Analytical Methods

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Journal:	*Analytical Methods*
Manuscript ID	AY-ART-08-2022-001394.R1
Article Type:	Paper
Date Submitted by the Author:	24-Oct-2022

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Analysis of solid uranium particulates on cotton swipes with an automated microextraction-ICP-MS system

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Manuscript to be submitted to *Analytical Methods*

Abstract

An automated microextraction method coupled to an inductively coupled plasma – mass spectrometer (ICP-MS) was developed for the direct analysis of solid uranium particulates on the surface of cotton swipes. The microextraction probe extracts particulates from the sample surface, in a flowing solvent, and directs the removed analyte to an ICP-MS for isotopic determination. The automated system utilizes a mechanical XY stage that is software controlled with the capability of saving and returning to specific locations and a camera focused to the swipe surface for optimal viewing of the extracted locations (i.e., material present). Here, particulates (n=135) were extracted and measured by ICP-MS, including 35 depleted uranyl nitrate hexahydrate (UN) (used for mass bias corrections), 50 uranyl fluoride (UO_2F_2), and 50 uranyl acetate (UAc) particulates. Blank extractions were performed on the cotton swipes between triplicate sample analyses. Between each swipe extraction, the probe was sent between two wells containing 10% and 5% HNO_3 to clean the probe head and to eliminate any analyte carryover between particulates. The measured $^{235}U/^{238}U$ and $^{234}U/^{238}U$ isotope ratios for the UO_2F_2 particulates were 0.00725(8) and 0.000054(4), a percent relative difference (% RD) of -0.041% and -1.7% from the reference isotope ratios determined in-lab through multi-collector ICP-MS analysis of dissolved aliquots of the U material. The UAc samples had a measured $^{235}U/^{238}U$ isotope ratio of 0.00206(7), a -0.96% relative difference from the reference value of 0.00208(1). The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios were 0.000008(1) and 0.000031(4), -5.1% RD and -4.3% RD, respectively. The automated sample stage enabled seamless and rapid particle analysis, leading to a significant increase in throughput versus what was previously possible. Additionally, the saved location capability reduced user sampling error as sampling locations were easily stored and recalled. Analysis of U particles on the swipe surface – including blanks, mass bias, and triplicate extractions– was completed in less than an hour without any sample preparation necessary.

Introduction

Much effort in modern analytical chemistry is focused on increasing the speed of analysis and sample throughput while minimizing sample handling and this is especially true in nuclear analytical chemistry disciplines such as forensics and safeguards[1-4]. Automation has been increasingly explored in nuclear laboratories as a way of increasing sample throughput and minimizing personnel radiation exposure[5]. Our laboratory has placed an emphasis on automated and rapid analytical methods for analyzing trace elements in bulk uranium / thorium samples[6-9], analyzing trace fission products in a variety of complex radiological matrices[10-13], and separating U and Pu in environmental swipe samples [14]. Particle analysis methods, utilized in a host of nonproliferation and safeguards activities, are also being improved by automation. Large geometry secondary ion mass spectrometers (LG-SIMS) can employ an automated screening process, called automated particle measurement (APM) which decreases the time required to sort through large numbers of particles[1, 15-19]. Automated secondary electron microscopy systems, like TESCAN integrated mineral analyzer (TIMA), have been used to map samples and can obtain chemical and textural information for a 1 cm^2 section of a geological sample in 30 minutes[20-22]. These improvements in automation have proven to be beneficial to nuclear safeguards programs by increasing sample throughput and decreasing personnel required for sample analyses while maintaining low measurement uncertainties.

