Title: New Particle Working Standards for NWAL Particle Laboratory Calibration and Quality Control - Operational Engineering for an Aerosol-Based Production Platform for the Synthesis of Plutonium-Containing Reference Particulate Materials

Authors: Spencer Scott[1], Benjamin Naes[2], Jonathan Christian[1], Bryan Foley[1], Travis Tenner[2], Wendy Kuhne[1], Kim Wurth[2], Thomas Shehee[1], Seth Lawson[1], Henry Ajo[1], Kyle Samperton[1], Matthew Wellons[1*]

[1] Savannah River National Laboratory

[2] Los Alamos National Laboratory

[*] Presenting Author

Doc# SRNL-STI-2023-00162

R&R Date: April 25, 2023

New Particle Working Standards for NWAL Particle Laboratory Calibration and Quality Control - Operational Engineering for an Aerosol-Based Production Platform for the Synthesis of Plutonium-Containing Reference Particulate Materials

Spencer Scott[1], Benjamin Naes[2], Jonathan Christian[1], Bryan Foley[1], Travis Tenner[2], Wendy Kuhne[1], Kim Wurth[2], Thomas Shehee[1], Seth Lawson[1], Henry Ajo[1], Kyle Samperton[1], Matthew Wellons[1*]

[1] Savannah River National Laboratory
[2] Los Alamos National Laboratory
[*] Presenting Author

Abstract

Novel mixed-element particle working standards are needed for instrument calibration and operational quality control within the International Atomic Energy Agency (IAEA) Network of Analytical Laboratories (NWAL). Historically, the microanalysis of mixed plutonium and uranium oxide materials has been challenging due to a deficiency of adequate particle working standards with well-characterized elemental and isotopic compositions. Savannah River National Laboratory (USA) previously developed the THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) production platform for the synthesis of uranium oxide particulate working standards. THESEUS uses aerosol-based technologies to generate, calcine, and aggregate monodispersed oxide-phase particle products. To synthesize Pu-containing U oxide microparticulates, the production platform was re-engineered and the microanalytical characterization methods were refined. THESEUS was redesigned to control the collection of targeted numbers of Pu/U particles on specific locations of microanalytical substrates. Physical modifications included a new thermal source and new electrostatic precipitator collection design. Analytical electron microscopy operations were improved with new automated particle measurement protocols which incorporated uranium oxide particle test specimens for quality assurance and control. A modified counting statistics method was developed to process large-geometry secondary ion mass spectrometry (LG-SIMS) data to assess both inter- and intra-particle elemental and isotopic homogeneity. These THESEUS and microanalytical developments were demonstrated with the syntheses of Pu/U oxide particulates with a 1:100 actinide elemental ratio. Other outcomes included spherical particle morphologies with an average particle diameter of one micrometer, and a constrained particle deposition on microanalytical substrates resulting in particulate loadings of < 2500 particles per planchet.

Introduction

The analysis of environmental samples by the International Atomic Energy Agency (IAEA) Network of Analytical Laboratories (NWAL) is contingent on the availability and measurement of reference materials with well-characterized and analytically useful isotopic compositions. For example, accurate isotope ratio analyses of sample unknowns require that analytical instruments are calibrated through measurements of reference materials. Such materials are also used for quality control (QC) and proficiency testing of the NWAL laboratories. Through the support of several IAEA member state support programs, research and development efforts have allowed for the production of QC reference material actinide particles via hydrothermal synthesis[1, 2] and aerosol-based generation

methods.[3-5] Within the US Support Program (USSP), the production of actinide-bearing QC reference microparticle materials is conducted at Pacific Northwest National Laboratory (PNNL) via hydrothermal synthesis and at Savannah River National Laboratory (SRNL) via aerosol-based generation; Los Alamos National Laboratory (LANL) supports the efforts of PNNL and SRNL through evaluation of sample particles by large geometry–secondary ion mass spectrometry (LG-SIMS) characterization. Mixed Pu/U actinide QC particulates with tailored isotopic, elemental, and morphological properties are of high value to the international safeguards community but still necessitate further development. Pu/U QC particulates are desired for several needs including the development and benchmarking of new analytical methods, refinement of U and Pu particle age-dating methods, QC operations to support international nuclear safeguards, and others.[6-8] Prototype specimens were manufactured two decades ago[9] and international programs have continued development efforts towards both Pu/U and Th/U reference microparticulates.[10-12] Our Pu/U particulate synthesis efforts have required solving chemistry and engineering challenges, which included enhancements to the production platform, modification to feedstock chemistries, and refinement of mass spectrometry methods.[13] This work focuses on development efforts within the context of prototype mixed actinide particulates with 1:100 Pu/U elemental ratios, their production chemistry, and analytical method development within the context of single-particle LG-SIMS analyses.

