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Direct analysis of cotton swipes for plutonium isotope determination by microextraction-ICP-MS

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Abstract

This study demonstrates a method for determining the isotopic composition of low-level (sub-pg) plutonium (Pu) directly from a cotton swipe. Environmental sample (ES) swipes are routinely employed as a tool for monitoring activities in nuclear facilities. Traditional ES swipe analysis, as employed in nuclear safeguards, utilizes laborious ashing, digestion, and chemical separation procedures prior to mass spectrometric (MS) analysis. Here, an innovative sample introduction technique employing a microextraction probe to extract Pu directly from the swipe surface is described. The microextraction probe lowers onto the swipe surface, seals on a small area (8 mm^2), and delivers solvent (2 % HNO_3) to extract actinide material that may be present. The extracted analyte is subsequently directed into a sector field inductively coupled plasma (ICP) - MS for isotope ratio determination. This microextraction-ICP-MS method successfully determined the isotopic composition ($^{240}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$) of three Pu certified reference materials (CRM 136, 137, and 138) that were deposited (1 pg) onto ES swipes. The percent relative difference from the certified value, uncorrected for instrumental fractionation, was <2 % for the $^{240}Pu/^{239}Pu$ ratio on all three CRMs and <10 % for the $^{242}Pu/^{239}Pu$ ratio on CRM 136 and 138. The percent relative standard deviation, an estimate of the sample-to-sample isotopic precision, was <4 % for the $^{240}Pu/^{239}Pu$ and <15 % for the $^{242}Pu/^{239}Pu$. Method limits of detection were determined, based on measurements of an enriched ^{244}Pu material, to be ~7 fg. Additionally, a mixed uranium (U) and Pu deposition was made to determine the method's ability to simultaneously extract U and Pu and determine the isotopic composition of both analytes.

Introduction

Accurate determination of trace actinide isotopic compositions on environmental sample (ES) swipes is a cornerstone of nuclear safeguards analysis.[1-4] Since the 1990's nuclear safeguards inspectors have employed environmental sampling (ES) to aid in verification of activities and material at nuclear facilities. The collected samples, typically woven cotton fiber swipes, are analyzed by the IAEA Network of Analytical Laboratories (NWAL) using a variety of nondestructive and destructive techniques targeting actinide isotopic composition and total content, most predominately uranium (U) and plutonium (Pu). The isotopic composition and content of the actinides and fission products contained on the ES swipes are routinely used to draw conclusions regarding the consistency of declared activities and the absence (or presence) of undeclared activities at facilities. For instance, perturbations in the U isotope abundances, or simply the presence of Pu, can provide information regarding enrichment and reprocessing activities.

Particle analysis techniques such as fission track (FT) thermal ionization mass spectrometry (FT-TIMS)[5] and secondary ionization mass spectrometry (SIMS).[6, 7] are used to characterize the isotopic content of individual actinide particles contained on the swipe. Other methods such as laser ablation (LA) inductively coupled plasma mass spectrometry (ICP-MS) have also demonstrated effectiveness for direct particle analysis[8-10], potentially eliminating the need for sample preparation. Alternatively, ES swipes can also be measured by bulk analysis, where the entire ES swipe is digested and dissolved. Chemical separations are performed on the dissolved sample to remove potential trace element impurities which may form interfering polyatomic ions and to separate U from Pu, providing purified aliquots of each element free from isobaric interferences.[11-13] The purified samples are then analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and/or thermal ionization mass spectrometry (TIMS).[14] Typical ES swipes contain ng-mg levels of U and up to ng levels of Pu (generally in the form of particulates), along with various elemental impurities.[15] The results from multiple NWAL round-robin exercises find that U in the ng range and in the pg Pu can be determined routinely across the NWAL with good accuracy and precision.[16] In general, bulk analysis of ES swipes provides reliable detection of trace amounts of Pu , but the average isotopic value bulk analysis returns may in some cases fail to yield a complete picture of possible uranium enrichment activities. This is a function of all collected particles, which may individually be indicative of different process streams in the facility or of different time periods in the facility's operational history, being homogenized during digestion to create a single blended isotopic U signature. Additionally, bulk analysis necessarily contributes 1-5 ng of natural uranium inherent in the cotton swipe itself to the measured sample[17], making small amounts of non-natural uranium difficult to detect.

New methods have recently targeted the ability to directly analyze the swipe surface for chemical and isotopic analyses. Coopersmith et al. explored a rapid paper spray ionization technique, coupled to a high-resolution time-of-flight (TOF) MS.[18] In this configuration, the uranium loaded swipe sample was solvated with an organic mixture (methanol) and ions were generated, similarly to electrospray ionization, upon application of a high voltage (~3.0 kV) to a narrow tip of the swipe matrix. Preliminary results on swipes doped with reference materials showed the ability to detect uranium molecular ions and ultimately determine the $^{235}U/^{238}U$ ratio via $[^{235}U^{16}O_2]^+/[^{238}U^{16}O_2]^+$.[18] Kim et al. explored Monochromatic Micro X-ray Fluorescence (MMXRF) to directly analyze the surface of the swipe as a pre-screening tool, particularly prior to SIMS analysis. This technique was able to provide spatially resolved information regarding uranium enrichment.[19]