These methods can also be directly applied to the analysis of environmental sample (ES) swipes. The International Atomic Energy Agency (IAEA) collects environmental samples (commonly utilizing cotton swipes) during on-site safeguards inspections of nuclear facilities. These samples are then sent to members of the IAEA's international Network of Analytical

Laboratories (NWAL) for analysis[23]. The swipe samples collect trace particles of nuclear material present in a facility which may be indicative of the types of activities and material present (i.e. enrichment, reprocessing, etc). Actinide-containing particles from IAEA swipes are often analyzed with LG-SIMS, or fission track thermal ionization mass spectrometry (FT-TIMS). FT-TIMS is a laborious process where particles are irradiated to identify those with appreciable amounts of fissile material, which are then loaded onto tungsten filaments for TIMS analysis. It requires access to a neutron source, typically a nuclear reactor, and can take weeks or months to isolate and then measure particles of interest[24, 25]. LG-SIMS were first implemented by the IAEA for environmental swipe samples in 2011, and have since become a utilized technique for particle analysis as they can achieve high mass resolution compared to compact SIMS instruments without reduction in sensitivity, and are usually fitted with multiple detectors[1]. One drawback to SIMS analysis is the formation of polyatomic interferences, in particular the ^{236}U signal can be affected by $^{235}U^{1}H$[1, 26]. Both FT-TIMS and LG-SIMS requires removing particles from the surface of a swipe sample before analysis, which runs the risk of missing particles or losing them in the transfer process. Laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) is being explored as a direct sampling alternative to TIMS and SIMS measurements[27-31]. It has been shown effective for measuring uranium and plutonium isotope ratios for particles on the order of 1 μm in diameter, with uncertainty varying depending on the type of ICP-MS used for the measurement, with multi-collector (MC) ICP-MS experiments reporting uncertainty much lower than that reported by single-collector instruments[28, 31, 32]. Explorations of LA- time of flight (TOF)-ICP-MS have shown even better precision than uranium isotope ratios obtained through LA-MC-ICP-MS, but may be limited by sensitivity and dynamic range[30].

A different direct analysis technique, microextraction-ICP-MS, has been explored for the measurement of uranium and plutonium isotope ratios on simulated ES swipes[33-35]. Marcus et al. analyzed U, deposited as solution residues, on swipes with a microextraction system coupled to a liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma[36] ionization source and an orbitrap mass spectrometer[35]. Regarding the microextraction-ICP-MS methodology, major and minor U isotope ratios of several certified reference materials were extracted from a cotton swipe containing deposited U solution, and preliminary detection limits were determined to be ~50 pg for ^{238}U[34]. Pu isotope ratios were determined on a cotton swipe by microextraction integrated with a sector field ICP-MS, and with detection limits for Pu in the sub-pg range[33]. Microextraction was also proven to successfully determine uranium isotope ratios for solid particulates of uranyl nitrate and uranyl fluoride placed on the surface of a cotton swipe[37]. The external precision (EP) of these measurements ranged from 1% for the $^{235}U/^{238}U$ ratio to 10% for the $^{234}U/^{238}U$ ratio. A major constraint to increasing throughput with this method is the difficulty in positioning the microextraction probe head directly over a small particulate that is only a few μm in diameter. The ultimate goal of the microextraction system is to develop a method capable of analyzing the entirety of the swipe by rastering across the surface with the probe head.

In the present work, 100 particulates, including 50 uranyl fluoride (UO_2F_2) and 50 uranyl acetate (UAc), were analyzed using an automated microextraction ICP-MS system with programmable location memories. Particulates of depleted uranyl nitrate hexahydrate (UN) were used for mass bias corrections. The automated system was evaluated for its accuracy in sampling particular swipe locations and its ability to increase sample throughput in comparison to the manual positioning previously employed[37]. The uncertainty of the quadrupole ICP-MS isotope ratio measurements was also evaluated with larger sample sizes compared to previous work[33, 34, 37].

