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Automated Clean Chemistry for Bulk Analysis of Environmental Swipe Samples – FY17 Year End Report

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OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

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Chemical Sciences Division

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ACRONYMS

ASTM	American Society for Testing and Materials
COTS	commercial off the shelf
CRM	Certified Reference Material
ESI	Elemental Scientific Incorporated
HRICPMS	high-resolution inductively coupled plasma mass spectrometer
IAEA	International Atomic Energy Agency
ICPMS	inductively coupled plasma mass spectrometer
IDMS	isotope dilution mass spectroscopy
IRMM	Institute for Reference Materials and Measurements
ISO	International Standards Organization
JCR-EC	Joint Research Center of the European Commission
LDPE	low density polyethylene
M/C	measured/certified
MCICPMS	multi-collector inductively coupled plasma mass spectrometer
MCTIMS	multi-collector thermal ionization mass spectrometer
NIST	National Institute of Standards and Technology
NWAL	Network of Analytical Laboratories
ORNL	Oak Ridge Nation Laboratory
PFA	perfluoroalkoxy alkane
PSI	pounds per square inch
SEM	scanning electron microscope
SOP	standard operating procedure
SRM	Standard Reference Material
ULPA	ultra-low penetration air

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EXECUTIVE SUMMARY

Sample preparation methods for mass spectrometry are being automated using commercial-off-the-shelf (COTS) equipment to shorten lengthy and costly manual chemical purification procedures. This development addresses a serious need in the International Atomic Energy Agency's Network of Analytical Laboratories (IAEA NWAL) to increase efficiency in the Bulk Analysis of Environmental Samples for Safeguards program with a method that allows unattended, overnight operation. In collaboration with Elemental Scientific Inc., the prepFAST-MC2 was designed based on COTS equipment. It was modified for uranium/plutonium separations using renewable columns packed with Eichrom TEVA and UTEVA resins, with a chemical separation method based on the Oak Ridge National Laboratory (ORNL) NWAL chemical procedure. The newly designed prep*FAST*-SR has had several upgrades compared with the original prep*FAST*-MC2. Both systems are currently installed in the Ultra-Trace Forensics Science Center at ORNL.

Initial verification experiments yielded small elution volumes, consistent elution profiles, ample separation, and good recovery without cross-contamination of the eluent. Separations of mixed uranium and plutonium samples containing certified reference materials were analyzed by multi-collector inductively coupled plasma mass spectrometry and yielded good results. Current efforts have demonstrated a wider applicability of the prep*FAST* system. Near-quantitative removal of metal interferences was achieved with the system in both uranium and plutonium separated fractions. Successful system validation was completed with several archived samples. Isotopic results from archived samples and certified reference materials were well within data quality limits for the IAEA NWAL. Additional COTS equipment has been evaluated for its potential to aid the prep*FAST*-SR system in reducing the time allotments and clean room infrastructure requirements for accurate separations. Overall, these efforts help ensure continued efficient and effective operation of the NWAL.

1. INTRODUCTION

Environmental swipes are one type of sample that the International Atomic Energy Agency (IAEA) may collect during inspections of facilities under safeguards to verify compliance with declared nuclear activities.[1] Bulk analysis is a particular form of destructive analysis that is performed on an entire swipe sample. It uses high-precision mass spectrometry of purified samples to measure the isotopic composition and concentration of the actinide elements, particularly uranium (U) and plutonium (Pu) collected on the swipe. Bulk analysis produces very accurate and precise data, but the chemical separations required to produce the purified samples are labor intensive and require significant laboratory infrastructure. The IAEA depends heavily on its Network of Analytical Laboratories (NWAL) to support the Bulk Analysis of Environmental Samples for Safeguards program. Timeliness and efficient sample processing are important for the NWAL facilities. Typical characteristics of collected field samples are 1 ng to 10 mg U per swipe and <1 ng Pu per swipe. The Measurement Quality Goals set forth by the IAEA for the bulk analysis program are a ≤2% relative expanded uncertainty for $^{235}U/^{238}U$ and ≤20% for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ at >10 ng U and ≤20% for all Pu isotope ratios at >1pg at a 95% confidence level.[2]

Multi-collector inductively coupled plasma mass spectrometry (MCICPMS) or multi-collector thermal ionization mass spectrometry (MCTIMS) is often employed for this analysis. However, these high-precision instruments require highly purified actinide fractions, free from interferences such as organics and heavy metals, to ensure the quality of the measurements. Current purification protocols include ashing samples individually in furnaces (or occasionally, chemical leaching with acid) and then manually loading gravity-driven separation columns—a process that is both costly and time consuming. From start to finish, the manual purification chemistry takes between 2 and 4 weeks and represents the longest single step in the analysis process for bulk environmental samples. The separation procedures are also typically carried out in certified International Standards Organization (ISO) clean room laboratories with heavily filtered air and high-purity reagents to limit the contribution of background contamination to the measurement of the nanograms or picograms of material that may be present in environmental samples. The installation and maintenance of clean room facilities represent a significant upfront financial investment and ongoing maintenance commitments that some laboratories may be unable to sustain.

Streamlining NWAL sample preparation methods for subsequent analysis by mass spectrometry using fully automated, commercial-off-the-shelf (COTS) equipment would address a serious need in the safeguards community by shortening lengthy, costly manual chemical digestion and purification procedures. Automating digestion and chemical separation, while still producing a highly purified sample fraction, would offer significant time and cost savings to the IAEA without sacrificing data quality. Additional benefits may include lower and more consistent blank levels for U and Pu and the ability to achieve clean room–level blanks without the infrastructure needs of ISO clean rooms. Finally, the use of COTS equipment would allow an automated method to be quickly and economically transferred to and implemented by any NWAL facility (or prospective NWAL member), helping the IAEA globally execute standard operating procedures (SOPs) for isotopic purification while addressing the ongoing challenge of increasing efficiency and preventing sample backlogs.

These goals directly address high-priority Milestones 10.2 and 10.3 in the IAEA Long-Term R&D Plan (STR-375)[3] by developing new technologies and techniques that will improve the NWALs' ability to provide analytical services to IAEA. By supporting STR-375, this work also addresses the short-term needs described in the *Development and Implementation Support Programme for Nuclear Verification 2016–2017* (STR-382).[4] Specifically, transfer of automated COTS technology to NWAL member laboratories supports SGAS-003, "Analysis Support and NWAL Coordination," and especially the top priority to "Ensure efficient and effective operation of the NWAL." [4]

To this end, Oak Ridge National Laboratory (ORNL) has worked with Elemental Scientific Inc. (ESI) to customize ESI's COTS sample preparation platform prep*FAST*-MC.[5] The prototype, dubbed prep*FAST*-MC2, has been installed at ORNL. It closely mirrors the manual ORNL NWAL chemistry but uses automation to perform chemical separations in unattended, overnight operation. The initial work is described in more detail previously,[6-7] with those results summarized here and new data added where available. Specifically, ORNL has documented significant labor savings through the use of this equipment without any associated impact upon final data quality. As hoped, the blank levels achieved with the system point to the potential for it to operate as a portable clean room in laboratories lacking that infrastructure. Finally, ORNL is evaluating additional COTS technologies to enable efficiencies in other parts of the chemical processing of environmental swipe samples, which are also briefly described herein.

1.1 INSTALLATION OF NEW SYSTEM AT OAK RIDGE NATIONAL LABORATORY

The original prototype, prep*FAST*-MC2, was received in FY 2016. During the initial studies in FY 2016 with the system, ORNL staff worked in collaboration with ESI to determine ways to improve the prep*FAST*-MC2. The new system incorporates upgrades to the valve assembly, case design, and autosampler, including a barcode reader for sample tracking. The extent of the upgrades prompted ESI to also upgrade the name; the new equipment is called the prep*FAST*-SR. Two new prep*FAST*-SR systems were procured at the end of FY 2017. ESI provided onsite support for the installation in the Ultra-Trace Forensic Science Center located at ORNL. One installed prep*FAST*-SR is shown in Figure 1.

