during the generation of the elution profile. This excluded the need for extra preconditioning, and extensive washes may be detrimental to cleanliness as breakdown of the extractant from the UTEVA resin is observed at ~6% per 60 mL of 2 M HNO_3 [14]. Reexamination of trace elements that were previously studied on the TEVA resin (Zr, Mo, Hg, Th) [15], or the UTEVA resin (Zr, Ru, Pb) [14] were used as verification of the separation method and eluted as expected from the cartridges. The importance of the remaining trace elements (W, Os, Pt, Au, Tl, and Bi), as well as Pb and Th, was based on the formation of molecular interferences [6,29] which could affect the measurement of U and Pu isotopes. In addition, these elements that could be present in facilities where ESS is conducted [5].

Table 2
Percent recovery (2σ) of total Pu from 1-mL TEVA cartridge with 0.1 M HCl-0.06 M HF-***X*** M NH_4I based on elution volume and initial ^{244}Pu spike.

^{244}Pu/ [NH_4I]	0.1 M HCl-0.06 M HF- *X* M NH_4I					Elution Vol
	0 M	0.001 M	0.005 M	0.01 M	0.02 M	
0.01 pg	74.5 ± 6.9%	74.5 ± 7.7%	–	–	26.3 ± 2.2%	6 mL
0.05 pg	107.2 ± 8.9%	91.0 ± 7.8%	–	–	21.5 ± 2.3%	6 mL
0.5 pg	99.6 ± 8.6%	103.1 ± 8.8%	–	–	27.5 ± 2.4%	6 mL
1 pg	102.7 ± 8.8%	91.0 ± 7.9%	–	–	–	6 mL
2 pg	62.8 ± 2.6%	50.5 ± 3.6%	28.3 ± 2.6%	20.7 ± 3.2%	34.5 ± 2.6%[a]	12 mL

[a] 6 mL elution volume was employed.

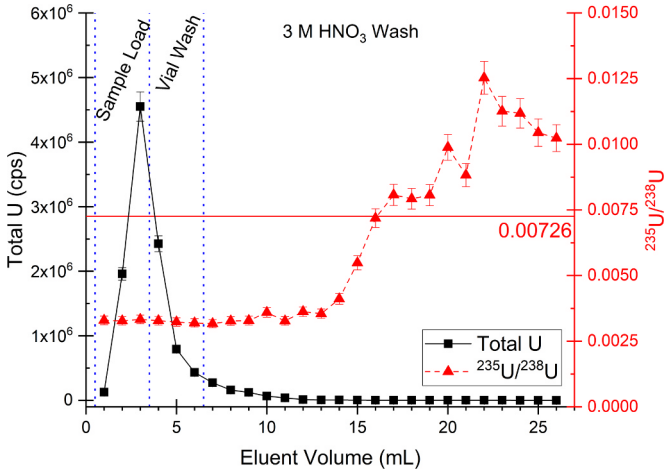

Fig. 2. Wash through of U on a preconditioned 1-mL TEVA cartridge with 3 M HNO_3 to compare total signal (cps) with the major $^{235}U/^{238}U$ ratio.

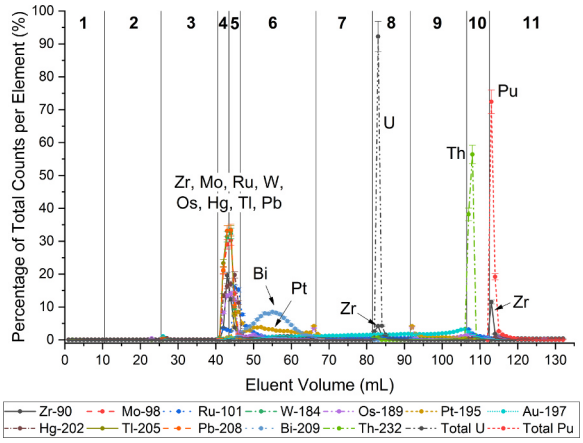

Fig. 3. Complete elution profile for TEVA and UTEVA cartridges following the elution profile steps outlined in Table 1, 'Expanded'.