Materials and Methods

Materials, Reagents, and Sample Preparation

All dilutions were performed with Optima™ grade nitric acid (HNO_3) from Fisher Scientific (Pittsburgh, PA, USA) diluted by volume with ASTM Type I water (18.2 MΩ-cm) generated from a Barnstead™ xCAD Plus ultrapure water purification system (Waltham, MA, USA. Reagent grade $UO_2(NO_3)_2 \cdot 6H_2O$ and UO_2F_2 were obtained from International Bioanalytics (Boca Raton, FL, USA) and $UO_2(CH_3CO_2)_2 \cdot 2H_2O$ was sourced from SPI Supplies (Structure Probe, Inc., West Chester, PA, USA). Sample particulates were transferred to pre-marked locations on cotton swipes (Texwipe TX304 10 × 10 cm, Kernersville, NC, USA) using an AxisPro Microsupport micromanipulator (Shizuaka City, Shizuaka, Japan) with two 1 µm tungsten probes. The micromanipulator housed within a glass enclosure to maintain the cleanliness of the swipe and preparation. Optical images of deposited particulates were obtained using the camera of the micromanipulator to estimate the size of individual samples.

Multi-collector ICP-MS Analysis of Uranium Compounds

Uranium isotopic analyses were performed on a Thermo Scientific Neptune *Plus* (Bremen, Germany) double focusing, multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). This MC-ICP-MS is equipped with ten Faraday cups, three secondary electron multipliers (SEM) and two compact discrete dynodes and was used for analysis of $^{234}U/^{238}U$,

$^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotopic ratios. The instrument is outfitted with an Apex Omega high efficiency introduction system (Elemental Scientific Inc., Omaha, NE, USA) using a nickel jet sample cone and a nickel X skimmer cone. The uranium analyses were made using a 10^{-11} **Ω** amplifier resistor on ^{238}U while the ^{234}U, ^{235}U and ^{236}U isotopes were measured using secondary electron multipliers. Throughout the analytical session, isotopic reference materials from the European Commission, Joint Research Centre-Geel [JRC-Geel, formally the Institute for Reference Materials and Measurements (IRMM)] were analyzed, bracketing the samples to correct for instrumental mass bias (IRMM-2025) and as quality controls (IRMM-2020 and IRMM-2022). Instrumental mass bias effects on samples and standards were corrected by direct comparison against IRMM-2025. Corrections were also made for instrumental blank and hydride contributions. The U isotopic measurements by MC-ICP-MS were used to define the reference isotopic ratio for the particle analyses. This was achieved by dissolving to represent the “true” U isotopic composition.

Automated Microextraction Device

A ProScan Motorized XY Stage (Prior Scientific, Rockland, MA, USA), with a travel distance of 154 × 154 mm and 40 nm step-resolution was fitted with an Advion Plate Express (Ithaca, NY, USA) TLC plate reader and a Keyence CA-H500C Vision System Camera (Itasca, IL, USA) to enable automated sampling of cotton swipes, with real-time visual inspection of the sample area. This stage has the capability to be operated with joystick or PC remote control (utilized for the studies here). The experimental set-up can be seen in **Figure 1**.

Insert Figure 1

To adapt the XY stage to the Plate Express®, it was necessary to remove the base of the Plate Express® and extend the housing. Dimensional information from the Plate Express® was documented for placement of the plate reader and the electronic and pneumatic controls and circuits in an extended housing. The top, sides, and base of the Plate Express were removed, modified parts for these elements were designed, fabricated, and installed, and the Plate Express control boards and circuitry were incorporated into the new housing.

The new housing for the Plate Express and the ProScan XY stage was mounted on a large aluminum base, which physically linked the two elements for precision alignment and operation. In addition, the Keyence CA-H500C was mounted to the same base via vertical supports and a crosspiece, which held the SL20/M (ThorLabs, Newton, NJ, USA) articulating base. The crosspiece could be moved in the Y-axis, while the mount for the SL20/M could be moved in the Y-axis.