Another recent technique for directly sampling a surface utilizes a microextraction probe originally developed for biomolecules and thin layer chromatography-based separations.[20-22] For ES analysis, the microextraction probe can be lowered onto the swipe surface, delivering an extraction solvent (2 % HNO_3) to desorb the uranium species doped on the swipe. In an initial study, the extracted U was delivered to a liquid sampling – atmospheric pressure glow discharge (LS-APGD) ionization source[23, 24] coupled to an Orbitrap-MS for isotopic anlaysis.[25] More recently, the microextraction sampling mechanism was coupled to a quadrupole-based ICP-MS and demonstrated its ability to accurately and precisely analyze various U certified reference materials (CRMs) for both the major ($^{235}U/^{238}U$) and the minor ($^{234}U/^{238}U$, $^{236}U/^{238}U$) isotope ratios. The work described here looks to improve the sensitivity of the microextraction technique by incorporating a high efficiency sample introduction system and a sector-based ICP-MS. Additionally, the determination of Pu directly from the swipe surface was investigated at sub-picogram levels to mimic ES swipes loadings. Plutonium isotopic abundances will vary depending on its source and intended use. Weapons usable plutonium has ~6% ^{240}Pu and ~93% ^{239}Pu while high burn up reactor fuel can be ~25 and ~58%, respectively[26]. The work presented here, employing the microextraction-ICP-MS methodology, will examine the ability to accurately discern these isotopic systems, specifically at the sub-picogram level which have been doped on a cotton swipe.

Experimental

Sample Materials and Preparation

All standards were prepared and gravimetrically diluted from stock solutions. For uranium analysis, a single element uranium standard (10 μg mL^{-1}), from High Purity Standards (Lot #1916841-250, North Charleston, SC) and a certified isotopic standard (2 mg U mL^{-1} 1 M HNO_3) from the European Commission – Joint Research Centre-Geel (JRC-Geel, formally the Institute for Reference Materials and Measurements, or IRMM, Geel, Belgium) was used, specifically IRMM 2027.[27] The plutonium standards used were a Highly Enriched ^{244}Pu spike[28] and certified reference materials (CRM) 136, 137, and 138 from New Brunswick Laboratory Program Office[29]. The ^{244}Pu was gravimetrically diluted from a stock solution (4.418 ± 0.021 ng Pu g^{-1} 4M HNO_3-0.05M HF) to concentrations ranging from 0.05-2.5 ng ^{244}Pu g^{-1} solution such that varying amounts ranging from 0.1-5 pg could be deposited onto the swipe surface with a 2 μL aliquot. The CRMs 136, 137, and 138 were diluted from stock concentrations of ~30 ng Pu g^{-1} solution to a working concentration of 0.5 ng Pu g^{-1} solution such that a 2 μL aliquot on a swipe sample would be ~1 pg. All dilutions were performed with Optima™ grade nitric acid (HNO_3) from Fischer Scientific (Pittsburgh, PA, USA) diluted to 2 % w/w with ASTM Type I (18.2 MΩ-cm) generated from a Barnstead™ xCAD Plus ultrapure water purification system (Waltham, MA, USA). Cotton swipes were prepared such that the 10 × 10 cm TX304 (Texwipe, Kernersville, NC, USA) was folded to create 9 sampling locations (at the fold crosshairs). The sample solutions were pipetted onto the respective locations in 2 μL volumes and allowed to dry prior to sampling.

Microextraction-ICP-MS

The extraction of the actinide species from a swipe surface was achieved via an Advion Plate Express (Ithica, NY, USA) and is referred to here as a microextraction probe.[30] Sampling is achieved by lowering the probe head onto the swipe surface while delivering an extraction solvent (2% HNO_3) to the probe head (2 × 4 mm). A 30 second probe contact time was used, as it was previously determined to be optimal for efficiently extracting the analyte form the surface[30]. The pumped 2% HNO_3 was delivered at a constant flow rate of 200 μL min^{-1} and directed, in-line, to the ICP-MS for analysis. Between extractions, a small burp of gas (N_2, ultrahigh purity, Airgas, Radnor, PA, USA) was delivered to the probe head to remove any debris that could be picked up from the swipe surface. Additionally, the probe head was cleaned by performing a blank extraction on a 10 x 10 cm piece of Teflon. For nebulization, two configurations were explored in the initial studies. First, a stable sample introduction (SSI) dual quartz chamber enclosed in a Peltier cooler (PC^3) and for improved sensitivity, an APEX high efficiency sample introduction system (all from Elemental Scientific Inc. (ESI), Omaha, NE, USA) was employed. For analysis, a Thermo Scientific sector field (SF) ICP-MS (Element 2) was utilized, and the cone configuration consisted of a traditional sample cone (H) and a high sensitivity skimmer cone (X) from ESI. The experimental set-up is depicted in graphically in **Figure 1**. For data acquisition, the isotopes ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{244}Pu were monitored in low resolution mode, along with respective half masses for peak-tailing corrections. The mass window was set to 5% with 1 ms settling time, 10 ms sampling time, 200 sample cycles per peak, in EScan mode utilizing both the counting and analog detectors. The instrument was tuned daily, and appropriate dead time and analog-counting corrections were made for optimal isotopic measurements. Data collection parameters were adjusted to target a 2 minute analysis. The parameters that were adjusted were number of isotopes monitored, number of points samples within the peak, and the duration of the sampling time.