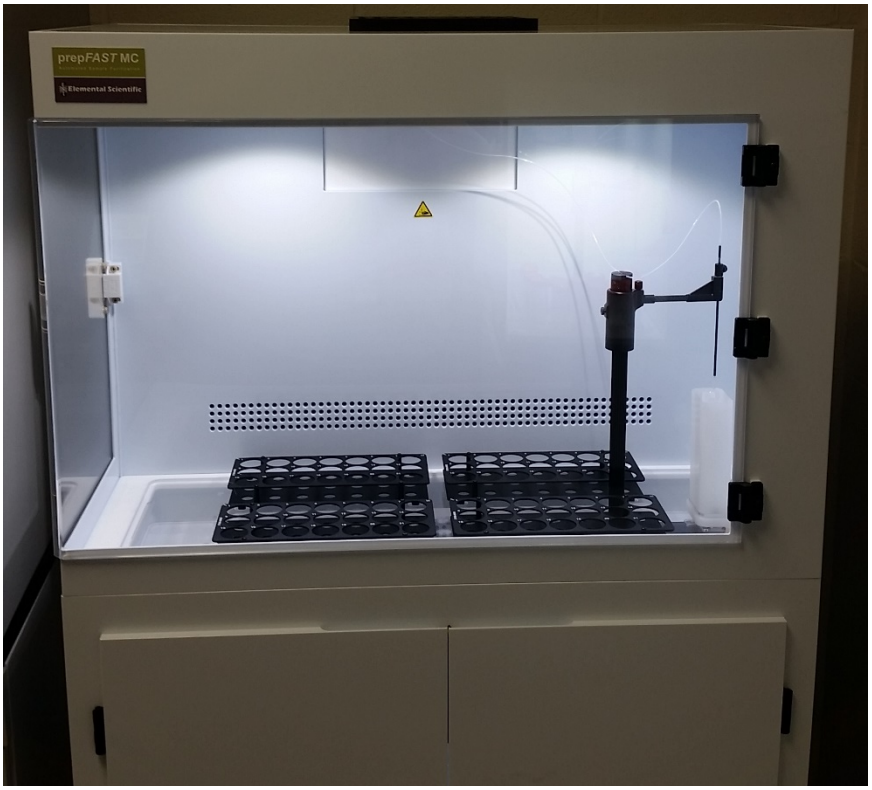

Figure 1. Installation of the prepFAST-SR at ORNL.

1.2 OVERVIEW OF THE NEW PREPFAST-SR SYSTEM

Figure 2 shows an image of the valves that make up the heart of the new separation system. Overall, the operation of the prep*FAST*-SR is similar to that of its predecessor, the prep*FAST*-MC2.[6-7] Briefly, samples

are introduced to the prep*FAST*-SR via the sample probe, which also serves to dispense separated sample aliquots into specified vials after column purification. The system is driven by four syringe pumps that are integrated with the seven valves shown in Figure 2. Column packing, and unpacking, is now controlled by three valves for each column to enable faster packing and unpacking, as well as more efficient column washing. Similarly, the entire sample line is closed, so that the sample contacts only the fluoropolymer tubing. Additionally, the new prep*FAST*-SR comes equipped with an ultra-low particulate air (ULPA) filter positioned above the autosampler enclosure to ensure samples are exposed only to clean air.

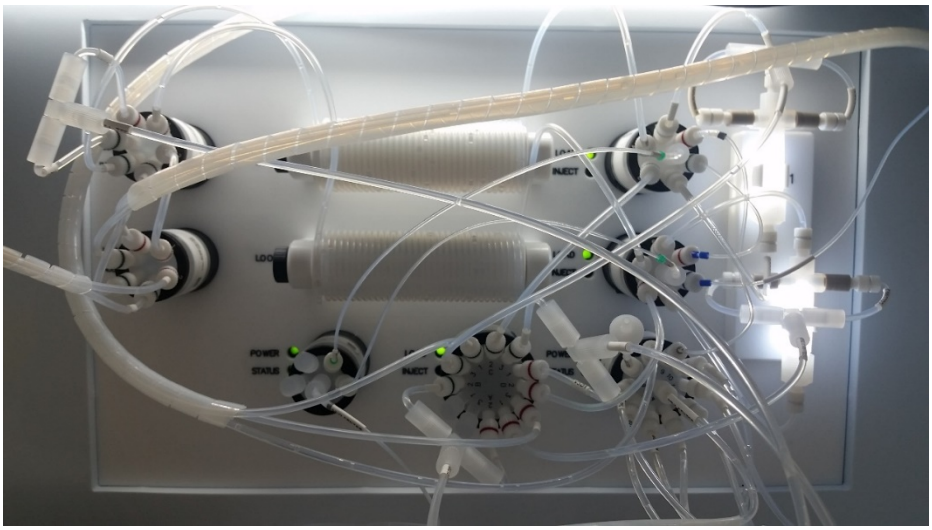

Figure 2. New ESI prepFAST-SR valve assembly.

The new system is controlled by a laptop computer (provided by ESI) that runs the same commercial ESI SC software as the prep*FAST*-MC2.[6] The chemistry methods employed on the prep*FAST*-SR are controlled and programmed through the software. Variables in the current configuration can be easily adjusted by modifying the separation program being used. Updated software will allow the user to adjust designated sub-method parameters (e.g., sample load volume, sample location).

1.3 OVERVIEW OF THE EVAPOCLEAN SYSTEM

The EvapoClean from Analab, a sub-boiling distillation apparatus, is pictured in Figure 3. It is a six-port vertical hotplate, with a programmable timer, that can distill acids from individual samples, each in a completely sealed fluoropolymer environment. The acid matrix of the sample is evaporated and then condensed into a separate vial, while the analytes of interest (i.e., actinides in a sample) remain in the original vial, as shown in Figure 5. The sealed environment limits the exposure of the samples to laboratory air, which will enable acid dry-down steps (or matrix conversions) to move out of a clean room and into a traditional chemical laboratory. An additional benefit of the equipment is that it can simultaneously be used to reflux acid into labware (via the ports on top of the unit), either to clean new vials or to acid leach previously used vials for reuse (Figure 5). The dual use of the EvapoClean enables both labware cleaning and sample dry-downs to occur outside a clean room.

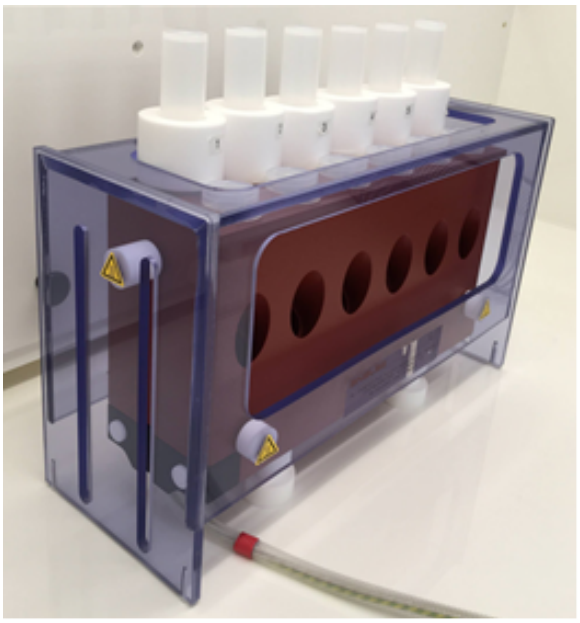

Figure 3. The Analab EvapoClean installed in a chemical hood at ORNL.

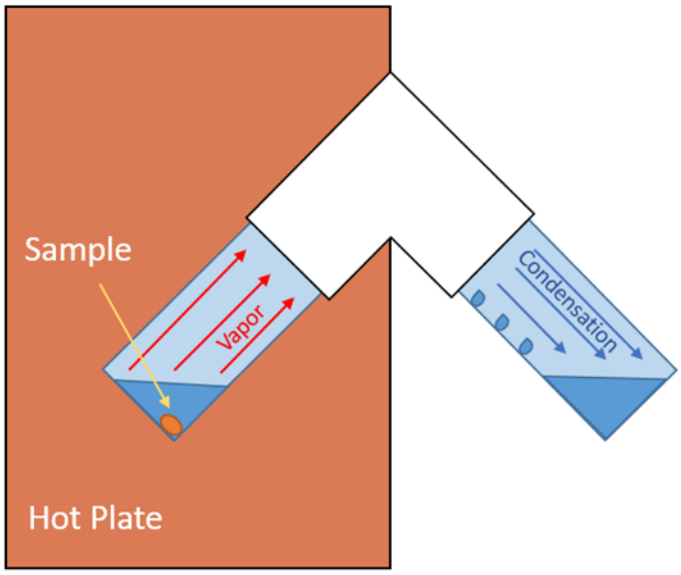

Figure 4. Distillation and matrix reduction setup for the EvapoClean system.

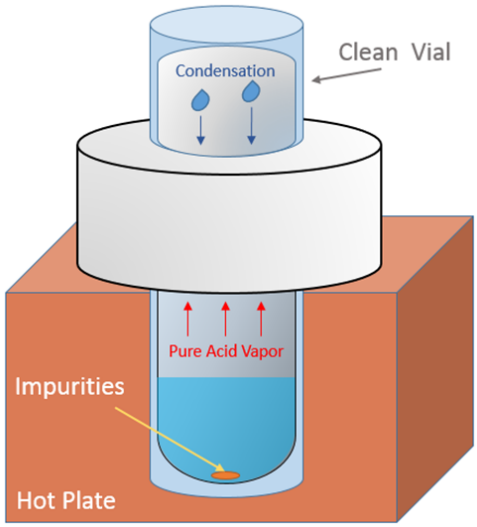

Figure 5. Leaching setup for the EvapoClean system.