The elution profile for the separation method detailed in Table 1 ("Expanded") is shown in Fig. 3. Excellent washout (> 99%) of Mo, Ru, W, Os, Hg, Tl and Pb from the cartridges was observed during quantitative sample loading. Bi and Pt demonstrated some affinity for the resins but were washed from the column with 3 M HNO_3 prior to U or Pu elution. The 1 mL TEVA cartridge did demonstrate ~5% breakthrough of Th at 5 μg g^{-1}, as can be expected with the smaller cartridge [15,22]; however, < 1% (0.05 μg g^{-1} Th) was observed in the U elution fractions and did not perturb the $^{233}U/^{238}U$ isotope ratio measurements. Higher Th concentrations could create mass interferences with the U isotopes from $^{232}Th^1H$, a sample prescreening or second UTEVA cartridge separation could resolve the potential interference. Examination of the $^{240}Pu/^{239}Pu$ suggests the elution of NBL PO CRM 137 occurred only during the Pu elution fraction. The elution profile for the trace metals using the stacked TEVA/UTEVA cartridge configuration was not significantly different from the profile for a single TEVA cartridge (data not shown).

The final optimized method for the separation of U and Pu was based on the elution profile. The optimized method uses the same sample load and vial wash volumes (Table 1) as the traditional ORNL method. After quantitative sample load, 10 mL of 3 M HNO_3 was used to rinse the stacked TEVA/UTEVA cartridges to ensure complete transfer of U onto the UTEVA cartridge and remove low affinity elements. The cartridges are separated and individually rinsed to ensure complete removal of matrix interferences prior to elution of U and Pu. Recovery of U or Pu from the UTEVA or TEVA cartridge, respectively, was based on the percentage of signal in each fraction versus the sum of the signal response throughout the total elution. Near quantitative (> 98%) recovery of U, with the IRMM 183 $^{235}U/^{238}U$ ratio, from the UTEVA cartridge was observed in 4 mL and no significant improvement was observed with increased elution volumes. During the Pu elution, > 95% of the total Pu with the NBL PO CRM 137 $^{240}Pu/^{239}Pu$ ratio were collected in the first 5 mL and elution continued through 10 mL with > 98% recovery. After separation, the final purified fractions are preconcentrated for matrix conversion prior to analysis by MC-ICP-MS in 2% HNO_3 (1.5 mL).

3.3. Blank characterization

Blank samples containing 3 M HNO_3, without U or Pu, were processed in conjunction with samples as process blanks. This enabled the determination of the amount of U or Pu which could be inherent to the 1 mL cartridges. While Pu is not generally found in the environment, natural U can be found throughout the environment including in labware and pure reagents [7,8,30,31]. The use of acid-leached vials and ultra-pure reagents are employed to reduce the natural U background. The amount of U and Pu in the process blanks was estimated based on count rates and the sensitivity of the day [5]. Process blanks yielded average ± 2σ values of 0.030 ± 0.031 ng and 0.00032 ± 0.00066 pg for U and Pu respectively, and were lower than previously reported process blanks for the traditional ORNL method [5].

Of additional interest during the characterization of the blanks was the count rates at ^{233}U and ^{242}Pu which can influence the concentration measurements during IDMS due to the isotope ratios of the spikes. Process blanks for the traditional ORNL method, based on data accumulated in 2018, displayed a range of 17–42 counts at 233 amu. These counts were considered significant as the value was greater than twice the expanded uncertainty of the measurement. In contrast, process blanks from the 1 mL columns consistently demonstrated no statistically significant counts (counts < 2σ) at 233 amu (< 6 cps on average). Spiked process blanks for Pu also demonstrated significantly less spike stripped counts of ^{242}Pu in 1 mL process blanks (32–83 counts) in comparison to traditional ORNL spiked process blanks (34–156 counts). It is predicated, that the cleaner blanks are attributed to the optimized volumes used for cartridge washing and elution in the final method. The smaller volumes are expected to contribute less overall to the process

Table 3
Measured and certified values (± 2σ) for the triplicate analysis of CRM IRMM 183 and NBL PO CRM 137 separated using the optimized method on 1 mL columns.