Particle Synthesis and Characterization Methods and Discussion

Syntheses with uranyl nitrate or uranyl oxalate feedstocks were explored to assess and compare their viability for Pu/U reference particles manufacturing. Mixed-element particles were generated using the SRNL-developed THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) production platform shown in Figure 1. Uniform droplets of tailored mixed-element feedstock solutions were aerosolized, dried, and calcined using an inline heater.[5, 14] Feedstock solutions for the mixed-element particulates consisted of a mixture of uranyl oxalate or uranyl nitrate, plus a plutonium nitrate solution at prescribed ratios based on the target Pu/U ratio for a given feedstock mixture. Uranium feedstock isotopic composition was depleted with a 1.7×10^{-3} $^{235}U/^{238}U$ ratio, and the plutonium feedstock isotopic composition was > 90 % ^{239}Pu. Select isotope and elemental ratio values are shown in Table 1. The uranium isotopic composition of the material used in the manufacture of this feedstock has been previously reported[5] and plutonium isotopic ratios were characterized by both inductively coupled plasma – mass spectrometry (ICP-MS) and gamma spectroscopy.

Solid uranyl oxalate trihydrate (31.7 mg) was dissolved using 37.6 mL of 0.1 M nitric acid to yield a 2.048 mM uranyl oxalate solution. Solid uranyl nitrate hydrate (20.7 mg) was dissolved using 20.1 mL of 0.1 M nitric acid to yield a 2.048 mM uranyl nitrate solution. Concurrently, an aliquot of a 0.0978 M plutonium nitrate solution (46 µL) was diluted to 2.2 mL using 0.1 M nitric acid to yield a 2.048 mM plutonium nitrate solution. Acidic solutions were employed to prevent the formation of polymeric Pu precipitates.[15, 16] These solutions were then combined in a nominal 1:100 Pu/U ratio to generate the feedstocks that were injected into the THESEUS particle production platform. The total concentration of the feedstock solutions was fixed at a vol./vol. ratio of 2.75×10^{-4} to yield particles with a targeted 1-µm diameter. The generated particles were heated at 600 °C as a flowing aerosol to

facilitate the conversion to a predominate oxide phase. The generated particles were then collected on 1-inch diameter, polished carbon planchets and/or silicon wafers located within a custom designed electrostatic precipitator. Collection substrates within the collector were masked with plastic overlays to restrict deposition to the center of the planchet for ease of future handling and microanalytical characterization.
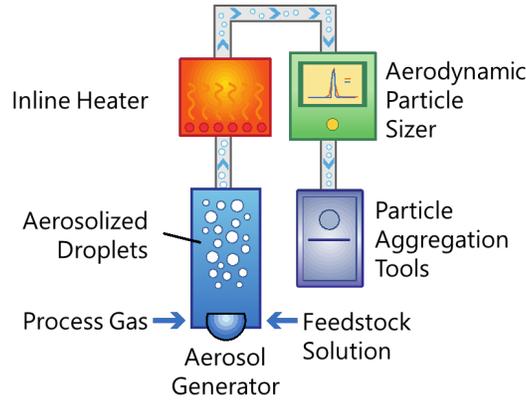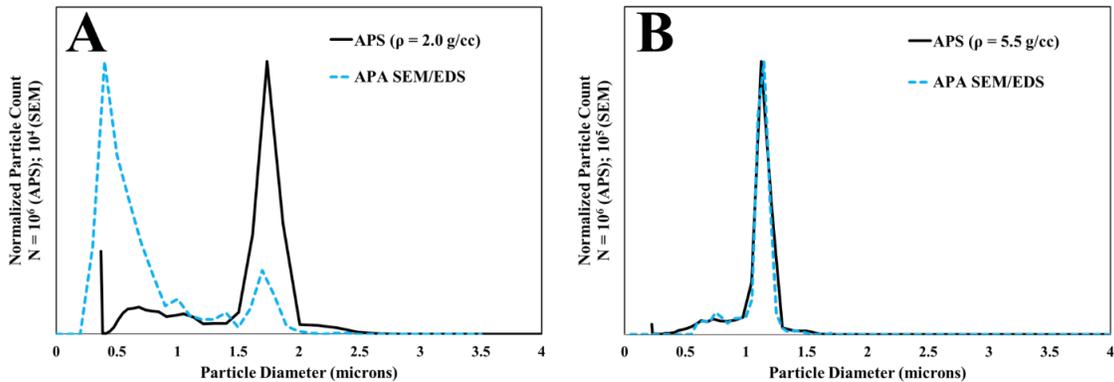

Figure 1. Cartoon diagram of the THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) production platform used in the development of Pu/U particulates at SRNL.