1.4 BARCODE READER

The prep*FAST*-SR comes equipped with a bar code reader to track individual samples via a barcode marking molded into the vial or a lab-made QR code sticker. The reader adds a layer of transcription protection from a sample tracking and chain-of-custody point of view. Additionally, it allows the system to check for the presence of the appropriate vial at each location in the sample tray before dispensing an aliquot, limiting the potential for loss of samples due to human error in the event of misloading vials.

2. EXPERIMENTAL METHODS

Only ultrapure reagents were used, with low trace metal content the major consideration in reagent selection. Optima HNO_3, HCl, and HF were purchased through Fisher Scientific and used without further purification. $NaNO_2$ (ACS, 95% min) and $FeSO_4$ Puratronic 99.999% (metals basis) were purchased through Alfa Aesar and used without further purification. ASTM Type I (18.2 MΩ) water was generated with a Thermo Scientific Barnstead GenPure Pro Water Purification System. TEVA-resin and UTEVA-resin (20–50 µm particle size) were purchased from Eichrom Industries Inc. Certified Reference Materials (CRMs) for U and Pu were purchased from the New Brunswick Laboratory (NBL-137, Pu) or the Institute for Reference Materials and Measurements (IRMM-183, U; IRMM-57, U; IRMM-82, Pu), now the Joint Research Center of the European Commission. An internal ORNL solution of high-purity 244Pu (RAL 22) was used as an isotope dilution spike to determine sample Pu recovery. Its concentration was determined relative to National Institute of Standards and Technology Standard Reference Material 4330C.

All mass spectrometric data presented in this report were collected on either a high-resolution inductively coupled plasma mass spectrometer (HRICPMS) or an MCICPMS. A ThermoScientific Element II (Bremen, Germany) was used for all HRICPMS measurements. The Element II is a single-collector magnetic sector mass spectrometer typically used for elemental analysis. It works by quickly scanning the magnetic field to direct ions sequentially onto the detector.

A ThermoScientific Neptune Plus (Bremen, Germany) was used for all MCICPMS measurements. The Neptune Plus is used for ORNL NWAL analysis of both U and Pu isotope ratio measurements and was

used in this study to characterize the mixed CRM samples that were separated on the ESI system. The MCICPMS obtains highly accurate and precise isotope ratio measurements by monitoring all isotopes of U or Pu simultaneously on different detectors. Uranium samples in the nanogram range are typically measured using faraday cup detectors, whereas the much smaller Pu samples (picograms) are measured using multiple ion counting detectors. As a result of the mass differences between U and Pu, as well as isobaric interferences such as ^{238}U and ^{238}Pu, U and Pu are measured in separate, purified aliquots during different analytical sessions.

Scanning electron microscope (SEM) images were taken on an FEI Phenom operating at 5 kV. The electron source was a tungsten emitter. The samples were affixed to an SEM stub with a carbon-conductive tab and then imaged at 500× magnification. Multiple image locations were selected at random on each sample and a representative image chosen.

General Procedures for Sample Preparation: In a class 100 or 1000 clean room, samples were prepared in 3 M HNO_3 in 15 mL perfluoroalkoxy alkane (PFA) vials. The valence state of the Pu was adjusted to Pu(IV) by adding $FeSO_4$ (0.2 mL, 1.7 M). The vial was capped and swirled to promote mixing. After approximately 5 min, a color change from clear to green and back to clear occurred; $NaNO_2$ (0.4 mL, 3 M) was then added, and the sample was mixed and allowed to degas for 15 min before column separation.

General Resin Preparation: TEVA resin contained in a disposable column was rinsed with 3 M HNO_3 (15 mL) via vacuum filtration and transferred to resin bottle 1 using 3 M HNO_3 in a 1:5 v/v ratio. UTEVA resin contained in a disposable column was rinsed with 0.01 M HNO_3 (15 mL) followed by 3 M HNO_3 (5 mL) via vacuum filtration and transferred to resin bottle 2 using 3 M HNO_3 in a 1:5 v/v ratio.

2.1 METAL INTERFERENCES

A mixed metal standard stock solution was made from single element standards of Tl, Hg, Ru, Au, Pt, Os, Zr, Bi, Mo, W, Pb, and Th procured from High Purity Standards. Metals solutions were added individually by volume to a 30 mL low-density polyethylene (LDPE) bottle and diluted with 3 M HNO_3 to a final volume of 20 mL following the guidelines outlined in Table 1. Samples were prepared by adding 1 mL of this working solution to either 3 M HNO_3 (blank samples) or U/Pu samples. Samples were then separated on the ESI prep*FAST*-MC2 as previously described.[6-7]

Table 1. Metal interference stock solution volumes

Element(s)	Stock concentration (µg/mL)	Volume added (mL)	Final concentration (µg/mL)
Tl, Hg, Ru, Au, Pt, Os	10.00	0.02	0.01
Zr, Bi, Mo, W	1000	0.02	1.00
Th	10.00	10.0	5.00
Pb	1000	0.20	10.0

2.2 MICROWAVE DIGESTION OF SWIPE BLANKS

Blank cotton swipes (three) were ashed overnight in separate Pyrex glass tubes using a Thermcraft tube furnace equipped with a Eurotherm 2404 temperature controller. The full furnace program is outlined in Table 2. Briefly, the samples were heated to 600 °C and then held at 600 °C for 12 h before being allowed to cool back to room temperature. The residual ash from the swipes was then transferred to Pyrex CEM microwave vessels using 8 M HNO_3 (5 mL). The samples were microwaved using a Discover SP-D from

CEM. The final microwave method is described in Table 3. Briefly, while being stirred at medium speed, the samples were heated for over 4 min to 200 °C and then held at 200 °C for 10 min before cooling back to room temperature. The pressure maximum was set to 400 pounds per square inch (psi) for venting. After microwave digestion, one of the three samples was transferred to a 15 mL PFA vial using 18.2 MΩ H_2O (5 mL). IRMM 183 (~80 ng total) was added to the sample, followed by HF (conc., 1 mL). The sample was then dried down on the EvapoClean system at 130 °C and constituted in 3 M HNO_3 (4 mL) before manual separation on a 2 mL UTEVA cartridge, following the ORNL manual chemistry separation SOP. Briefly, the UTEVA cartridge was pre-cleaned with 0.01 M HNO_3 (3 mL) and 3 M HNO_3 (12 mL). The sample was then loaded onto the column and the vial was rinsed with 3 M HNO_3 (3 × 1 mL). The UTEVA column was rinsed with an additional 3 M HNO_3 (20 mL) before elution of the U using 0.02 M HNO_3 – 0.05 M HF (5.5 mL). The sample was dried down using the EvapoClean system at 130 °C and resuspended in 2% HNO_3(1.5 mL). The sample and distillate U isotopics were then analyzed via MCICPMS.

Table 2. Furnace program for ashing cotton swipes.

Step	Initial T (°C)	Final T (°C)	ΔT rate (°C/min)	Hold time
1	RT	100	10	1 min
2	100	200	7.5	20 min
3	200	300	7.5	40 min
4	300	400	7.5	40 min
5	400	600	5	12 h
Cool down	600	RT	10	N/A

Table 3. ORNL microwave digestion method.

Stage	Ramp (min)	Pressure (psi)	Temperature (°C)	Hold (min)	Power (W)	Stirring
1	4:00	400	200	10:00	300	Medium

Additionally, six cotton swipes were sent to CEM for research and development testing on larger CEM microwaves to test complete digestion of swipes without furnace ashing. The report from CEM is attached in Appendix 1.