A sample holder (**Figure 2**) was designed and fabricated and was inset into the center of the XY stage. The sample holder is composed of four parts 1) a polyetheretherketone (PEEK) base mounted on the XY stage, 2) a PEEK insert which fit into the base, 3) a PEEK surround used to hold the cotton swipe on 4) a Teflon insert centered within the surround which fits closely inside the insert. Two wells were engraved in the PEEK base to hold HNO_3 for probe rinsing. The rinsing wells have a diameter of 16 mm and a depth of 1.5 mm and hold 400 μL of acid. The first well was filled with 10% and the second with 5% HNO_3.

Insert Figure 2

The ProScan XY stage was controlled using 64 Bit Prior Scientific DLL SDK proprietary software, which allowed for control of the stage using a sub-routine in the software. Specific points on the XY stage can be set in the software and retained in memory for revisiting the points in a given sampling plan. For example, in this procedure, coordinates were set for each washing well, and for all 25 sample locations on the swipe surface, so the probe could be sent immediately to the appropriate extraction location. The Plate Express was controlled with software from Advion, which activated both an area light for the sample, an indicating laser for the sample point, and raised and lowered the sampling head. The sampling head pressure was set to 300 N, and the extraction time set to 30 seconds. The Keyence Vision System Camera was controlled using Micro-Manager 2.0.0 Open-Source Microscopy Software.

Microextraction-ICP-MS Analysis of Solid Sample Particulates

The automated microextraction device was integrated to a Thermo Scientific (Bremen, Germany) iCAP TQ triple quadrupole ICP-MS. The microextraction probe applies 300 N of force on the surface of the swipe, forming a seal. The extraction solvent of 5% HNO_3 flows at a rate of 0.2 mL min^{-1} through the probe, extracting the U particulates from the surface and carrying them into the ICP-MS nebulizer. After extraction, the probe head is cleaned by performing extractions first in a well containing 10% HNO_3 and then in a well containing 5% HNO_3. The cleaning extractions were performed 3 times between samples, defined in this work as a single location on the swipe surface containing a particulate (or particulates) of solid U, until the U count rates in the cleaning extractions returned to background levels. Blank analyses were performed by extracting the swipe surface with no particulates present. The microextraction probe was integrated to the ICP-MS via a PFA concentric nebulizer housed within a Peltier cooled glass cyclonic spray chamber. The nebulizer gas flow rate was predetermined via instrument tuning to be 1.2 mL min^{-1}. The ICP-MS was operated in kinetic energy discrimination mode, with a He gas flow rate of 4.65 mL min^{-1} and a dwell time of 0.01 s for ^{234}U, ^{235}U, ^{236}U, and ^{238}U.

The transient signal was integrated in the Qtegra software using the ICIS peak detection algorithm. The integrated total counts under the peak were used to determine the isotopic abundances[38]. The mass bias correction was applied to each isotopic system, utilizing the known comparator value from a calibration standard, using equations described by Mathew et al[39]. External precision (EP) was used in this work to describe the variation in isotope ratios in the population of measured particles (standard deviation of the 50 particulates). Internal precision (IP) describes the propagated uncertainty of a single isotope ratio measurement and is calculated from 2× the relative standard deviation of all mass bias measurements from a given analysis day and the percent relative difference (% RD) of the measured mass bias sample and its expected value. The % RD is defined as the percent difference of the measured isotope ratio to a reference value, which in this work was the isotope ratio measured via solution-based MC-ICP-MS.

Each environmental swipe was pre-stamped in a 5 × 5 grid to mark sample locations where the first position in each row was a blank spot followed by a mass bias reference particle and the subsequent three spots were triplicate samples of the same material (either UO_2F_2 or UAc). The automated XY stage was programmed to have all 25 stage locations saved, so the stage can rapidly center each location as needed. The automated stage allowed for rapid sample measurements, and therefore a much larger sample size (100 particulates compared to 20) in a similar total analysis time compared to the previous manual method. The ability to return to the same pre-programmed locations reduced human error in lining up the swipe with the probe head, eliminating the possibility of missing particulates due to misalignment of the probe with the swipe surface.