Aerodynamic particle sizing data from 0.5 to 20 micrometers was captured during THESEUS operations with the Aerodynamic Particle Sizer (APS) from TSI Inc. APS aerodynamic sizing data was scaled with respect to particle characterization data generated via automated particle analysis (APA) scanning electron microscopy (SEM) methods and density approximation. APA SEM was performed with a Zeiss Crossbeam field emission SEM coupled to an Oxford Energy Dispersive Spectrometry (EDS) with the AZtecFeature software. This setup allowed for automated search, identification, and characterization of Pu/U particles located on the THESEUS-generated particle-laden sample planchets. Overlay of density-scaled APS and APA SEM particle size distributions shown as two histograms is shown in Figure 2. High-resolution SEM imaging was performed on the same instrumentation and representative particle images are shown Figure 3.

Figure 2: Overlays of APS and APA SEM/EDS particle sizing data acquired during or post synthesis, respectively, for 1:0100 Pu/U particles synthesized with uranium nitrate (A), or oxalate (B) feedstock. Shown APS data was density-scaled to fit signal patterns and enable assessment of any correlation between data sets.
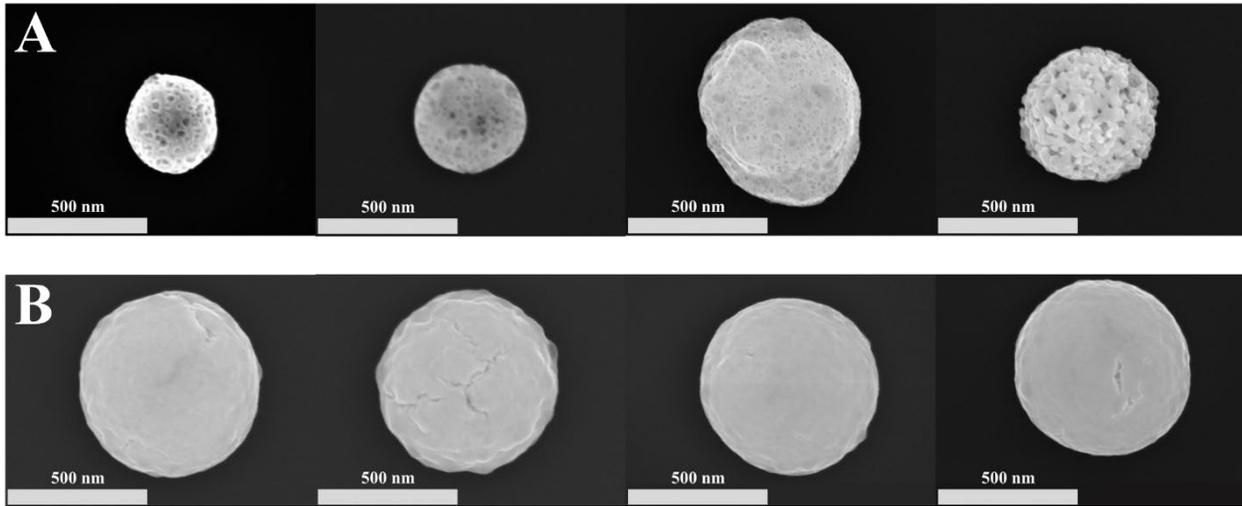

Figure 3: Representative high resolution secondary electron images of 1:100 Pu/U particles synthesized with uranyl nitrate (A), or oxalate (B) feedstock. All images captured via the Zeiss InLens detector with magnification of 65 kX, working distance of 13 mm, probe current of 500 mA, and electron high tension of 20 kV.