2.3 MATRIX REDUCTION USING EVAPOCLEAN SYSTEM

2.3.1 Reducing Background Counts through Leaching

A six-position EvapoClean heating block (as shown in Figure 3) with an Analab P116 temperature controller was used to leach six new 15 mL Savillex vials. Each 15 mL vial was fitted with an adapter, which was connected to a 25 mL vial placed in the heating block, as shown in Figure 5. 8 M HNO_3 (5 mL) was added to each set of vials, which were placed in the top of the EvapoClean system. Vials were then heated at 130 °C for 2 h. The 12 mL vials were then rinsed three times with 18.2 MΩ H_2O and allowed to dry in an ISO class 100 clean room. Six additional Savillex vials were subjected to the conventional ORNL clean room leaching method (6 M HCl, 8 M HNO_3, 18.2 MΩ H_2O for 16 h each, three rinses with 18.2 MΩ H_2O between each and at the end) and six new vials were left untreated. After the cleaned vials were dried overnight, 2% HNO_3 (2 mL) was added to each of the vials (unleached, leached new, and EvapoClean) and left to soak for 16 h. The acid was then analyzed via HRICPMS for ^{232}Th, ^{235}U, and ^{238}U content. Vials previously used for IRMM 183, ^{233}U (~1 ng), NBL 137, or ^{244}Pu (~2 pg) sample analysis were also leached on the EvapoClean system and through conventional leach

methods as described above to evaluate the potential for cleaning and reusing vials. Then 2% HNO_3 (2 mL) was placed in all vials and allowed to set overnight (16 h) before analysis via HRICPMS.

2.3.2 Decreasing Cross-Contamination via Sample Concentration in a Closed Environment

The same six-position EvapoClean heating block with an Analab P116 temperature controller was used as a small closed distillation apparatus as shown in Figure 4. A sample solution (5 mL) containing 0.5 ppb of 40 different elements (Al, Sb, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Ga, Ge, Au, In, Fe, La, Pb, Li, Mg, Mn, Mo, Ni, Nb, Pd, P, Pt, K, Ag, Na, Sr, Ta, Tl, Sn, Ti, W, V, Zn, and Zr) in 2% HNO3 was distilled in a 30 mL PFA vial. Temperature was decreased over the course of the experiment (2 h) to from 145 to 135 °C as the sample volume decreased. The residue was resuspended in 2% HNO3 (2 mL) for analysis via HRICPMS.

The recovery of U and of Pu was examined separately in a similar fashion. Samples of U with 5 ng IRMM 183 in 11 mL of 3.6 M HNO3 – 2.5 M HF were distillated at temperatures ranging from 110 to 150 °C (Δ = 10 °C). Distillation time was linked to temperature and ranged from approximately 7 h at the lower temperature to 2.5 h at 150 °C. Residues were dissolved in 2% HNO_3 (2 mL) and analyzed by HRICPMS and MCICPMS. Recovery of Pu was examined using NBL 137 (2 pg) in 1 mL of 3 M HNO_3. Samples were distilled at 120 °C for approximately 90 min. Sample residues were dissolved in 2% HNO_3 (1 mL) and spiked with high-purity ^{244}Pu (50 µL, 38.90 ± 0.75 pg/g). Sample distillate was transferred to pre-weighed vials and spiked with high-purity ^{244}Pu (50 µL, 38.90 ± 0.75 pg/g). Samples were then heated on a hot plate at 50 °C overnight before analysis by MCICPMS. Conventional matrix conversion methods for the sample Pu solution (1 mL) were also carried out for comparison. Conventionally dried samples were reconstituted with 2% HNO_3 (1 mL), spiked with high-purity ^{244}Pu (50 µL, 38.90 ± 0.75 pg/g), and heated overnight at 50 °C before analysis by MCICPMS. The concentration of the original NBL 137 solution used in the Pu studies was determined through isotope dilution mass spectroscopy (IDMS) calculations.

2.4 AUTOMATED IDMS SPIKING

The new prep*FAST*-SR system was programmed to perform automated IDMS spiking using 18.2 MΩ H_2O at several volumes (0.10, 0.12, 1.0, 5.0, and 10.0 mL). Briefly, in this method, the inside and outside of the probe was rinsed twice with 2% HNO_3 in the probe wash stations before the "spike" was loaded. Once the spike was loaded, the outside of the probe was rinsed twice more with 2% HNO_3 in the probe wash stations. The spike was then dispensed into the designated vial. After dispensing, the inside and outside of the probe was again rinsed twice with 2% HNO_3 in the probe wash stations. The mass of the dispensed spike was then manually determined on an analytical balance and recorded.

2.5 ARCHIVED SWIPE SAMPLES

Archived samples, were used for validation of the original prep*FAST*-MC2 system and chemistry methods. For the first sample, 500 µL of 3 M HNO_3 was added and the sample was then heated overnight at 60 °C. This sample was not spiked before separation. The remaining samples were treated first with small amounts of HF to yield a final concentration of ~50 mM before being heated at 80 °C overnight, dried down, and reconstituted in 3 M HNO_3. The second set were all spiked with a high-purity ^{244}Pu spike before sample preparation. Blanks (3 M HNO_3) and standard solutions (CRM IRMM 183, 5 ng; NBL 137, 2 pg) were also prepared. The general sample preparation method listed earlier was followed for each set of samples, standards, and blanks. Briefly, $FeSO_4$ (0.2 mL, 1.7 M) was added to each sample and, after the color change, $NaNO_2$ (0.4 mL, 3 M) was added. The samples were degassed for ~15 min before separation on the original prep*FAST*-MC2.

3. RESULTS AND DISCUSSION

3.1 METAL INTERFERENCES

Significant amounts of heavy metals such W, Pt, Pb, and Th are known to create interferences in an ICPMS plasma that can affect the measurement of U and Pu. Additionally, significant quantities of any metals may occupy binding sites in the resin columns and impact the successful purification of U and Pu aliquots. To test for these issues, elements either expected to be present in swipe samples in high abundance (Pb, Th) or elements, however rare, that are known to cause interferences in the ICPMS (Pt, Au, Bi) were spiked into samples and separated on the original prepFAST-MC2. Initial separations were verified with blanks spiked with the metals. The samples showed near-quantitative removal of all elements in the distinct fractions.

After initial verification with blanks, the same contaminants were spiked into samples containing U and Pu CRMs. A fraction of each purified aliquot was measured by HRICPMS to quantify the removal of the contaminants, and the remainder was submitted for MCICPMS analysis to ensure no negative impact on the actinide isotope ratio determinations. The list of contaminants examined and their starting and final concentrations in the CRM spiked samples are shown in Table 4. The results confirm that removal of all species, even at significant quantities, was accomplished by the system for both the U- and Pu-containing fractions. Furthermore, no significant deviations were observed in the major or minor U or Pu isotopic ratios.

Table 4. Percent reduction of contaminant elements in U and Pu fraction by the prepFAST-MC2.

Element	U fraction			Pu fraction	
	Starting concentration (ng/mL)	Final concentration (ng/mL)	Percent reduction	Final concentration (ng/mL)	Percent reduction
Zr	1000	17.0	98	0.4	100
Mo	1000	0.2	100	0.4	100
Ru	10	0.1	99	0.1	100
W	1000	0.2	100	0.2	100
Os	10	-0.3	103	-0.1	101
Pt	10	0.1	100	0.1	99
Au	10	0.2	98	0.1	100
Hg	10	0.2	100	0.2	100
Tl	10	-0.2	101	0.0	100
Pb	10000	0.8	100	0.6	100
Bi	1000	0.2	100	0.1	100
Th	5000	5.1	100	0.6	100

During the metal interferences studies, column clogging occurred after eight sample separations. Imaging of the frits from previous studies also demonstrated clogging.[6] Imaging of the resin slurry after 24 h showed breaking of the resin beads within the slurry bottles. New resin slurry was made, and initial SEM images were taken directly after slurry generation; they demonstrated no breakage. The slurry was stirred relatively fast and SEM images were taken after 1, 8, 24, and 48 h. Stirring was then slowed by ~15% of the previous value and SEM imaging was repeated at 1, 8, 24, and 48 h. The reduction in stirring speed significantly limited the breakage observed in the resin, as shown in Figure 6. After 24 h of sample

separations (ten samples), the frits and columns remained unclogged. To limit the possibility of resin breakage and subsequent frit clogging in the future, it was decided to change column frits with each new batch of resin slurry and to stir the resin at a speed that creates minimum breakage, while ensuring that the slurry remains mixed and relatively homogenous. Additionally, resin breakage should be minimized in the new prep*FAST*-SR, as updated stir plates are controlled by the ESI software, which turns the stir bars off between sample runs.