Data Analysis

Data processing was accomplished using OriginPro, Version 2020 (OriginLab Corporation, Northampton, MA, USA). The raw transient signal was smoothed using adjacent-averaging techniques within the Signal Processing portion of OriginPro. This allows the user to define the number of points used for smoothing the transient signal. This method has been shown to be successful for accurate isotopic analysis on quadrupole-based machines when employed in the ChromControl plugin within Qtegra software (Thermo Scientific)[31, 32]. After smoothing, the peak area was integrated using the Peak Analyzer feature within OriginPro. Peak area comparisons are traditionally used in HPLC and HPIC for accurate quantification and have also been previously shown to result in the highest precision when looking at isotope ratios on quadrupole-based instruments.[31, 32] A recent study by Wanna et al. confirmed that this practice also applies to sector field-based mass analyzers[33]. To best determine accurate signal processing, replicate runs (n=9) of blank swipes and swipes doped with IRMM 2027 using both the SSI and APEX sample introduction systems were processed using the OriginPro software. The transient signal for ^{235}U and ^{238}U were processed for the blanks and the samples to determine the major ^{235}U/^{238}U ratio. Integration of the peaks was performed on the raw transient signal, and on multiple levels of smoothing of the transient signal (2, 5, 10, 15, and 20 window points for adjacent - averaging). The eluted peak was analyzed using various baseline subtraction modes within the peak analyzer in OriginPro. The method precision and accuracy are defined by the percent relative standard deviation (%RSD) and percent relative difference (%RD) respectively in the isotope ratio for the replicate runs. The method precision presented here, is solely meant to encompass sample to sample precision only. The %RD is defined in equation 1. The Peak Analyzer feature requires a manual peak width selection; the lowest uncertainty (lowest %RSD and %RD) was achieved by integrating the whole peak using the same peak width for each sample and blank transient without making any baseline adjustments. After smoothing and integrating the sample, the blank (smoothed and integrated) was then subtracted from the sample. All transient signals were smoothed with 20 adjacent-averaging points prior to full peak integration and blank subtraction.

$$(1) \qquad \%\,RD = \frac{experimental - actual}{actual} \times 100$$

Results and Discussion

High efficiency sample introduction

A high efficiency sample introduction system is routinely used for enhanced sensitivity. Typically, the detection of actinides in low levels (fg or pg) would require the use of a high efficiency introduction system.[34] Peak transient and sensitivity improvements were studied with respect to coupling the microextraction probe to two different sample introductions systems. The first was the stable sample introduction (SSI) dual quartz spray chamber housed within a Peltier cooler and the second was an APEX HF high efficiency sample introduction system. To study the effects of these introduction systems, varying concentrations of uranium, ranging from 0.02 – 1 ng, were deposited onto the swipe surface for analysis by the microextraction-ICP-MS method. Overall, the sample transients remained unchanged with the two different nebulization processes, as seen in **Figure 2a (SSI) and 2b (APEX)**. A pertinent difference, however, is the observed sensitivity, which can be seen in the count rate for the transient signals. For the 1 ng deposit, the transient signal peaked at ~6.5×10^5 and 8.5×10^6 counts per second (cps) for the SSI and APEX introduction systems, respectively. Examination of the slope, in **Figure 2c**, demonstrates a ~15× improvement in the sensitivity between the SSI and the APEX, which is commonly found.[34-37] The method limit of detection (LOD) is defined in equation 2 and encompasses the standard deviation of multiple blank measurements (σ_{blank}) and the slope of the response curve (m). The LOD for ^{238}U was found to be 3 pg U for the APEX sample introduction system. It is assumed that this LOD would be lower for Pu extractions due to the inherent lack of naturally occurring Pu in the swipes and the reagents.

$$LOD = \frac{3 \times \sigma_{blank}}{m} \qquad (2)$$

Plutonium extraction

A highly enriched ^{244}Pu isotopic standard[28], was loaded onto a swipe surface in masses ranging from 0.12-5.7 pg. The deposits were analyzed by the microextraction-ICP-MS method in triplicate. The general elution profile, depicted in **Figure 3a**, remains relatively unchanged in comparison to the uranium extraction in the present and previous studies[25, 30]. Overall, there was good reproducibility in the extraction of the ^{244}Pu. The elution profile in **Figure 3a** plots the average of the three replicates and highlights the standard deviation of the transients by the shaded areas around the elution profile. The elution profiles generated from the three extractions of the smallest deposit, 0.1 pg of ^{244}Pu, are presented as an insert of **Figure 3a**. Quite remarkably, there is good precision (<5 %RSD) in this profile, and excellent signal-to-noise ratio with respect to a blank extraction seen in the insert. The < 5 %RSD is comparable to other transient analysis of actinides at ultra-trace levels.[31, 38] While the precision is likely compromised at these concentrations the ability to detect 100 fg of ^{244}Pu, with ~400 signal-to-noise ratio, bodes well for low level Pu analysis. The sensitivity curve, with inclusion of sample-to-sample standard deviation, is shown in **Figure 3b**. While not intended to be a fully quantitative technique, the microextraction-ICP-MS method was able to successfully analyze varying concentrations of ^{244}Pu and yielded a correlation coefficient (R^2) of 0.997. To determine the method LOD, the same equation from above was applied, and the LOD for ^{244}Pu was determined to be 7 fg.