Particles generated via the uranyl nitrate and plutonium nitrate feedstock combination exhibited a multi-modal size distribution (Figure 2a) with two aggregate histogram maxima centered at approximately 0.5 and 1.7 μm diameter. Note the APS instrumentation is not designed to measure particles with <0.5 μm aerodynamic diameter but does show a histogram maximum near 1.7 μm. This particle population appears to correlate with the overlaid APA SEM measurements assuming a notional particulate density $\rho = 2.2$ g/ml. This low-density approximation relative to solid uranium oxides (U_3O_8 $\rho = 8.3$ g/ml) is consistent with SEM imaging, which shows particulates with highly porous surface structure and complex morphologies (Figure 3a). Particles synthesized with the uranyl nitrate feedstock were predominantly of sub-micron diameters, well below the THESUES recipe target size of 1 μm. Particles generated using the uranyl oxalate and plutonium nitrate feedstock combination demonstrated a mono-modal size distribution with a single histogram maximum centered at approximately 1.1 μm, consistent with the THESUES recipe target particle diameter of 1 μm (Figure 2b). This particle population correlates well with the overlaid APA SEM measurements, assuming a particulate density of approximately 5.5 g/ml. This value is less than typical solid uranium oxide particulates but consistent with SEM images of particulates with uniform surface features and minimal visible porosity (Figure 3b). The specific chemical and physical phenomenon responsible for the microparticle product differences between uranyl nitrate and oxalate feedstocks is unknown but is likely due to disparate drying and thermally-induced decomposition dynamics.

A Cameca IMS 1280 LG-SIMS was used for isotopic ratio particle analysis at LANL using methods as previously reported.[13] Typical analyses of particles with Pu and U used four of five multicollectors positioned to detect signal from masses 235, 238, 239, and 240 (i.e., typically the most abundant isotopes of U and Pu), with the fifth multicollector positioned for a desired minor isotope of Pu or U. Importantly, at mass 241, [241]Pu and [241]Am are not resolved under the aforementioned operating

conditions. Also, no mathematical estimate of hydride interference signal can be employed for simultaneous detection of U and Pu isotopes (e.g., $^{238}U^1H$ and ^{239}Pu, $^{239}Pu^1H$ and ^{240}Pu, $^{240}Pu^1H$ and $^{241}Pu + ^{241}Am$, $^{235}U^1H$ and ^{236}U). However, the hydride abundance can be estimated from measurements of the substrate surrounding particles and is used to correct raw data[13]. Cameca's Automated Particle Measurement (APM) software was used to initially locate Pu/U particles of interest. The data presented herein is from high-precision single particle analysis using a small primary ion beam raster (5 μm² to 10 μm²)[13].

Two different LG-SIMS single particle analysis methods were explored: (1) A traditional single particle measurement strategy, where the signal collection duration (150 s) was selected based on the "flattest" region of the depth profile or most temporally consistent isotope compositions, and (2) consumption analyses, where data were accumulated beginning with the onset of sputtering and ending once the particle was fully consumed (900 s). Figure 4 shows comparisons of single particle depth profile datasets collected, and the time windows for which traditional and consumption methods for particles generated from both feedstocks were explored. When plotted together, it is apparent that the consumption method produces higher average Pu/U ratios and smaller uncertainties than those from traditional single particle analyses. In addition, plotting the average data points demonstrates the relationships between the depth profiles and single particle measurement results. With respect to the consumption method of analysis, the contribution of signal from the whole profile leads to a higher average Pu/U ratio; this is in contrast to the lower average Pu/U ratios from the traditional single particle analysis approach, from which signal is only compiled from the earlier, "flatter" regions of the profiles. Also, the uranyl oxalate feedstock samples have relatively high Pu/U values over the first 1000 seconds. This suggests that the oxalate feedstock allows incorporation of more Pu into the particulate. These results are tabulated below in Table 1.
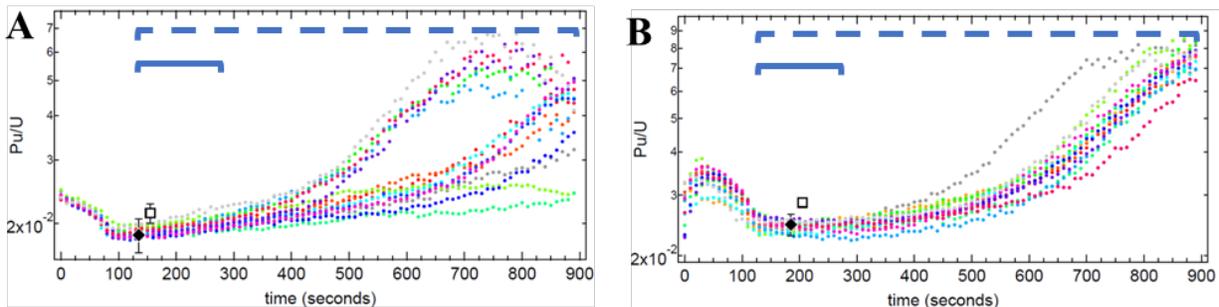