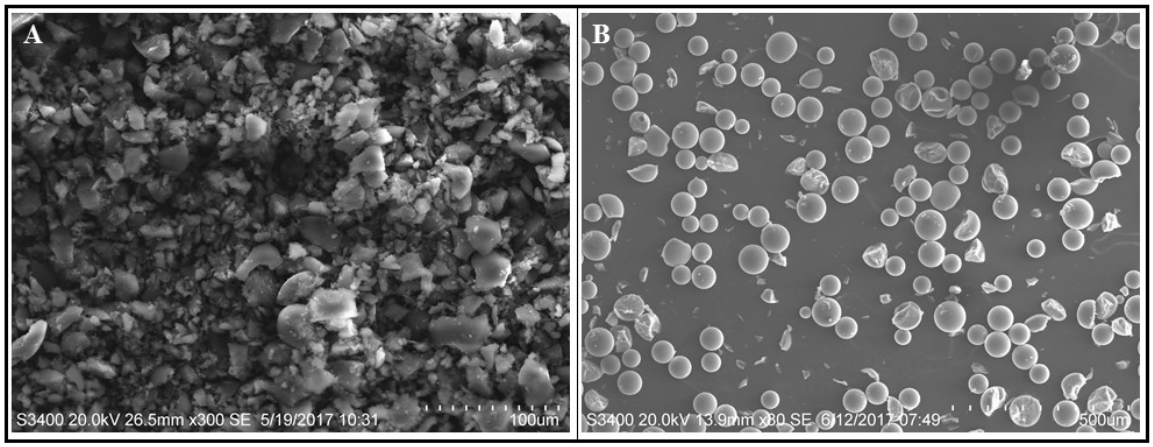

Figure 6. SEM images of TEVA resin with fast stirring after 24 h (A) and slower stirring after 48 h (B).

3.2 MICROWAVE DIGESTION OF SWIPE BLANKS

Based on tests conducted by CEM, the manufacturer of the microwave system in use at the analytical lab at ORNL, microwave digestion of swipes alone is not a suitable replacement for furnace ashing of cotton swipes. The amount of organic material present in the swipe itself presents a significant challenge for this digestion method. However, ORNL conducted a further study looking at a hybrid ashing method consisting of a single furnace ashing step, followed by microwave digestion of the ash residue. If suitable, this could be a faster method, and more suitable to automation, compared with the multiple (two or more) dry ashing steps that are often required to achieve full digestion of a swipe.

Using the hybrid method (one furnace ashing step followed by the microwave digestion method outlined in Table 3), it was possible to fully digest the blank swipe material. After the swipe was digested in the microwave and the solution was allowed to cool to room temperature, the residue was transferred to a PFA vial and IRMM 183 (~80 ng) was added to the sample. The resulting sample was then dried down and resuspended in 3 M HNO_3 before being separated on a 2 mL UTEVA cartridge following the ORNL manual NWAL chemistry method. The MCICPMS results showed good agreement with the certified isotopic values. Although this hybrid digestion option is viewed as promising, it would need to be more fully investigated in a separate research effort.

3.3 MATRIX REDUCTION USING EVAPOCLEAN SYSTEM

3.3.1 Reducing Background Counts through Leaching

The conventional ORNL clean room method of leaching calls for separate solutions of reagent-grade 6 M HCl, 8 M HNO_3, and Type 1 water, each at a volume of approximately 2 L. New vials are rinsed with deionized water, placed in 6 M HCl at 45 °C for 16 h, rinsed, and followed in the same manner with 8 M HNO_3 and then finally water. The process takes a total of 3 days and 3 to 4 h of labor for approximately 25 vials. While the EvapoClean system would take roughly an equivalent number of labor hours, the

system would require only ~8 h to clean the same number of vials. A big advantage of the EvapoClean is the reduced acid volume requirement. Each position (six lids, six vials) uses 5 mL of 8 M HNO_3, totaling 60 mL of acid. The acid is heated, channeling ultra-pure vapors into the top container, which then condenses and flows downward (Figure 5). It is not necessary to renew the acid often because the contaminants remain at the bottom of the refluxing vial, while the rising vapor remains clean.

A comparison of counts of ^{235}U and ^{238}U from new unleached PFA vials, new leached PFA vials, and new PFA vials leached through the EvapoClean system is shown in Figure 7. Conventional leaching methods and the EvapoClean leaching method both reduced the counts by an order of magnitude compared with the unleached PFA vials. EvapoClean leaching methods further reduced the counts of U by half compared with conventional leaching methods.

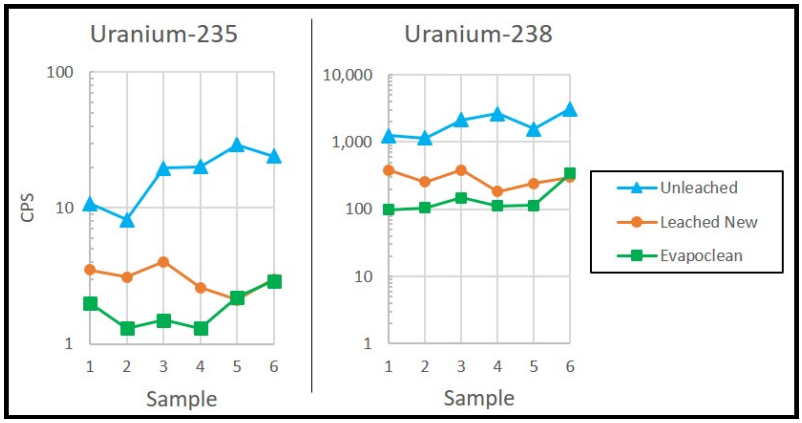

Figure 7. Comparison of background counts in three sets of PFA vials for selected isotopes.

Of further interest was the efficacy of leaching vials after they had been used for sample containment. To test this, vials that had previously held ~1 ng of ^{233}U were submitted to both methods of leaching. There was not a noticeable difference in the counts of ^{233}U and ^{235}U between the leaching methods, as shown in Figure 8. However, ^{238}U counts were five times lower on average with the EvapoClean method than with the conventional method. This is likely because the EvapoClean method distills the acid used for cleaning as part of the process itself, while acid in the traditional leaching method, using the 2 L vats, will become slightly contaminated over time. The used PFA vials cleaned on the EvapoClean system had lower counts of ^{238}U and ^{235}U than a new vial. Vials that were previously used for NBL 137 (2 pg) were also cleaned through the EvapoClean system, and counts were reduced to sub-femtogram levels (data not shown).

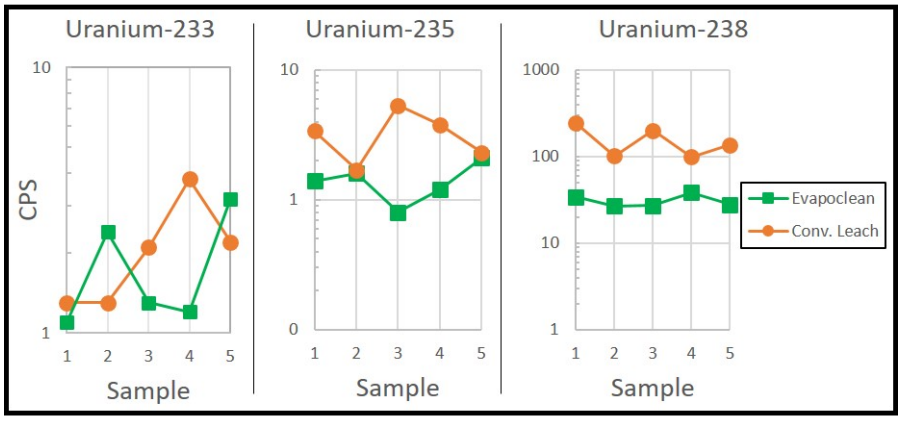

Figure 8. Counts of selected isotopes from previously used PFA vials after conventional leaching and EvapoClean leaching method.

3.3.2 Decreasing Cross-Contamination via Sample Concentration in a Closed Environment

Matrix reduction and conversion is one of the most time-consuming steps in the sample preparation process. Current methods can expose samples to cross-contamination from other samples processed concurrently through traditional ORNL acid dry-down methods. The individual enclosures for each sample used by the EvapoClean, illustrated in Figure 4, protect them from cross-contamination. Initial studies to determine recovery were carried out using a mixture of metals at 0.5 ppb (not including U or Pu) in dilute HNO_3. The results of this study are outlined in Table 5. Briefly, of the 40 metals, only 3 metals (Au, Pd, and Ta) demonstrated recoveries below 85%; three additional metals (Pt, W, and Sn) were below 90% recovery. The remaining 34 elements showed recoveries greater than 90% at 130 °C.