Plutonium isotopic analysis

To determine the microextraction-ICP-MS method's ability to make accurate and precise isotope ratio measurements on low-level Pu, three different CRMs (CRM 136, 137, and 138) were deposited (1 pg in 2 μL) onto swipe surfaces. As a point of comparison, while the work presented here is not intended to demonstrate the technique as a means for particle analysis, the 1 pg sample load represents a similar amount of material to what has been previously correlated with 1 μm^3 U particles.[39, 40] The certified isotopic values of the CRMs are presented in **Table 1**. It should be noted that ^{241}Pu/^{239}Pu was not reported as the doping solutions were not chemically cleaned from the ingrowth of ^{241}Am. The samples were analyzed such that blanks, 2 μL of 2 % HNO_3 deposited on the swipe surface, were analyzed between each sample. There were no mass bias corrections made for this data set, and each sample was analyzed 5 times, except for CRM 137, which was analyzed 4 times due the microextraction probe missing the sample location in one instance. Overall, the agreement with the ^{240}Pu/^{239}Pu ratios for all three CRMs is within 2 % of the certified value. The percent relative difference for the ^{240}Pu/^{239}Pu was 1.06, 1.48, and 1.93 for CRM 136, 137, and 138, respectively. The ^{242}Pu/^{239}Pu ratios are slightly less precise but are within 10 % of the certified values for CRM 136 and 137. Impressively, for CRM 136, the atom percent of the ^{242}Pu is 0.578 %; this would roughly equate to 5 fg of ^{242}Pu based on the 1 pg deposit. The ability to determine the ^{242}Pu/^{239}Pu ratio, with only 5 fg of ^{242}Pu, highlights the utility of the microextraction-ICP-MS technique. The ^{242}Pu/^{239}Pu was unable to be determined for CRM 138 as the ^{242}Pu was ultimately below the method detection limit for the microextraction-ICP-MS approach. For CRM 138, assuming 1 pg was deposited and the certified ^{242}Pu abundance is 0.0330%, the amount of ^{242}Pu that would have been deposited would be 0.33 fg. This also agrees with the LOD determined previously for ^{244}Pu (7 fg). Regarding the analysis of CRM 137, the sample transients of the respective isotopes are shown in **Figure 4.** For CRM 137, the ^{240}Pu and ^{242}Pu have an atom percent of ~19 and ~1, which equates to ~190 and ~10 fg for the respective isotope. These sample transients had slightly more variability, when compared to the transients in **Figure 3**; however, this is not a major concern as the isotope ratio of the Pu is the target measurement. The sample-to-sample %RSD of the ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu was 3.5 and 4.6 % respectively.

Mixed U – Pu analysis

The detection of plutonium in the presence of uranium using mass spectrometry is particularly challenging. Many factors hinder the measurement of ^{239}Pu in the presence of U, including the hydride formation of ^{238}U^{1}H and the high mass peak tailing of ^{238}U onto the ^{239}Pu (abundance sensitivity). Traditionally, chemical separation of the U and Pu using ion exchange resins (e.g. UTEVA and/or TEVA) is performed prior to analysis by ICP-MS to alleviate these interferences[12, 13]. Other research has been devoted to using collision gasses within the mass spectrometer to shift the interfering U away from the Pu measurement mass range. However, if high accuracy and low uncertainty isn't required, the measurement can still be performed with appropriate corrections. Additionally, employment of a high efficiency introduction system can aid in the measurement by decreasing the formation of the ^{238}U^{1}H ion. Here, an extraction of a mixed U/Pu sample was performed. The U (IRMM 2027) was mixed with Pu (CRM 137) prior to being deposited onto the swipe, such that the Pu concentration remained constant at 1 pg and the U concentration varied with concentrations of 0, 1, 5, 10, and 50 ng. While typically a chemical separation is warranted for precise and accurate measurement of these isotopic systems[12, 13], the microextraction-ICP-MS was able to effectively demonstrate its ability to extract both analytes simultaneously, and perform the isotope ratio measurement, albeit with a hindered performance. The results from this experiment are depicted in **Figure 5**. Triplicate analysis of each sample combination was performed, and the resulting measured / certified values are depicted, with the sample-to-sample %RSD depicted by the error bars. It should be noted that no mass bias adjustments were performed due to the relatively low precision associated with the replicate measurements. For U analysis, ($^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$) the results remained reasonably consistent such that the average %RD, in comparison to the certified values, was <3.5 %, <1.5 %, and <5 % for the three isotopic systems, respectively. The sample-to-sample precision, for all extractions, in all three uranium isotopic systems, was <6 %RSD. Regarding the Pu isotopic determinations, unlike the data presented in the previous section, the $^{242}Pu/^{239}Pu$ was unable to be determined as the ^{242}Pu was below the method detection limit (as determined in the presence of uranium). The $^{240}Pu/^{239}Pu$ was determined after correcting for the $^{238}U^{1}H$. The $^{238}U^{1}H$ was monitored by extracting a sample that only contained uranium for nine replicates, and the hydride ratio was determined to be 7.4×10^{-5}. This application of this correction greatly hindered the sample-to-sample precision as shown in **Figure 5**, which plots the $^{240}Pu/^{239}Pu$ measured over certified values. Despite the inherent shortcomings of correcting for the presence of U in a Pu measurement, the rapid and direct microextraction-ICP-MS method was able to achieve a % RD within 7 percent for the $^{240}Pu/^{239}Pu$ CRM. While this value does not include full expanded uncertainty analysis, for reference the IAEA measurement quality goal for ES analysis of $^{240}Pu/^{239}Pu$ ratio in 1 pg total Pu is ≤20 %.[15]