Figure 4: LG-SIMS single particle depth profiles for (A) 1:100 Pu/U (nitrate feedstock) and (B) 1:100 Pu/U (oxalate feedstock). Each color represents a distinct single particle analysis. Pu/U (y-axis) is shown as a function of sputtering time (x-axis). Scatter in the Pu/U ratio approaching the 900 second mark is indicative of particle consumption/low count rates. The solid and dashed brackets denote the traditional versus consumption signal collection windows, respectively. The black diamond represents the average of the traditional single particle analysis approach while the white box shows the average for the particle consumption method, with uncertainties displayed at 2SD (standard deviation). Note: Pu/U data are not relative sensitivty factor (RSF) corrected/calibrated.

Figure 5 (uranyl nitrate feedstock) and Figure 6 (uranyl oxalate feedstock) show single particle intra- and inter-elemental isotopic ratios for the analyzed 1:100 Pu/U particulates. The figures include data from both traditional and consumption method single particle LG-SIMS measurements. All data are

R&R Date: April 25, 2023

summarized in Table 1, which also includes nominal laboratory referenced values. Regardless of LG-SIMS analytical protocol, measured $^{235}U/^{238}U$ ratios are consistent with particle production feedstock values ($^{235}U/^{238}U$: 1.70 x 10^{-3}). The $^{240}Pu/^{239}Pu$ ratios are also consistent with reference values, and regardless of measurement type, albeit slightly elevated due to uncertainties of the instrument bias correction. The (^{241}Pu + ^{241}Am) /^{239}Pu ratio was consistent between particles and feedstocks with minor deviation, with no dependence on analysis type. As detailed in previous reports, a particle homogeneity/heterogeneity assessment includes use of a counting statistics-based predictive model developed at LANL.[13] This is represented by a Gaussian distribution factor wherein 99+% of data (particle scatter) would fall inside the upper and lower bounds of the model curves if/when a homogeneous particle population exists. If a significant number of particle data plot outside of the calculated bounds of the model, the particle population is resolvable as isotopically heterogeneous. The calculated models for each isotope system are shown in Figure 5 and Figure 6 as red curve overlays. Both sample types and both LG-SIMS methods are shown to be isotopically homogeneous with respect to their intra-element ratios ($^{235}U/^{238}U$ and $^{240}Pu/^{239}Pu$), as most data fall within the counting statistics-based models of predicted scatter about the averages. In contrast, the Pu/U datasets for each sample are notionally heterogenous, as the data are scattered beyond the model predictions. However, and if only considering the consumption method datasets, the particles synthesized from uranyl oxalate feedstock have a significantly lower Pu/U two-standard deviation (2SD) (±5.95E-4) than that of the particle dataset from the uranyl nitrate feedstock (±1.65E-3) (Table 1).

Table 1: LG-SIMS average isotope or elemental ratio for each of the two methods of analysis (single particle consumption and traditional single particle measurement) per sample type, 1:100 Pu/U oxalate feedstock and 1:100 Pu/U nitrate feedstock. Uncertainties are 2SD of the mean for the accumulated particle data. Reference data were calculated from U and Pu feedstock isotopic compositions and laboratory assay values. Apparent Pu/U relative sensitivity factor (RSF) values are calculated as the ratio of LG-SIMS (e.g., raw/measured) and laboratory feedstock (e.g., known) Pu/U values.