Results and Discussion

Particle Mass Considerations

Particle images collected during micromanipulation were imported into the FIJI software suite[40] and converted to monochromatic images using the "split channels" function. For each image, the blue channel had the sharpest contrast and was thus chosen for particulate measurements. Scale bars from the original micromanipulator images were used to create an internal scale within FIJI. Image thresholds were adjusted and applied to segment particles from background. An example of each uranium particulate (UO_2F_2 and UAc) placed onto the swipe, with the subsequent segmented image, can be seen in **Figure 3**. The "analyze particles" function in FIJI was used to determine the area of each particulate that was visible in the image. Although likely an overestimation, 50% of the area calculated for each particle was chosen as an approximation of the particle depth. It is highly unlikely that the longest dimension of the particulates is orthogonal to the field of view, e.g., anisotropic particles are likely to orient themselves parallel to the two dimensional plane with the largest area [41], therefore, this is a justified assumption. Following volume estimations from particle size measurements, experimentally determined densities for each material of interest were used to calculate approximate particulate masses [42-44]. The approximate uranium content for each particulate was then determined using the weight percent uranium obtained from the formulae for each phase. For example, the particulate in **Figure 3a** (UO_2F_2) has a visible area of 45 μm^2 and a calculated mass of 5 ng. The particulate in **Figure 3b** (UAc) has a visible area of 88 μm^2 and a calculated mass of 9 ng.

Insert Figure 3.

The estimated particulate mass was plotted against the log of the total measured ^{238}U signal integrated under the peak and presented in a logarithmic scale for 95% of the particles (**Figure 4**). The particles that were excluded (5% of the population) had a signal significantly different than the visible area of the particle would indicate. It is hypothesized that these particles may not have oriented themselves as expected, and therefore the volume of the particles were larger than estimated. There is indeed a positive correlation between the mass of the particulate and the measured U signal. While the correlation shouldn't be considered strong, this is likely due to the volume estimation not being completely accurate. Particulates with different depths but the same length and width would be considered the same size in this estimation, but if one particle has a higher depth it should also have a higher signal. For example, for a particulate with a measured area of 100 μm^2, the estimated depth of the particle would be considered 50 μm, as that is half of the area, leading to a mass estimation of 32 ng. If, however, the actual depth of the particulate was a quarter of the measured area, 25 μm, the mass of the particle would then be 16 ng, leading to a much different U signal after ICP-MS analysis. Figure 4 shows that the particulate mass calculation is a useful but imperfect way of estimating the amount of U measured by microextraction.

Insert Figure 4

Isotope Ratio Measurements

Accurately determining U isotope ratios is important for IAEA safeguard inspections, as measured ratios that deviate from those reported by the facility could indicate the presence of undeclared activities or material. Here, UO_2F_2 and UAc particulates were evaluated for their isotopic composition. For the UO_2F_2 samples, the measured $^{235}U/^{238}U$ ratio was 0.00725(8) which had a -0.041 % RD from the reference value of 0.007248(2) and an EP of 1%. Regarding a comparison to a previous study utilizing microextraction-ICP-MS for uranium particulate analysis, the %RD was improved by ~10×, while the EP did not change[37]. One possible factor in the improvement in % RD for this study was the increase in sample throughput that allowed for a much larger sampler size. Additionally, the increased sample throughput allowed for a mass bias measurement after every three sample measurements while the previous study only performed one mass bias per day, and the mass bias samples were actual particles as opposed to deposited solutions. These factors may have led to a more accurate mass bias correction in this study. **Figure 5** shows the measured isotope ratios for each individual sample in order from smallest to largest estimated U load, along with the average ratio and the reference value. A 2σ outlier test was performed on the data set, and samples with isotope ratios that fell outside the 2σ range were excluded, and the average and standard deviation of the isotope ratios were recalculated. A total of 2 data points were rejected for the ^{234}U/^{238}U isotope ratio, and none were rejected for the ^{235}U/^{238}U ratio. The estimated mass of U in each sample ranged from 2 ng to 200 ng, meaning that the mass of ^{235}U ranged between 10 pg and 1000 pg. There is not a significant difference in the isotope ratio measurements based on the particulate size, with the smaller particulates having a similar spread in precision and deviation from the reference ratio compared to the larger U deposits. This shows that the estimated masses of U extracted are above the limit of quantitation for this method. The measured ratio for ^{234}U/^{238}U was 0.000054(4) with a -1.7% RD from the reference value of 0.0000546(1). The EP of the ^{234}U/^{238}U ratio was 7%. The mass of ^{234}U deposited ranged from 0.1 pg to 10 pg. The ^{236}U signal was 20× lower than the ^{234}U signal and fell below quantitation limits for the majority of samples, and therefore was not included in this study.