Sample/ratio	Sample 1	Sample 2	Sample 3	Certificate
$^{234}U/^{238}U$	$1.456 \times 10^{-4} \pm 2.1 \times 10^{-6}$	$1.460 \times 10^{-4} \pm 1.9 \times 10^{-6}$	$1.466 \times 10^{-4} \pm 1.9 \times 10^{-6}$	$1.48358 \times 10^{-4} \pm 2.7 \times 10^{-8}$
$^{235}U/^{238}U$	$3.204 \times 10^{-3} \pm 3.5 \times 10^{-5}$	$3.196 \times 10^{-3} \pm 3.7 \times 10^{-5}$	$3.201 \times 10^{-3} \pm 3.2 \times 10^{-5}$	$3.21570 \times 10^{-3} \pm 8.0 \times 10^{-7}$
$^{236}U/^{238}U$	$1.986 \times 10^{-5} \pm 3.0 \times 10^{-7}$	$1.976 \times 10^{-5} \pm 3.5 \times 10^{-7}$	$1.984 \times 10^{-5} \pm 2.9 \times 10^{-7}$	$1.9755 \times 10^{-5} \pm 1.1 \times 10^{-7}$
$^{240}Pu/^{239}Pu$	0.2410 ± 0.0036	0.2412 ± 0.0028	0.2400 ± 0.0044	0.24100 ± 0.00037
$^{241}Pu/^{239}Pu$	$6.10 \times 10^{-3} \pm 4.6 \times 10^{-4}$	$6.08 \times 10^{-3} \pm 4.6 \times 10^{-4}$	$6.04 \times 10^{-3} \pm 4.4 \times 10^{-4}$	$6.200 \times 10^{-3} \pm 1.7 \times 10^{-5}$
$^{242}Pu/^{239}Pu$	$1.530 \times 10^{-2} \pm 8.4 \times 10^{-4}$	$1.543 \times 10^{-2} \pm 5.8 \times 10^{-4}$	$1.552 \times 10^{-2} \pm 5.9 \times 10^{-4}$	$1.5600 \times 10^{-2} \pm 5.2 \times 10^{-5}$

blanks while ensuring adequate interference removal without degradation of the organic extractant.

3.4. CRM validation

Validation of the optimized separation method detailed in Table 1 was conducted on triplicate samples of CRMs (IRMM 183 mixed with NBL PO CRM 137). The measured ratios are displayed in Table 3 and show no significant difference from the certified values. A quantitative comparison of the measured values ($x_{measured}$) with a standard uncertainty ($u^2(x_{measured})$ with the certified value ($x_{certified}$) and its associated standard uncertainty ($u^2(x_{certified})$ was done by calculating zeta (ζ) scores using Eq. (1) [32,33]. Results were in good agreement with the certified value if $|\zeta| < 2$ (95% confidence) or if $|\zeta| < 3$ (99% confidence). Calculated zeta scores were very small ($|\zeta|$ 0.01–1.35) for each measured ratio for IRMM 183 and NBL PO CRM 137 and are shown in Fig. 4.

$$\zeta = \frac{x_{measured} - x_{certified}}{\sqrt{u^2(x_{measured}) + u^2(x_{certified})}} \quad (1)$$

3.5. Archived ESS validation

The optimized 1-mL method was validated using archived ESS analyzed by ORNL from 2015 to 2016. Samples were analyzed only for U and Pu isotope ratios, as analyte concentrations change over time. The samples represent a variety of isotopic and content range for U and Pu and were split into three groups: depleted U, natural U, and enriched U based on the $^{235}U/^{238}U$ ratio regardless of Pu content as shown in Table 4. The U and Pu content in the samples varied greatly over the three groups with samples ranging from < 1 ng to 1500 ng of U and < 0.01–6 pg of Pu. One sample in the depleted U group had sufficiently high U and Pu content (2.4 μg U and 45 pg of Pu) that three replicate separations were performed on the sample. The originally reported minor Pu isotope ratios had expanded uncertainty values

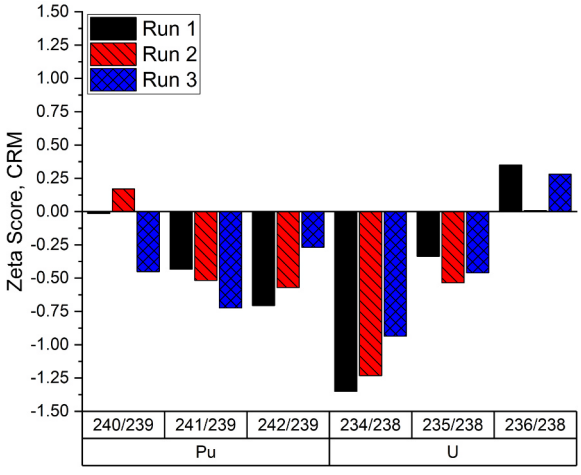

Fig. 4. Zeta scores for NBL PO CRM 137 and IRMM 183 after separation.