|	SIMS Analysis and No. Particles	$^{235}U/^{238}U$	$^{240}Pu/^{239}Pu$	(^{241}Pu + $^{241}Am)/^{239}Pu$	Pu/U	Pu/U RSF
Particles w/ uranyl nitrate feedstock	Consumption (15)	1.76E-03 ± 1.46E-04	7.00E-02 ± 6.12E-03	2.41E-03 ± 3.38E-04	2.15E-02 ± 1.65E-03	2.15
	Traditional (30)	1.75E-03 ± 1.02E-04	6.99E-02 ± 5.71E-03	2.23E-03 ± 7.26E-04	1.85E-02 ± 2.01E-03	1.85
Particles w/ uranyl oxalate feedstock	Consumption (17)	1.77E-03 ± 1.58E-05	7.56E-02 ± 2.85E-03	2.26E-03 ± 1.43E-04	2.85E-02 ± 5.95E-04	2.85
	Traditional (21)	1.74E-03 ± 1.15E-04	7.60E-02 ± 3.00E-03	2.22E-03 ± 3.45E-04	2.46E-02 ± 1.76E-03	2.46
Nominal Feedstock Ref. Values	-	1.70E-03	6.36E-02	1.83E-03	1.01E-02	-
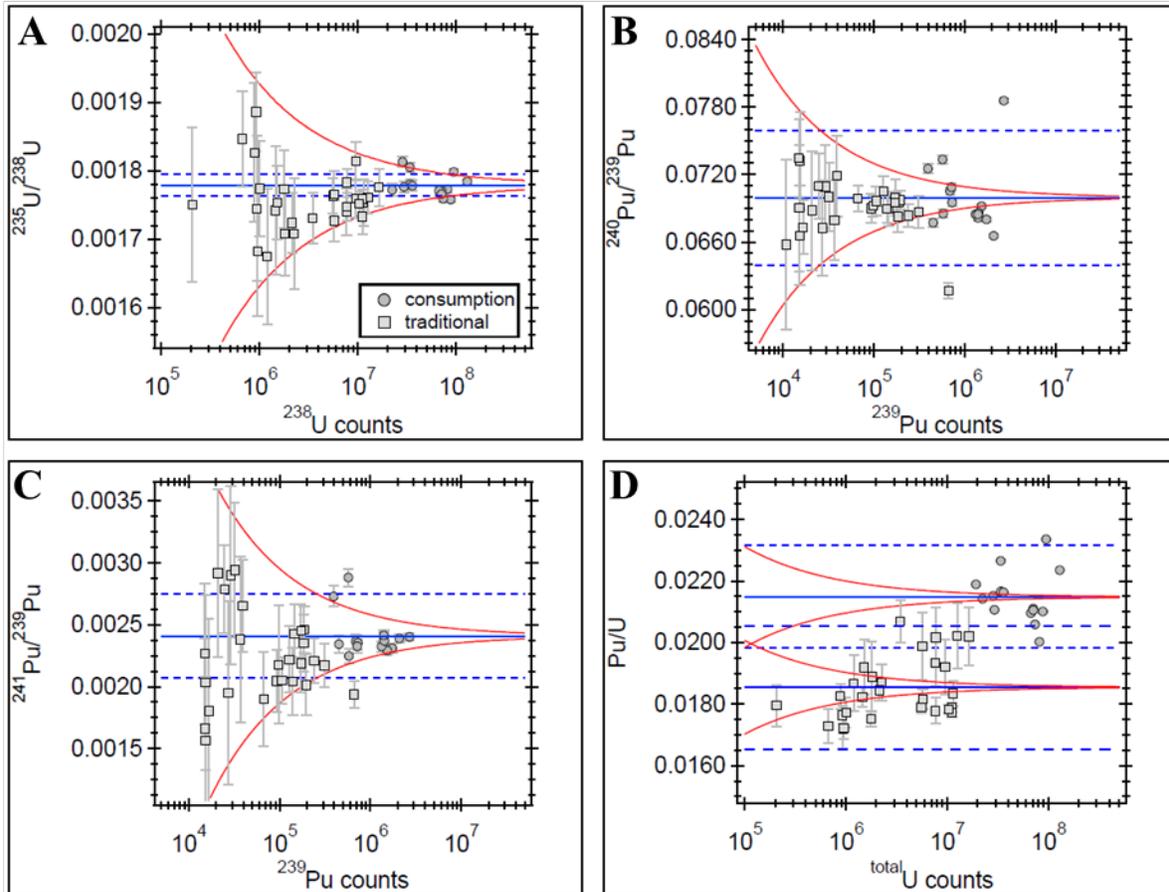
Figure 5 : LG-SIMS single particle analysis isotope ratio (particle distribution) plots for the 1:100 Pu/U sample (nitrate feedstock). Results from the traditional and consumption methods of analysis are shown in (A) $^{235}U/^{238}U$, (B) $^{240}Pu/^{239}Pu$, (C) $^{241}Pu/^{239}Pu$, and (D) Pu/U. Averages and uncertainties of all datasets are provided in Table 1. The solid and dashed blue lines represent the average and expanded standard deviation (2SD), while the solid red curves represent the counting statistics-based