Insert Figure 5

The average measured UAc isotope ratio for ^{235}U/^{238}U was 0.00206(7) and is shown in Figure 6. It has a -0.96% RD from the reference value (0.002080(1)) and an EP of 4%. The ^{234}U/^{238}U ratio was 0.000008(1) with an EP of 15% and a -5.1% RD from the reference value of 0.00000860(7). The ^{236}U/^{238}U isotope ratio was found to be 0.000031(4) with an EP of 13% and a -4.3% RD from the reference value of 0.0000323(2). The estimate of the deposited U mass ranged from 0.1 ng to 300 ng, and over half of the samples had a U load of less than 10 ng. The ^{234}U mass load was between 0.001 pg and 3 pg, the ^{235}U mass was between 0.2 pg and 600 pg, and the ^{236}U mass load ranged from 0.004 pg to 10 pg. A 2σ outlier test was performed as above. For the ^{234}U/^{238}U ratio two data points were rejected for falling outside 2σ and two others were not included as the ^{234}U signal was below detection limits. Two outliers were rejected from the ^{235}U/^{238}U data set, and three were rejected from the ^{236}U/^{238}U data set. The UO_2F_2 samples had better precision and accuracy compared to the UAc for the ^{235}U/^{238}U ratio especially, because the UO_2F_2 samples are natural abundance while the UAc samples are depleted, so there was a higher ^{235}U count rate for UO_2F_2, leading to improved counting statistics. Also, the U mass load was on average much higher for the UO_2F_2 samples, which likely lead to lower EP and % RD compared to the samples with UAc.

Insert Figure 6

Sample Washout

After each sample extraction a series of extractions were performed in wash stations located to the side of the sample holder. The wash stations consisted of a well containing 10% HNO_3 and one with 5% HNO_3. The probe alternated between the two for 3 wash cycles (6 total washing extractions). The ICP-MS detected U signal in the washes, which dropped significantly from the sample to the first wash and decreased even further over the course of the subsequent washes. By the final wash the total uranium counts detected in the wash station were approximately 0.01% of the counts detected for a particle extraction. This shows that there is some amount of uranium that remains in the probe head and tubing after an extraction of a uranium particle, and the probe head must be cleaned before another particle can be extracted without impacting the isotope ratio measurement of the subsequent particle. **Figure 7** shows each of the washes for every sample as a % of uranium counts from the previous particle extraction. A 5-point boxcar smoothing applied, and the x-axis shows the averaged % of uranium counts detected during probe washing extractions as a continuum, with the two uranium compounds separated to explore differences in the speed of uranium washout between the two compounds. The UO_2F_2 appears to wash out faster than the UAc. For UO_2F_2 the first wash contained on average 0.8% of sample signal, while the UAc samples averaged 2% of counts in the first wash. By the 3rd wash the U signal drops to an average of 0.04% for UO_2F_2 and 0.08% for UAc, and by the 6th wash both U compounds averaged 0.01% of counts. Based on this data, 3 washes are likely sufficient to eliminate any U carryover effects from the previous sample extraction. The additional decrease of < 0.1% between the 3rd wash and the 6th wash would not likely impact the isotope ratio measurement enough to justify doubling the wash time between each sample.