Table 5. Percentage recovery of selected metals that were evaporated at 130 °C from a metal concentration of 0.5 ppb in 2% HNO_3

Element	Percent recovery	Element	Percent recovery	Element	Percent recovery
Al	102 ± 19	Mg	92 ± 12	Ta	73 ± 2
Sb	91 ± 3	Mn	93 ± 3	Tl	93 ± 3
As	98 ± 4	Mo	96 ± 3	Sn	89 ± 5
Ba	92 ± 3	Ni	95 ± 3	Ti	93 ± 4
Be	108 ± 13	Nb	105 ± 2	W	89 ± 3
Bi	96 ± 7	Pd	68 ± 16	V	93 ± 1
B	154 ± 42	P	104 ± 25	Zn	108 ± 20
Cd	90 ± 1.5	Pt	85 ± 14	Zr	100 ± 6
Ca	100 ± 47	K	100 ± 65	In	91 ± 6
Cr	97 ± 7	Ag	93 ± 3	Fe	105 ± 42
Co	95 ± 2	Na	93 ± 15	La	97 ± 4
Cu	145 ± 12	Sr	92 ± 3	Pb	90 ± 5
Ga	95 ± 2	Au	46 ± 15	Li	100 ± 7
Ge	93 ± 4	-	-	-	-

Uranium recovery was examined using a solution matrix similar to that of the standard NWAL digestion matrix (3.6 M HNO_3 – 2.5 M HF) and IRMM 183 (5 ng). To determine the optimum operating

temperature, U recovery was examined over the temperature range of 110 to 150 °C (Δ = 10 °C). No significant change was observed in the percentage recovery at different temperatures, shown in Figure 9. However, as expected, there was a correlation between the temperature and the amount of time required for complete matrix reduction. The lower the temperature, the longer the amount of time needed: ~7 h for 110 °C and ~2.5 h for 150 °C. MCICPMS results showed no significant difference in the major or minor isotopic ratios for U after reconstitution in 2% HNO_3. Complete sample recovery required supervision near the end of the dry-down cycle, or moderate heating. Compared with standard ORNL techniques, the time required for moderate temperatures (120 to 130 °C) still provided a significant improvement in the amount of time need for matrix reduction—from overnight to 4–6 h.

Plutonium recovery was examined at 130 °C and compared with standard dry-down box techniques. The Pu source was NBL 137 with a ^{244}Pu tracer added to quantify the recovery. Samples dried down using the standard ORNL method yielded an average recovery of 72 ± 39% (n = 3). The EvapoClean system yielded higher recoveries at 89.0 ± 6.3% (n = 4). Distillate from the EvapoClean system demonstrated near blank values with an average of 15.9 ± 1.5 fg (n = 4) of Pu. In the dry-down boxes, any loss of sample would remain unaccounted for; however, the closed setup of the EvapoClean allows for both the sample and the distillate to be examined for the presence of the sample. This would ensure that if sample were lost to the distillate, it could be transferred back to the sample vial and dried down again without significant loss or contamination from an external source. Additionally, the dry-down boxes took twice as long (~3 h) to completely dry the samples as did the EvapoClean method (90 min).

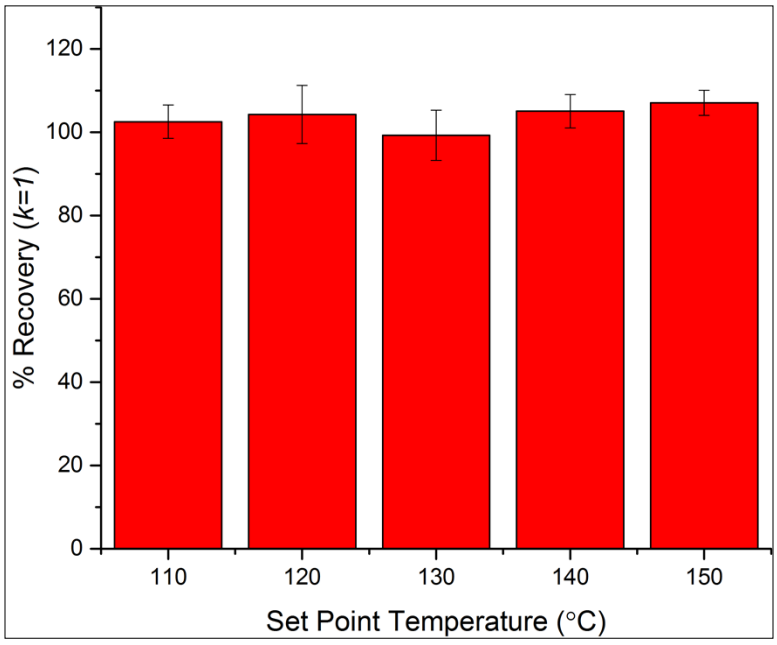

Figure 9. Percent recovery of U from matrix reduction using the EvapoClean system at various temperatures.

3.4 AUTOMATED IDMS SPIKING

Initial experiments that transferred various volumes (0.1 – 10 mL) of water between vials were carried out on the prep*FAST*-SR to evaluate the potential of the system for automated IDMS spiking. These experiments called into the question the ability of the software-controlled syringe pump to deliver exactly the specified amount of spike solution to a sample. Although the system exhibited high precision on the volume of spike solution delivered, the accuracy was unsatisfactory. At the typical spike volumes employed by ORNL (50–100 µL), the instrument delivered on average ~85% of the expected value (by

weight). At larger volumes, the relative offset between the user-defined value and the delivered value decreased, but the use of a more dilute spike has drawbacks for shelf life and spike equilibration. Automation of the spiking is possible, but manual weighing is still required for high confidence in the final IDMS result. Thus, automation of this step does not lead to any time savings over manual spiking using a pipette and will not continue to be pursued without a significant advancement in technology from ESI.

3.5 ARCHIVED SWIPE SAMPLES

The final method of validation using archived samples (with explicit IAEA approval for this activity) was conducted using samples from 2014–2016. The samples were analyzed for U and Pu isotopic ratios only, as sample concentrations may change over time as a result of evaporation or loss to vial walls. Typically, after processing, only 10–20% of the original sample is saved for archiving. Four samples were chosen from archived IAEA samples to test a variety of isotopic and concentration ranges for U and Pu. In the original total samples, Sample 1 had ~30 ng of low-enriched U and ~3 pg of Pu; Sample 2 had ~8 ng of natural U and ~10 pg of Pu; Sample 3 had 10 ng of low-enriched U and <2.5 fg of Pu; Sample 4 had ~3 µg of depleted U and ~50 pg of Pu. Samples 1–3 archived only ~15% of the original sample, whereas the U and Pu content in Sample 4 allowed ~85% of the sample to be archived. The minor Pu isotope ratios previously reported were not larger than their 2σ value and, although they were measured here, were not a point of focus for these studies.

Sample 1, from 2014, had experienced some degree of evaporation after being removed from archive storage, so 3 M HNO_3 was added to bring the volume up to ~1.5 mL before separation. MCICPMS results for U isotopics showed very good agreement with the previously reported values. However, the analyzed Pu isotopic results did not match the reported values (Table 6). This result was likely due to the affinity of Pu for PFA vials—which is well known to impact the concentration of Pu solutions over time—and the age of the archived aliquot. It was further confirmed by the significantly lower number of counts of Pu in the mass spectrometry analysis than was expected, based on the estimated amount of Pu remaining in the archived portion of the sample. To ensure all Pu was in solution in the remaining samples, HF was added to give a final concentration of ~50 mM. The samples were heated overnight to help leach the Pu from the PFA vial and then dried down to remove the HF from the sample. The samples were resuspended in 3 M HNO_3 before separation.

The major U and Pu isotopic ratios for Sample 2 were consistent with previously reported values. Although the $^{234}U/^{238}U$ isotopic ratio matched the reported value, the $^{236}U/^{238}U$ isotope ratio was off from the previously reported value (Table 6). This result is attributed to the very low number of ^{236}U counts in the sample (which represents ~15% of the total U content in the original sample); it made the measurement of the minor isotopes challenging.

Table 6. Comparison of measured vs. reported values for major and minor U isotopic ratios and major Pu isotopic ratios.

Measured/Reported	$^{234}U/^{238}U$	1σ	$^{235}U/^{238}U$	1σ	$^{236}U/^{238}U$	1σ	$^{240}Pu/^{239}Pu$	1σ
Sample 1	99.88%	0.70%	99.92%	0.95%	99.40%	0.64%	210.7%	17.6%
Sample 2	99.48%	1.54%	99.80%	0.65%	180.27%	60.00%	100.7%	2.3%
Sample 3	97.04%	1.09%	98.35%	0.81%	96.28%	1.52%	-298%	1118%
Sample 4 – 1	100.12%	0.69%	99.95%	0.79%	99.42%	0.94%	100.5%	2.9%
Sample 4 – 2	99.87%	0.57%	100.11%	0.79%	99.65%	0.89%	100.9%	3.6%
Sample 4 – 3	99.95%	0.70%	100.10%	0.79%	99.53%	0.95%	100.2%	4.7%

Sample 3 had a very low count rate for Pu, as expected based on the sample concentration (Table 6). The measured $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios were within 2σ of the reported values, and the measured $^{236}U/^{238}U$ ratio was within 3σ. Although the $^{235}U/^{238}U$ ratio was not statistically different from the reported values, it was slightly smaller. The slightly lower than expected values point to a small amount of contamination. Because this is a real sample that was handled and archived 2 years ago, the exact source of the contamination is difficult to determine. However, ~60 pg of natural U contamination would explain the observed result, compared with a typical clean room blank of ~25 pg. Additionally, the measured values were well within IAEA NWAL data quality limits.