model of predicted scatter for a homogeneous source[13]. Uncertainites of individual particle data from the consumption method are based on counting statistics, whereas uncertainites for the single particle method are 2SE (standard error) of the 10 cycles of accumulated data. Note: Pu/U data are not RSF corrected/calibrated.
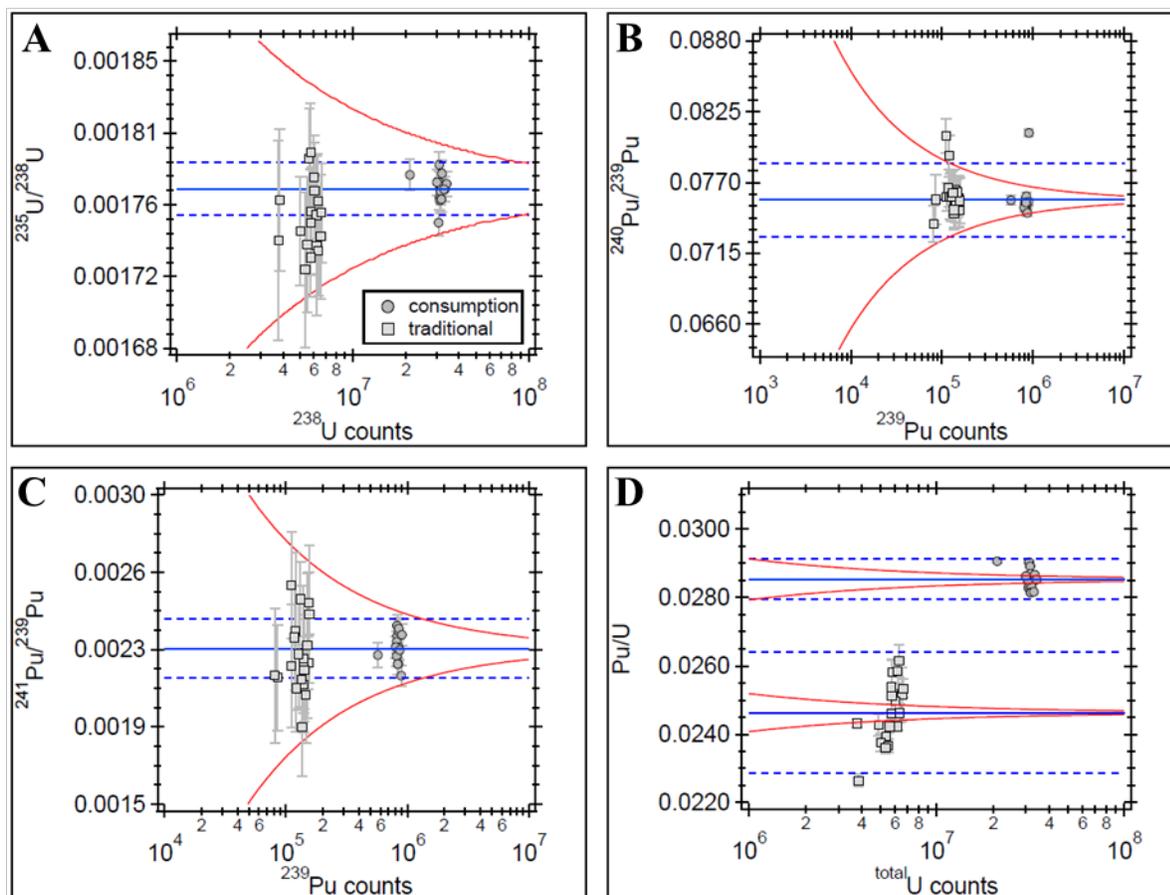
Figure 6: LG-SIMS single particle analysis isotope ratio (particle distribution) plots for the 1:100 Pu/U samples (oxalate feedstock). Results from the traditional and consumption methods of analysis are shown in (A) $^{235}U/^{238}U$, (B) $^{240}Pu/^{239}Pu$, (C) $^{241}Pu/^{239}Pu$, and (D) Pu/U. Averages and uncertainties of all datasets are provided in Table 1. The solid and dashed blue lines represent the average and expanded standard deviation (2SD), while the solid red curves represent the counting statistics-based model of predicted scatter for a homogeneous source (see model equation in main text). Uncertainties of individual particle data from the consumption method are based on counting statistics, whereas uncertainties for the single particle method are 2SE of the 10 cycles of accumulated data. Note: Pu/U data are not RSF corrected/calibrated.