Conclusions

The utilization of a microextraction-ICP-MS method for determining Pu isotope ratios directly from swipe surfaces has been achieved. While traditional bulk swipe analysis requires a complete digestion of the swipe, the microextraction-ICP-MS methodology allows for the extraction of actinides (U and Pu) from the swipe surface directly and delivers the analyte to an ICP-MS for analysis. This method could allow the ability to identify the presence of different isotopic systems that may be present, whereas a bulk digestion method would ultimately homogenize the presence of multiple isotopic compositions. This method could be particularly beneficial for monitoring enrichment activities, especially since spatially resolved analysis across the swipe surface could be achieved. The results presented here demonstrate the microextraction-ICP-MS method to be effective for extracting as little as 1 pg of Pu, while still maintaining accurate isotope ratio measurements for CRM 136, 137, and 138. The ^{240}Pu/^{239}Pu ratio had <2 %RSD and <2 %RD from the certified value for all three standards while the ^{242}Pu/^{239}Pu had <15 %RSD and <10 %RD from the certified value of CRM 136 and 137 (the ^{242}Pu in CRM 138 was below the detection limit). When mixing Pu with a U matrix (100-50,000 × U/Pu) the measurement of the major and minor U isotopics was easily achieved; the ^{240}Pu/^{239}Pu ratio was also determined, albeit with larger uncertainty. Overall, the present results show the effectiveness of this innovative methodology to extract and successfully determine the isotopic composition of Pu on swipe surfaces, particularly at sub-pg levels. Detection limits for the microextraction-ICP-MS method, in conjunction with a high efficiency sample introduction system, X-skimmer cones, and the sector-based ICP-MS were determined to be ~3 pg for ^{238}U and ~7 fg for ^{244}Pu. Future efforts may need to be applied to address potential problems regarding the ability to extract particulates on the cotton swipe surface.

Additionally, the presence of elemental contaminates which could interfere with the isotopic measurement of U and Pu, would need to be evaluated and/or eliminated.

Conflicts of Interest

There are no conflicts of interest to declare.

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FIGURE / TABLE CAPTIONS:

Figure 1. Experimental set-up of the microextraction probe coupled to a sector field-based ICP-MS with a high-efficiency sample introduction system.

Figure 2. Analysis of uranium deposited onto a cotton swipe at difference concentrations (0.02-1 ng) with the microextraction-ICP-MS method with a SSI and APEX introduction systems. The average sample transients are depicted for the SSI (A) and the APEX (B), along with the generated response curve (C).

Figure 3. Analysis of a ^{244}Pu elemental standard deposited onto a cotton swipe at difference loadings (0.13-5.76 pg), by the microextraction-ICP-MS method. The average sample transients of the ^{244}Pu signal are depicted (A), along with the transient from the lowest concentration (inset to A). The generated response curve is also presented (B).

Figure 4. Signal transients for ^{239}Pu, ^{240}Pu, and ^{242}Pu as a result from analysis of 1 pg of CRM 137 deposited on a swipe surface by the microextraction-ICP-MS methodology.

Table 1. Results from the analysis of CRM 136, 137, and 138 by the microextraction-ICP-MS methodology. The certified value is reported with an expanded uncertainty (k=2). The measured value is reported as the standard deviation of the replicate runs. The value in the parenthesis applies to the last digit(s). The % relative difference from the certified value is also reported.

Figure 5. Analysis of a mixed Pu:U sample, containing 1 pg of CRM 137 and different levels (0-50 ng) of IRMM 2027, is reported as the average measured / certified ratio using the standard deviation of the replicate runs. Presented are the isotope ratios of ^{234}U/^{238}U, ^{235}U/^{238}U, ^{236}U/^{238}U, ^{240}Pu/^{239}Pu.

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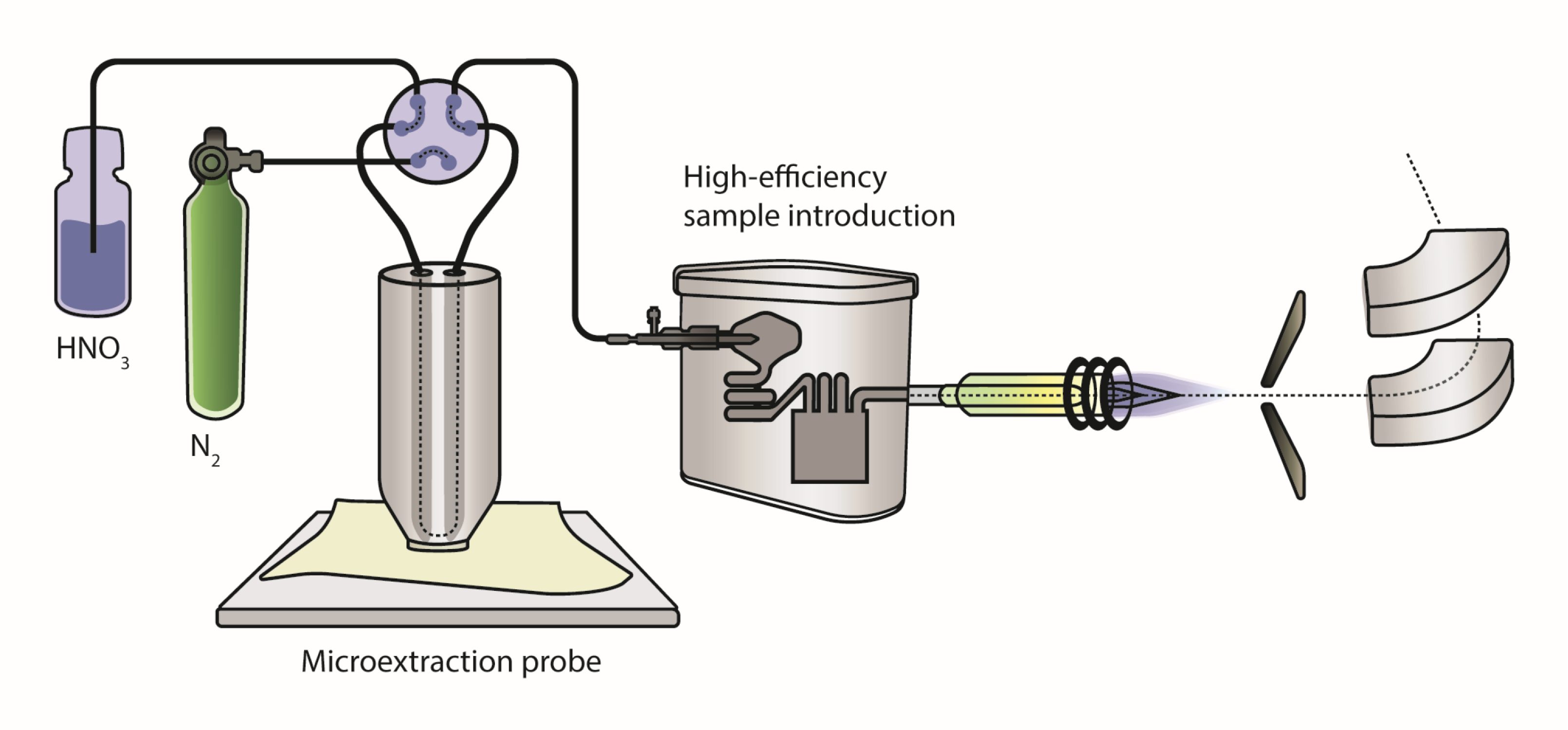
High-efficiency
sample introduction
HNO_3
N_2
Microextraction probe