Table 4
Overview of archived ESS for optimized method validation including estimates of U and Pu content in archived samples portions.

U grouping	Approximate U content archived	Approximate Pu content archived
Depleted U	8–2400 ng	< 0.01–45 pg
Natural U	< 1–1300 ng	< 0.01–0.07 pg
Enriched U	3–1500 ng	< 0.05–6 pg

(k = 2) that were greater than the measured ratios and therefore not examined during validation.

Table 5 shows the comparison of measured over reported values for U and Pu isotopic ratios for the archived ESS. MC-ICP-MS results for the Pu isotopics in all samples demonstrated good agreement with the previously reported values. Very low count rates (< 50 cps) of ^{240}Pu in samples 6, 9, and 10, led to large errors in the measurement of the $^{240}Pu/^{239}Pu$ ratio and subsequent comparison to reported values as expected based on the archived amounts in each sample. Triplicate runs of sample 2 showed no perturbation of the U or Pu isotopes measured in comparison to the reported values. The higher archived content of U and Pu enabled good counting statistics for each measured isotope. The U isotopes were in very good agreement with the reported values (< 0.2% difference in minor ratios, < 0.06% difference in major ratio). Additionally, the major Pu isotope ratio measurement was within 1% of the reported values. The average values of sample 2 in Table 5 reveal the high precision and accuracy of the MC-ICP-MS measurement, and reproducibility of the associated separation method. Further examination of the remaining samples showed good agreement of the measured and reported values for all three groups (depleted, natural, and enriched U) with 99% confidence and were within IAEA data quality limits [3].

4. Conclusions

The work presented here provides further characterization of Eichrom TEVA and UTEVA resins and demonstrates the successful separation of ultra-trace levels of U and Pu using stacked 1 mL cartridges. Recovery of Pu from the TEVA column during elution was improved through the elimination of the reducing agent in the eluent. The complete elution profile generated allowed for the optimization of the volume of reagents used in each step. This contributed to improved process blanks with lower U and Pu content when measured by MC-ICP-MS. Purification of U and Pu CRMs were successful and isotope ratios agreed well with the certificate values. Further success of the method was demonstrated with archived ESS and yielded high accuracy results well within data quality limits for the IAEA. Lastly, the optimized method takes approximately three hours and uses 35% less reagents; a significant improvement to the eight-hour traditional method. The optimized method demonstrates the necessity of established method re-evaluation in the safeguards community as ultra-trace detection limits improve. Furthermore, the optimized method is applicable to a wide range of environmental samples where high precision, accurate, low-level measurements are necessary.

Table 5
Comparison of measured vs reported values for the major and minor U and major Pu isotope ratios with 2σ errors for archived ESS.

U-Group	Measured/reported	$^{234}U/^{238}U$	2σ	$^{235}U/^{238}U$	2σ	$^{236}U/^{238}U$	2σ	$^{240}Pu/^{239}Pu$	2σ
Depleted	sample 1	99.9%	2.6%	99.76%	1.2%	100.3%	2.2%	99.1%	3.2%
	sample 2.1	99.88%	1.2%	99.99%	1.5%	100.06%	1.8%	99.3%	5.8%
	sample 2.2	99.92%	1.1%	99.99%	1.5%	99.87%	1.7%	98.9%	5.4%
	sample 2.3	99.80%	1.1%	99.94%	1.5%	100.00%	1.8%	99.7%	5.6%
	average sample 2	99.87%	0.88%	99.98%	1.1%	99.98%	1.4%	99.3%	4.2%
	sample 3	99.5%	5.6%	99.95%	1.2%	98.4%	7.0%	104.3%	10.2%
Natural	sample 4	104.5%	3.4%	99.62%	1.1%	99.0%	4.4%	98.7%	5.0%
	sample 5	99.0%	3.0%	99.42%	1.8%	96.2%	2.4%	100.4%	3.2%
	sample 6	99.42%	0.84%	99.98%	1.5%	99.7%	3.8%	91%	34%
Enriched	sample 7	102.95%	1.5%	102.99%	1.5%	103.3%	4.4%	100.3%	9.4%
	sample 8	98.73%	1.5%	98.59%	1.5%	99.0%	2.0%	118%	38%
	sample 9	97.85%	0.78%	98.62%	1.5%	99.56%	1.6%	96%	56%

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Conflicts of interest

There are no conflicts of interest to declare.