Insert Figure 7

The automated sampling stage greatly improves sample washout time and ease over the previous incarnation of the microextraction system. The wash wells on the translation stage contain a pool of acid in which the probe head is submerged, leading to faster rinse out than the previous method where the washout was performed on a Teflon pad after the removal of the swipe matrix. Having wash locations separate from the sample location, made possible by the addition of the automated, moveable sample stage, allowed for the performance of rinse extractions without removing the sample.

Conclusions

The newly developed mechanical stage succeeded in decreasing analysis time and reducing sampling error compared to a manual microextraction system. The current automated set-up processed a total of 15 samples along with 5 mass biases and 5 blanks in a single sequence in approximately 4.7 h. As 100 samples were analyzed in this study, the total time required to complete data collection was approximately 30 h. The probe washout wells enabled faster sample washout, only 3 wash extractions needed to reduce U signal to 0.04% of UO_2F_2 sample signal, and 6 wash extractions required to return the system to background prior to the measurement of the following sample. The $^{235}U/^{238}U$ isotope ratio was 0.00725(8) and 0.00206(7) for UO_2F_2 and UAc, respectively. The UO_2F_2 ratio had a % RD of -0.041% and the UAc had a % RD of -0.96%. The $^{234}U/^{238}U$ isotope ratio was 0.000054(4) and 0.000008(1) for UO_2F_2 and UAc, respectively. This method succeeded in measuring 100 U particulates rapidly, with good accuracy and precision. In the future, the precision of the isotope ratio measurements could be improved by connecting the microextraction system to a MC-ICP-MS.

Acknowledgements

This work was supported by the Department of Energy’s National Nuclear Security Administration under contract DE-AC05-000R22725 with UT-Batelle, LLC. Oak Ridge National Laboratory is managed by UT-Batelle for the Department of Energy under contract DE-AC-05-000R22725. The authors would like to acknowledge Jaimee Janiga (ORNL) for the assistance with graphics.

Figure Captions

1. Experimental set up for the automated microextraction system, including a mechanical XY stage containing two washing wells, a sample holder fitted with a swipe loaded with particulates in a 5 x 5 grid; a microextraction probe head with a switching valve, a camera, and a laptop with the software to control the different components
2. Swipe sample holder composed of a PEEK base (1) with a 10.4 x 10.4 cm inset which houses a PEEK insert (2), a PEEK clamp (4) which is used to hold a cotton swipe onto a square Teflon insert (3).
3. Image of deposited UO_2F_2 (A) and UAc (B) particulates with their respective converted monochromatic images.
4. Plot of total ^{238}U signal as a function of particle size for samples of UN (red square), UO_2F_2 (blue circle), and UAc (black triangle) samples.
5. Measured UO_2F_2 isotope ratios for $^{234}U/^{238}U$ (left) and $^{235}U/^{238}U$ (right). The blue dashed lines represent average measured isotope ratio ± 2σ. The black solid line denotes reference isotope ratio. Error bars on individual particles is the IP of the measurement, based on the expanded relative uncertainty of the mass bias measurements.
6. Measured UAc isotope ratios for $^{234}U/^{238}U$ (left), $^{235}U/^{238}U$ (center) and $^{236}U/^{238}U$ (right). The blue dashed lines represent average measured isotope ratio ± 2σ, the black solid line denotes reference isotope ratio. Error bars on individual particles is the IP of the measurement, based on the expanded relative uncertainty of the mass bias measurements.
7. Plot of the ^{238}U % carryover in various subsequent washing steps (1-6) for the UO_2F_2 (left) and UAc (right) samples with a moving average smoothing applied.

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