Figure 1

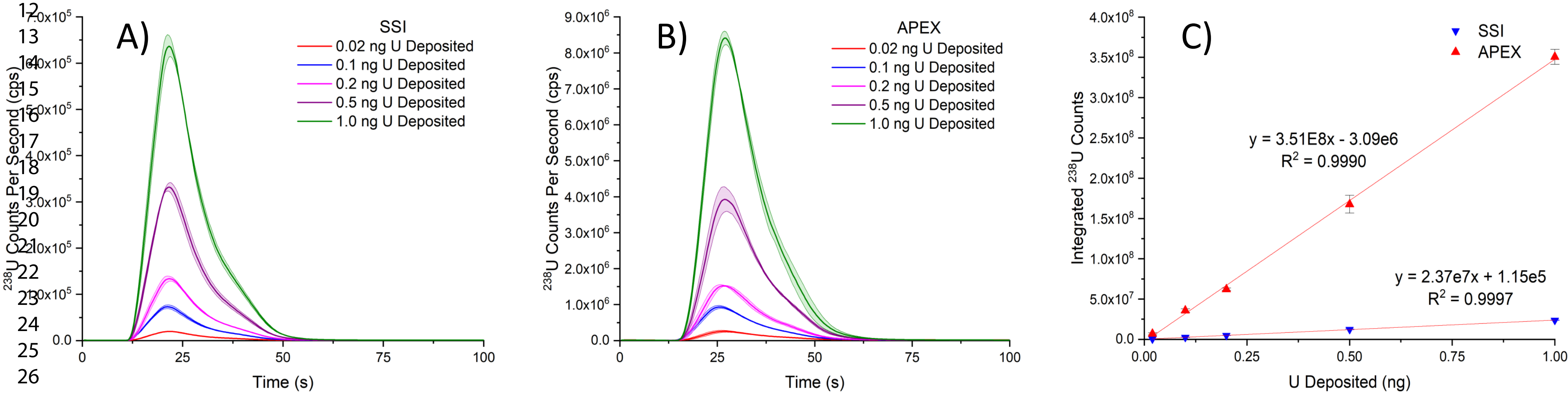
A)
SSI
0.02 ng U Deposited
0.1 ng U Deposited
0.2 ng U Deposited
0.5 ng U Deposited
1.0 ng U Deposited
^{238}U Counts Per Second (cps)
7.0x10^5
6.0x10^5
5.0x10^5
4.0x10^5
3.0x10^5
2.0x10^5
1.0x10^5
0.0
0
25
50
75
100
Time (s)
B)
APEX
0.02 ng U Deposited
0.1 ng U Deposited
0.2 ng U Deposited
0.5 ng U Deposited
1.0 ng U Deposited
^{238}U Counts Per Second (cps)
9.0x10^6
8.0x10^6
7.0x10^6
6.0x10^6
5.0x10^6
4.0x10^6
3.0x10^6
2.0x10^6
1.0x10^6
0.0
0
25
50
75
100
Time (s)
C)
SSI
APEX
y = 3.51E8x - 3.09e6
R^2 = 0.9990
y = 2.37e7x + 1.15e5
R^2 = 0.9997
Integrated ^{238}U Counts
4.0x10^8
3.5x10^8
3.0x10^8
2.5x10^8
2.0x10^8
1.5x10^8
1.0x10^8
5.0x10^7
0.0
0.00
0.25
0.50
0.75
1.00
U Deposited (ng)