References

[1] D.L. Donohue, Strengthening IAEA safeguards through environmental sampling and analysis, J. Alloy. Compd. 271 (1998) 11–18, https://doi.org/10.1016/s0925-8388(98)00015-2.
[2] IAEA, Development and Implementation Support Programme for Nuclear Verification 2018–2019, International Atomic Energy Agency, Vienna, 2018.
[3] IAEA, Qualification Procedure for the Network of Analytical Laboratories for Environmental Sampling, International Atomic Energy Agency, Vienna, 2011.
[4] IAEA, Environmental Sampling for Safeguards, International Atomic Energy Agency, Vienna, 2005.
[5] 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 (15) (2018) 9441–9448, https://doi.org/10.1021/acs.analchem.8b02095.
[6] S. Boulyga, S. Konegger-Kappel, S. Richter, L. Sangely, Mass spectrometric analysis for nuclear safeguards, J. Anal. At. Spectrom. 30 (7) (2015) 1469–1489, https://doi.org/10.1039/c4ja00491d.
[7] S.F. Boulyga, A. Koepf, S. Konegger-Kappel, Z. Macsik, G. Stadelmann, Uranium isotope analysis by MC-ICP-MS in sub-ng sized samples, J. Anal. At. Spectrom. 31 (11) (2016) 2272–2284, https://doi.org/10.1039/c6ja00238b.
[8] D. Lariviere, V.F. Taylor, R.D. Evans, R.J. Cornett, Radionuclide determination in environmental samples by inductively coupled plasma mass spectrometry, Spectrochim. Acta Part B 61 (8) (2006) 877–904, https://doi.org/10.1016/j.sab.2006.07.004.
[9] P. Goodall, C. Lythgoe, Rapid separation of uranium and plutonium by extraction chromatography for determination by thermal ionisation mass spectrometry, Analyst 124 (3) (1999) 263–269, https://doi.org/10.1039/A809219B.
[10] J.W. Grate, M.J. O'Hara, A.F. Farawila, M. Douglas, M.M. Haney, S.L. Petersen, T.C. Maiti, C.L. Aardahl, Extraction chromatographic methods in the sample preparation sequence for thermal ionization mass spectrometric analysis of plutonium isotopes, Anal. Chem. 83 (23) (2011) 9086–9091, https://doi.org/10.1021/ac202150v.
[11] J. Veliscek-Carolan, Separation of actinides from spent nuclear fuel: a review, J. Hazard. Mater. 318 (Supplement C) (2016) 266–281, https://doi.org/10.1016/j.jhazmat.2016.07.027.
[12] S.A. Ansari, P.K. Mohapatra, A review on solid phase extraction of actinides and lanthanides with amide based extractants, J. Chromatogr. A 1499 (Supplement C) (2017) 1–20, https://doi.org/10.1016/j.chroma.2017.03.035.
[13] K.L. Nash, C. Madic, J.N. Mathur, J. Lacquement, Actinide separation science and technology, in: L.R. Morss, N.M. Edelstein, J. Fuger (Eds.), The Chemistry of the Actinide and Transactinide Elements, Springer, Netherlands, Dordrecht, 2006, pp. 2622–2798.
[14] E.P. Horwitz, M.L. Dietz, R. Chiarizia, H. Diamond, A.M. Essling, D. Graczyk, Separation and preconcentration of uranium from acidic media by extraction chromatography, Anal. Chim. Acta 266 (1) (1992) 25–37, https://doi.org/10.1016/0003-2670(92)85276-C.
[15] E.P. Horwitz, M.L. Dietz, R. Chiarizia, H. Diamond, S.L. Maxwell, M.R. Nelson, Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions, Anal. Chim. Acta 310 (1) (1995) 63–78, https://doi.org/10.1016/0003-2670(95)00144-O.
[16] Y. Muramatsu, S. Uchida, K. Tagami, S. Yoshida, T. Fujikawa, Determination of plutonium concentration and its isotopic ratio in environmental materials by ICP-MS after separation using ion-exchange and extraction chromatography, J. Anal. At. Spectrom. 14 (5) (1999) 859–865, https://doi.org/10.1039/a900071b.