The high U and Pu concentrations in Sample 4 allowed for the separations and analyses to be carried out in triplicate on two different days. Table 6 shows isotopic results from the MCICPMS analysis of the separated U and Pu fractions, which demonstrate excellent agreement with the reported values. The major and minor U isotope ratios show no significant difference from the reported values. Also notable is that the $^{240}Pu/^{239}Pu$ isotopic ratio was also consistent with the previously reported value. The values for all three replicates of sample 4 were within 1σ of the reported values.

4. NEWLY DESIGNED PREPFAST-SR SYSTEMS

The newly designed prep*FAST*-SR was installed in August 2017, with the help of ESI representatives. Initial quality control tests by ESI were successful and demonstrated functionality of the syringe pumps and autosampler. Preliminary column calibration methods demonstrated good separation of U and Pu CRMs from a mixed sample. Elution profiles were similar to those generated on the original prototype (the prep*FAST*-MC2) system. Updates to the new prep*FAST*-SR, highlighted in Figure 10, include a new plastic enclosure with a minimal amount of exposed metal. The new enclosure also includes an ULPA filter at the top to provide filtered air in the autosampler region (Figure 10A). In the lower cabinet, the valve assembly (Figure 10B) and column design (Figure 10C) have been updated to allow for faster packing and unpacking of the bulk resin. The resin loops allow for the resin to be individually preloaded through the loops at a significantly faster flow rate. The additional ports at the top of the columns allow for a flow of acid solution to help expel loose resin during unpacking. ESI has added additional ventilation holes in the autosampler region and changed the ventilation of the lower cabinet to reduce the buildup of acid fumes. Lights in the upper and lower cabinet region have been replaced with brighter LED lights, enabling better viewing of samples.

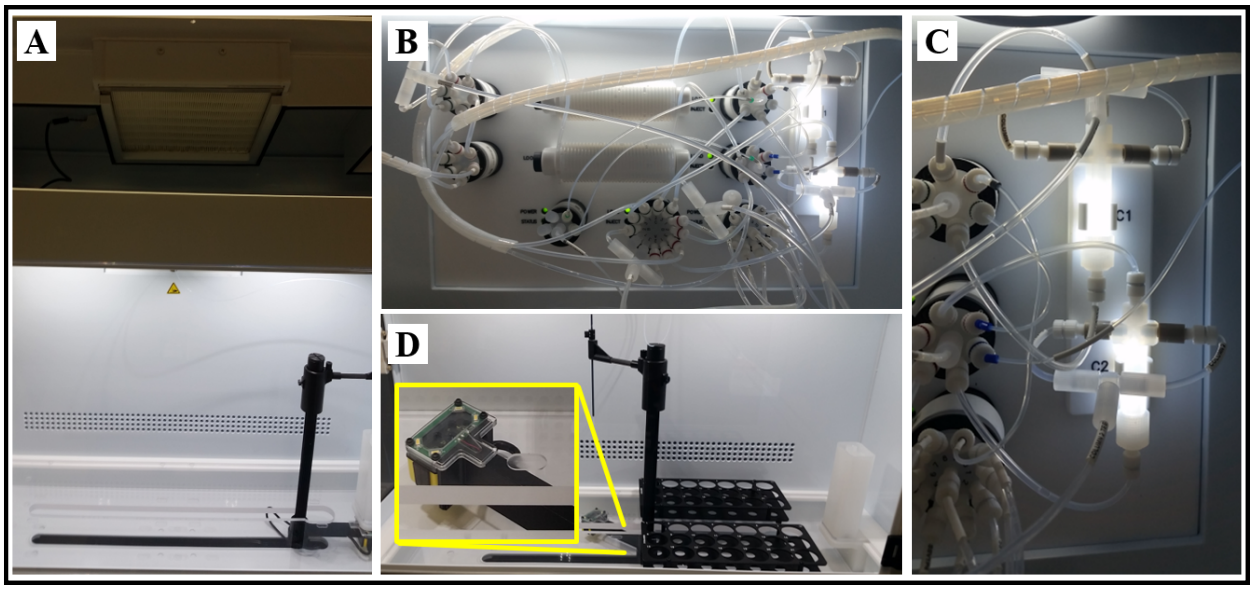

Figure 10. Highlighted updates to the prep*FAST*-SR: (A) ULPA filter at the top of the new enclosure; (B) updated valve assembly; (C) updated PFA columns; (D) barcode reader with specialized racks.

After verification of consistent elution profiles between the prototype and the prep*FAST*-SR, individual and mixed CRM samples were prepared with U and Pu for separation. MCICPMS results showed no perturbation of major or minor isotopic ratios for U or Pu fractions. However, the number of washes was initially reduced from three to one to help determine the extent of washing needed with the new column designs, and carryover of U and Pu was observed in the blank samples run between each sample. Therefore, additional washes will be necessary in the future to ensure adequate washout of the columns between samples. A more formal testing and validation of the new system will be completed in FY 2018 as part of the field deployment preparation task.

4.1 BARCODE READER

The new systems are equipped with the hardware for the barcode reader, shown in Figure 10D. However, upon installation, the software to enable the use of the barcode reader was still under development by ESI. Currently, the systems operate properly without the barcode reader functionality. We expect that working software will be delivered to ORNL by the end of FY 2018 Q1, when the testing of the barcode reader will be completed. No impact on the schedule of any potential FY 2018 activities is expected from this delay.

5. CONCLUSIONS

The prep*FAST*-SR, from ESI, is a COTS automated sample preparation system that has been customized by ORNL to perform U and Pu separations on digested swipe samples in support of the IAEA's Bulk Analysis of Environmental Samples for Safeguards program. It packs and unpacks bulk Eichrom TEVA and UTEVA resins into columns for each individual sample purification. Separation was initially verified by the use of mixed U and Pu CRM samples at various concentrations. Heavy metal contaminants were also spiked into samples to ensure purification of the final U and Pu aliquots. Validation of the automated system with archived IAEA samples was successfully demonstrated, and results matched reported values. The use of the prep*FAST*-SR, along with other COTS equipment like the EvapoClean from Analab, creates the opportunity to conduct clean room–level separations without the expensive infrastructure.

6. REFERENCES

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7. Ticknor, B. W.; Bottorff, S. C.; Tevepaugh, K. N.; McBay, E. H.; Bostick, D. A.; Hexel, C. R.; Kim, H.; Field, M. P. Automated Clean Chemistry for Bulk Analysis of Environmental Samples for Safeguards, *39th ESARDA Symposium on Safeguards and Nuclear Non-Proliferation*, 2017.

APPENDIX A. CEM MICROWAVE DIGESTION REPORT

CEM CORPORATION

LAB REPORT

APPENDIX A. CEM MICROWAVE DIGESTION REPORT

MARS 6

Laboratory Report
(Acid Digestion)
2 Step

Date: November 16, 2016

Customer: Oak Ridge National Laboratory
Cole R. Hexel
One Bethel Valley Road
Oak Ridge TN, 37830
865-574-2449
Hexelcr@ORNL.GOV

CEM Sales: Lee Daugherty

Sample(s): Cotton Swipe, Texwipe 304, Lot #L308AD

Equipment: Mars 6, Xpress Plus iWave

Heating Program One Touch
Organic
Ramp to Temperature
Step #1

Stage	Ramp (min)	Pressure (psi)	Temperature (°C)	Hold (min)	Power (W)
1	20:00	N/A	120	10:00	280-1800

Ramp to Temperature
Organic
Step #2

Stage	Ramp (min)	Pressure (psi)	Temperature (°C)	Hold (min)	Power (W)
1	20:00	N/A	175	10:00	290-1800

Analytes: U, and Pu

CEM Lab Number: D16-024-1

Reagents: HNO_3 and Di Water

Number of Vessels: 8

Procedure:

1. Fold into a small square and place one swipe (approximately 2 grams) into the Xpress Plus vessel.
2. Add 10 ml of HNO_3 and 10 ml of Di Water to the vessel.
3. Assemble the vessel without the plug by torqueing on the vessel cap.
4. Program the MARS 6 as outlined in Step #1.