Figure 2

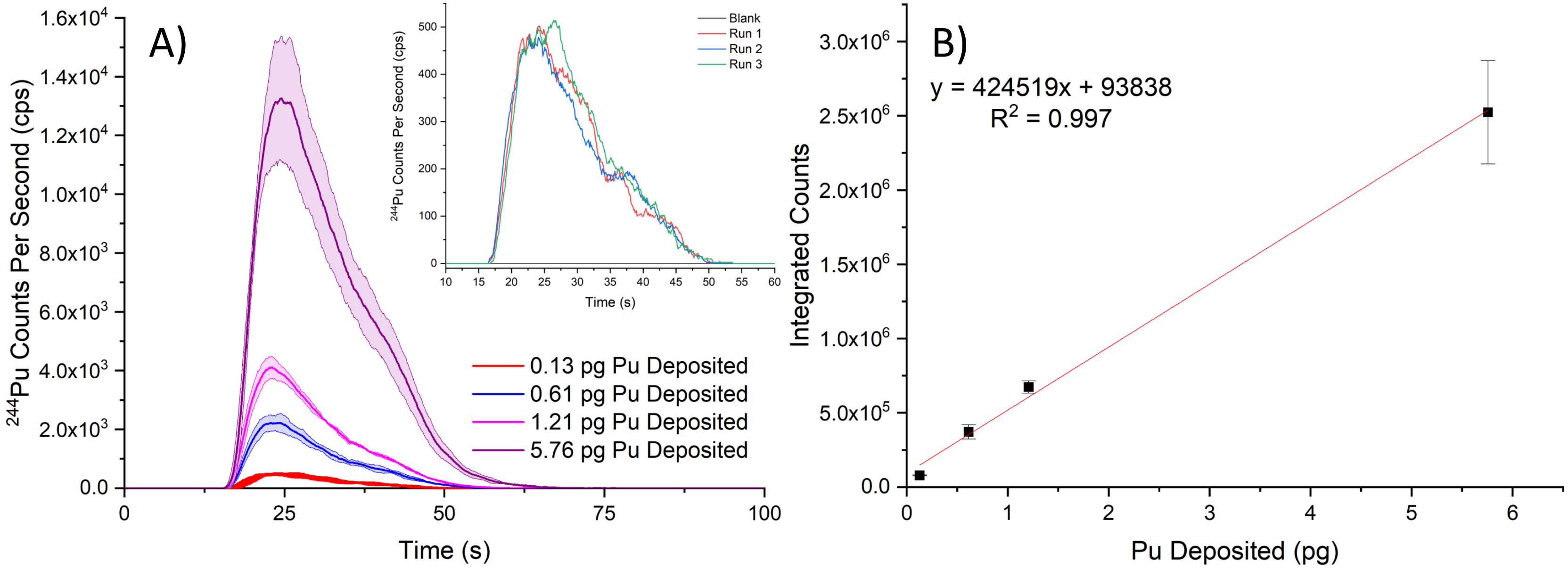
A)
1.6x10^4
1.4x10^4
1.2x10^4
1.0x10^4
8.0x10^3
6.0x10^3
4.0x10^3
2.0x10^3
0.0
^{244}Pu Counts Per Second (cps)
0
25
50
75
100
Time (s)
0.13 pg Pu Deposited
0.61 pg Pu Deposited
1.21 pg Pu Deposited
5.76 pg Pu Deposited
^{244}Pu Counts Per Second (cps)
500
400
300
200
100
0
10
15
20
25
30
35
40
45
50
55
60
Time (s)
Blank
Run 1
Run 2
Run 3
B)
y = 424519x + 93838
R^2 = 0.997
3.0x10^6
2.5x10^6
2.0x10^6
1.5x10^6
1.0x10^6
5.0x10^5
0.0
Integrated Counts
0
1
2
3
4
5
6
Pu Deposited (pg)

Figure 3

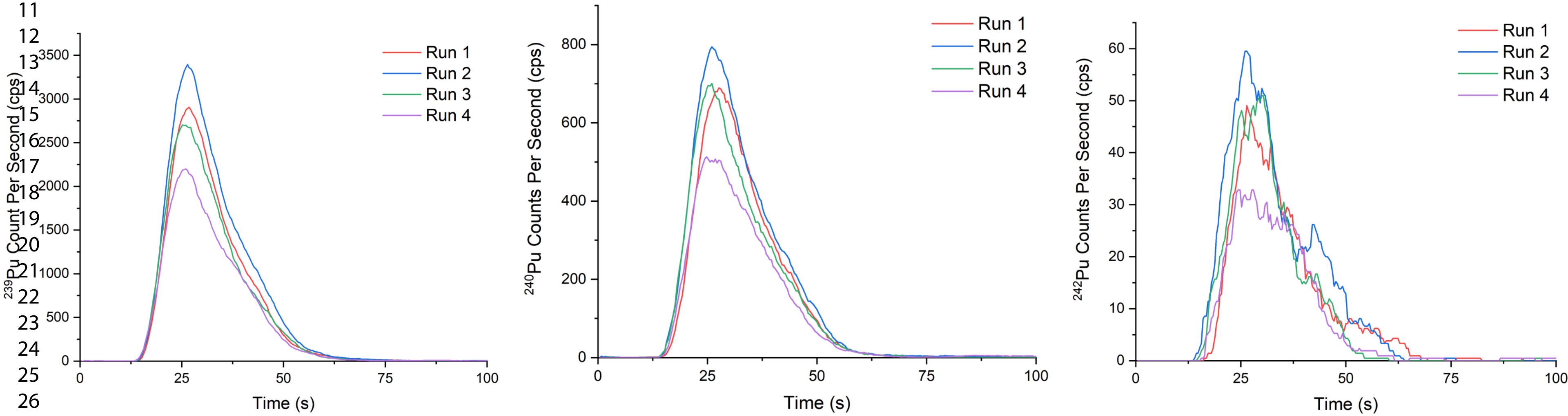
^{239}Pu Count Per Second (cps)
0
500
1000
1500
2000
2500
3000
3500
Time (s)
0
25
50
75
100
Run 1
Run 2
Run 3
Run 4
^{240}Pu Counts Per Second (cps)
0
200
400
600
800
Time (s)
0
25
50
75
100
Run 1
Run 2
Run 3
Run 4
^{242}Pu Counts Per Second (cps)
0
10
20
30
40
50
60
Time (s)
0
25
50
75
100
Run 1
Run 2
Run 3
Run 4