[17] J. Qiao, X. Hou, P. Roos, M. Miró, Rapid isolation of plutonium in environmental solid samples using sequential injection anion exchange chromatography followed by detection with inductively coupled plasma mass spectrometry, Anal. Chim. Acta 685 (2) (2011) 111–119, https://doi.org/10.1016/j.aca.2010.10.029.
[18] Eichrom Technologies, Available Methods Home Page, 2017. 〈http://www.eichrom.com/eichrom/methods/eichrom-methods/〉. (accessed 24 January).
[19] C.D. Quarles, B.T. Manard, E.M. Wylie, N. Xu, Trace elemental analysis of bulk uranium materials using an inline automated sample preparation technique for ICP-OES, Talanta 190 (2018) 460–465, https://doi.org/10.1016/j.talanta.2018.08.031.
[20] E.M. Wylie, B.T. Manard, C.D. Quarles, L.A. Meyers, N. Xu, An automated micro-separation system for the chromatographic removal of uranium matrix for trace element analysis by ICP-OES, Talanta 189 (2018) 24–30, https://doi.org/10.1016/j.talanta.2018.06.063.
[21] Eichrom Technologies, Eichrom Technologies' Product Catalog for 2014. 〈https://www.eichrom.com/wp-content/uploads/2018/02/eic-2014-product-catalog-web.pdf〉. (Accessed 19 October 2018), 2014.
[22] S.C. Metzger, Personal communication, Oak Ridge, TN, 2017.
[23] P. Markl, E.R. Schmid, Chapter 3 Techniques in column extraction chromatography, in: T. Braun, G. Ghersini (Eds.), Extraction Chromatography, Elsevier, 1975, pp. 45–67.
[24] Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM 100:2008 (GUM 1995 with minor corrections), BIPM Joint Committee for Guides in Metrology, Paris, 2008.
[25] ASTM, C1411-14, Standard Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis, ASTM International, West Conshohocken, PA, 2014 (10.1520/C1411-14), 〈http://www.astm.org/cgi-bin/resolver.cgi?C1411-14〉.
[26] H. Ziegler, K. Mayer, Development of an optimized method for faster and more reliable automated U/Pu/Np separations, Radiochim. Acta (1999) 123.
[27] Z. Varga, A. Nicholl, J. Zsigrai, M. Wallenius, K. Mayer, Methodology for the preparation and validation of plutonium age dating materials, Anal. Chem. 90 (6) (2018) 4019–4024, https://doi.org/10.1021/acs.analchem.7b05204.
[28] J. Qiao, X. Hou, M. Miró, P. Roos, Determination of plutonium isotopes in waters and environmental solids: a review, Anal. Chim. Acta 652 (1–2) (2009) 66–84, https://doi.org/10.1016/j.aca.2009.03.010.
[29] N. Daskalova, I. Boevski, Spectral interferences in the determination of trace elements in environmental materials by inductively coupled plasma atomic emission spectrometry, Spectrochim. Acta Part B-At. Spectrosc. 54 (7) (1999) 1099–1122, https://doi.org/10.1016/s0584-8547(99)00043-9.
[30] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, The actinide elements, in: Sixth (Ed.), Advanced Inorganic Chemistry, Wiley-Interscience, New York, 1999, pp. 1130–1164.
[31] F. Pointurier, R.W. Williams, S.P. LaMont, R.E. Steiner, D.A. Bostick, K.B. Olsen, N.A. Wogman, Round-robins in the area of uranium and plutonium bulk analysis of environmental samples, J. Radioanal. Nucl. Chem. 296 (2) (2013) 599–608, https://doi.org/10.1007/s10967-012-1985-6.
[32] K.T. Rogers, J. Giaquinto, R.M. Essex, S.C. Metzger, B.W. Ticknor, C.R. Hexel, Trace impurity analysis in uranium oxide via hybrid quantification techniques—gravimetric standard addition and isotope dilution mass spectrometry, J. Radioanal. Nucl. Chem. (2018), https://doi.org/10.1007/s10967-018-6106-8.
[33] Analytical Methods Committee, AMCTB No. 74, z-scores and other scores in chemical proficiency testing—their meanings, and some common misconceptions, Anal. Methods 8 (28) (2016) 5553–5555, https://doi.org/10.1039/C6AY90078J.