Summary of Conditions During Digestion of Cotton Swipes Step #1			
Temperature at End of Ramp (°C)	119	Pressure at End of Ramp (psi)	N/A
Temperature at End of Hold (°C)	119	Pressure at End of Hold (psi)	N/A

5. Allow the sample to cool. Vent and remove the vessel cap.
6. Look inside vessels to be sure the swipes have begun to dissolve. If swipes still appear completely intact then add 5 ml of HNO3, put the vessel caps back on and repeat Step #1.
7. Add 5 ml of HNO3 to the sample
8. Assemble the vessel with the plug by torqueing the vessel cap.
9. Program the MARS 6 as outlined in Step #2

Summary of Conditions During Digestion of Cotton Swipes Step #2			
Temperature at End of Ramp (°C)	176	Pressure at End of Ramp (psi)	N/A
Temperature at End of Hold (°C)	174	Pressure at End of Hold (psi)	N/A

10. Allow the sample to cool. Vent and remove the vessel cap.
11. Transfer the solution to a 50 mL volumetric flask and dilute to volume with deionized water

Discussion:
Due to the large size (4 x 4 inches) and weight (2 grams) of this sample, it must be run in 2 steps. The first step is run without the plug to a low temperature of 120C to allow for the sample to pre-digest. The second step is run with the plugs up to 175C for a complete digest.

Some of these samples can go exothermic causing excessive venting. In these cases, the sample might lose volume and not be acceptable for recoveries of the analytes of interest.

Sample was clear, colorless and particle free upon dilution.

Note: This procedure has not been optimized for acid volume, temperature, pressure, and time. Acid mixtures may need optimization for some analytes and sample types.

Prepared By: Tina Restivo
Sr. Applications Chemist

APPENDIX B. PREPFAST-SR SOP

APPENDIX B. PREPFAST-SR SOP

1. Apparatus and Materials
   - 1.1. prep*FAST*-MC-SR System
   - 1.2. Leached sample vials and tops
   - 1.3. 0.75 in. egg-shaped stir bars
   - 1.4. Eichrom TEVA and UTEVA bulk resin (50–100 um mesh size)
   - 1.5. Balance, 150 g or greater capacity, having an accuracy of at least ± 0.0001 g
   - 1.6. Fume hood (or ventilation for the prep*FAST*-MC-SR)
   - 1.7. Adjustable pipets and leached pipet tips (5 mL, 1 mL, 100 uL)
   - 1.8. Self-adhesive labels for sample vial identification
   - 1.9. 10-mL disposable plastic columns set
   - 1.10. Vacuum line or vacuum pump
   - 1.11. 125–250 mL side arm filter flask with rubber septum
   - 1.12. Vacuum tubing
   - 1.13. 125 mL PFA squirt bottle
   - 1.14. 50 mL centrifuge tubes
   - 1.15. 20 mL graduated cylinder (or pipets can be used to measure out the volumes for washing the resin before transfer to resin bottle)
   - 1.16. 15 mL centrifuge tube holder
   - 1.17. 50 mL centrifuge tube holder

2. Standards and Reagents
   - 2.1. ASTM Type II reagent-grade water, 18MΩ
   - 2.2. HNO_3, Ultrex grade (or equivalent)
   - 2.3. HF, Ultrex grade (or equivalent)
   - 2.4. HCl, Ultrex grade (or equivalent)
   - 2.5. H_2O_2, Ultrex grade (or equivalent)
   - 2.6. 8 M HNO_3
   - 2.7. 8 M HNO_3–0.1 M HF
   - 2.8. 3 M HNO_3
   - 2.9. 0.01 M HNO_3
   - 2.10. 9 M HCl
   - 2.11. 0.02 M HNO_3–0.005 M HF
   - 2.12. 0.1 M HCl–0.06 M HF
   - 2.13. 2% HNO_3
   - 2.14. 5% HNO_3
   - 2.15. 3 M $NaNO_2$, ultra-pure, 0.51g dissolved in 2.4 mL water (0.4 mL/sample)
   - 2.16. 1.7 M $FeSO_4$, ultra-pure, 0.96 g dissolved in 2 mL water (0.2 mL/sample)

3. Preparation of TEVA and UTEVA Bulk Resin
   - 3.1. Prepare 10 mL plastic disposable columns with a frit at the bottom of each column and place a cap on the bottom tip of the column. Place prepared empty column into a 50 mL centrifuge tube or 15 mL centrifuge tube rack holder.

3.2. Tare empty column (in centrifuge tube). Add ~4.00–4.04 g of respective resin to the column and reweigh. Record results as the "Resin Weight." (Weight range should be ~1%.) Label column with resin type and weight and place top cap on column for storage until use.

3.3. TEVA cleaning and suspension:

3.3.1. Remove top and bottom cap from column (do not dispose of bottom cap). Place column in rubber stopper in side arm vacuum flask and start vacuum. Rinse TEVA resin with 3 M HNO_3 (15 mL).

3.3.2. Stop vacuum and remove column from rubber stopper.

3.3.3. Replace bottom cap on column.

3.3.4. Weigh out 50 mL of 3 M HNO_3 (~55.0 g) into a PFA squirt bottle. Record weight as "Resin Suspension Weight."

3.3.5. Using the squirt bottle, resuspend the resin in the column in small increments and pour resin into TEVA resin bottle for use on the prep*FAST*-SR.

3.3.6. Once all resin is in resin slurry bottle, use any remaining 3 M HNO_3 to rinse the tip of the squirt bottle into the slurry bottle.

3.4. UTEVA cleaning and suspension:

3.4.1. Remove top and bottom cap from column (do not dispose of bottom cap). Place column in rubber stopper in side arm vacuum flask and start vacuum. Rinse TEVA resin with 0.01 M HNO_3 (15 mL). Followed by 3 M HNO_3 (5 mL).

3.4.2. Stop vacuum and remove column from rubber stopper.

3.4.3. Replace bottom cap on column.

3.4.4. Weigh out 50 mL of 3 M HNO_3 (~55.0 g) into a PFA squirt bottle. Record weight as "Resin Suspension Weight."

3.4.5. Using the squirt bottle, resuspend the resin in the column in small increments and pour resin into UTEVA resin bottle for use on the prep*FAST*-SR.

3.4.6. Once all resin is in resin slurry bottle, use any remaining 3 M HNO_3 to rinse the tip of the squirt bottle into the slurry bottle.

3.5. Attach resin slurry feed lines to designated vial and place slurry bottles on stir plates in prep*FAST*-SR lower cabinet.

3.6. Stir resin mixture for ~20 min or until all fines are mixed in from the top of the solution. (This step can occur while samples are loaded into autosampler trays and methods are loaded into the ESI software.)

4. Column Separation of U and Pu (assuming samples are already digested, spiked if necessary, and in 3 M HNO_3 [1–3 mL])

4.1. Add 0.2 mL 1.7 M $FeSO_4$ to each vial and mix for ~5 min. When the solution color changes from dark to light, add 0.4 mL 3 M NaNO2 and wait for the solutions to degas (~15 min). Samples should be capped immediately after adding the $NaNO_2$ solution.

4.2. Place samples in autosampler tray in prep*FAST*-SR.

4.3. Place labeled collection vials into autosampler tray(s) in prep*FAST*-SR.

4.4. Software Setup:

4.4.1. Click "Configure"

4.4.2. Choose "prepFAST Offline"

4.4.3. Select "Enable prepFAST-MC2"

4.4.4. Complete the sample log for Sample ID, Sample Vial, and Destination 1 and 2 vial locations

4.4.4.1. Sample ID: Name of sample

4.4.4.2. Sample Vial: Autosampler tray location of sample
4.4.4.3. Destination 1 Vial: U fraction vial collection location
4.4.4.4. Destination 2 Vial: Pu fraction vial collection location
4.4.4.5. Destination 3 Vial: blank

4.4.5. Select FAST Method File: IAEA in sample one. Right click on the method name and select "Set Submethod Parameters."
4.4.5.1. Double check submethod parameters are correct for the samples selected and save any changes.

4.4.6. Right click on the method name in Sample 1 and select "Copy Cell Contents To All Cells Below."

4.5. Uncap all vials, double check vial locations, and select "Start prepFAST."
4.6. Cap samples after all samples are complete.

5. Matrix Conversion
5.1. Dry down the U and Pu fractions in an evaporation box or on the EvapoClean system.
5.2. Remove column organics by adding 25 µL 8 M HNO_3 plus 25 µL H_2O_2 and heating the sample at 60 °C for 20 min; dry down, repeat.
5.3. Add 15 µL 8 M HNO_3 to dissolve the residue before adding 1.5 mL 2% HNO_3 to the vials containing the U and Pu fractions.
5.4. Submit for MS analysis.

6. If the U/Pu in the original sample was >1e04, as determined by initial screen results, the Pu fraction may need to be passed through a second TEVA column to reduce the U in the final Pu fraction.