Figure 4

	$^{240}Pu/^{239}Pu$			$^{242}Pu/^{239}Pu$		
CRM	**Certified Value**	**Microextraction-ICP-MS**	**% RD**	**Certified Value**	**Microextraction-ICP-MS**	**% RD**
136	0.14463(23)	0.1462(46)	1.06	0.006801(35)	0.0074(11)	8.11
137	0.240688(37)	0.2442(84)	1.48	0.015599(52)	0.01709(78)	9.58
138	0.086097(12)	0.0880(33)	1.93	0.0003595(33)	<DL	NA

Table 1

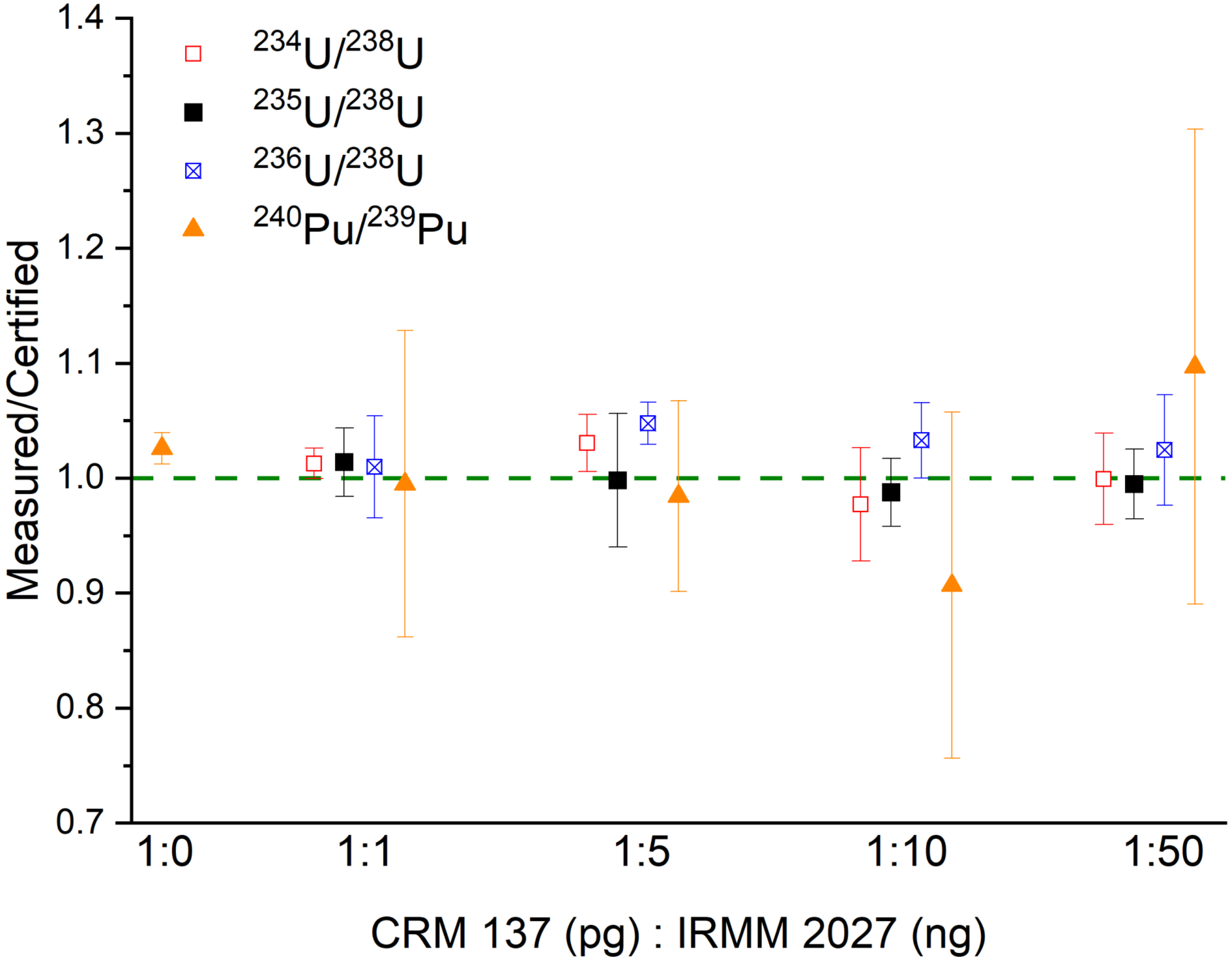
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
Measured/Certified
$^{234}U/^{238}U$
$^{235}U/^{238}U$
$^{236}U/^{238}U$
$^{240}Pu/^{239}Pu$
1:0
1:1
1:5
1:10
1:50
CRM 137 (pg) : IRMM 2027 (ng)

Figure 5