Without certified Pu/U elemental ratio reference materials to calibrate the instrument, raw SIMS Pu/U ratios cannot be evaluated on an absolute basis for accuracy. This is due to a known observation that Pu and U have different ionization efficiencies during sputtering. This effect is known as the relative sensitivity factor (RSF), which is defined as $(Pu/U)_{raw}/(Pu/U)_{known}$. Note that samples of the same matrix type should theoretically have the same RSF if measured under the same analytical conditions, meaning that regardless of Pu abundance, test material samples should yield similar Pu/U RSF values. Prior LG-SIMS efforts to characterize particles with mixed Pu and U have determined a Pu/U RSF value of 2.4.[17, 18] Here, it is assumed that the $(Pu/U)_{known}$ values are 0.01 (i.e., 1:100 Pu/U) based on the laboratory manipulations to synthesize the feedstocks. As such, the $(Pu/U)_{known}$ can be combined with the LG-SIMS $(Pu/U)_{raw}$ values to estimate Pu/U RSF as shown in Table 1, using the raw averaged values of the single particle datasets from both the traditional and the consumption analysis methods. The Pu/U RSF values determined from the samples range from 1.85 to 2.85 and are dependent on the analysis method (e.g., consumption versus traditional) and feedstock.

For a given Pu abundance and analysis method, the Pu/U RSF values from samples produced using oxalate feedstocks are 0.6 to 0.7 units higher than those values from samples produced using nitrate feedstocks. For example, the RSF determined for uranyl oxalate feedstock derived particulates (consumption method) is 2.85 while the RSF from nitrate derived particulates (consumption method) is 2.15. It is possible that the uranyl nitrate and oxalate feedstocks yield different Pu/U RSF values due to varied resultant material phases from thermal conversion in the particle generation process. However, the more likely explanation is that the samples produced from nitrate feedstocks have relatively lower abundances of Pu than those produced from the oxalate feedstocks. Also of note is that for a given sample, the Pu/U RSF determined from consumption single particle analyses is 0.3 to 0.4 units higher than that determined from the traditional single particle analysis method. This disparity is due to differences in data acquisition between methods and is likely related to the single particle depth profiles (e.g., Figure 4).

Collectively, the range of calculated Pu/U RSF values are similar to a value of 2.4, determined from previous studies mentioned above, suggesting that the actual Pu abundances of the test material samples are close to the nominal value. The Pu/U RSF values of the oxalate feedstock-derived samples (2.46 and 2.85) more closely match the previously determined value of 2.4 than those from the nitrate feedstock-derived samples (1.85 and 2.15); the oxalate feedstock-derived sample values are also similar to an RSF of 2.8 determined by LANL LG-SIMS characterization of an additional mixed Pu/U test material generated by SRNL.[13] As such, we hypothesize the oxalate feedstock-derived samples have actual Pu abundances that more closely match the targeted Pu abundances. However, confirmation of Pu abundances requires further bulk characterization of these samples, such as by multicollector (MC) ICP-MS and/or thermal ionization mass spectrometry (TIMS). In the future, if working reference material particles with mixed U and Pu become available, with *fully verified* intra-element and inter-element ratios via MC-ICP-MS and/or TIMS characterization, such particles can serve to calibrate the LG-SIMS instrument, which will allow for generation of accurate measurements (e.g., RSF corrected Pu/U ratios) of unknown particle samples with mixed U and Pu.

Conclusions

This study has resulted in a modified particle synthesis approach and new measurement methods to improve the quality of future reference microparticle products. It was determined that uranyl oxalate precursors outperformed uranyl nitrate precursors for the production of Pu/U particulates within the SRNL operational scenario. In addition, selecting a total consumption single particle LG-SIMS approach improved the accuracy of the measured Pu/U elemental ratios. Future efforts will include destructive analysis for isotopic and elemental ratio measurements of sacrificial particle-laden planchets via MC-ICP-MS. The planned activity will select U and Pu reference spikes to unambiguously characterize aggregate particle composition and provide qualified reference information to assist particle synthesis and LG-SIMS data analytical method development.

6   References

1.   Trillaud, V.; Maynadie, J.; Manaud, J.; Hidalgo, J.; Meyer, D.; Podor, R.; Dacheux, N.; Clavier, N., Synthesis of size-controlled UO 2 microspheres from the hydrothermal conversion of U (IV) aspartate. *CrystEngComm* **2018**, *20*, (48), 7749-7760.
2.   Pope, T. R.; Arey, B. W.; Zimmer, M. M.; II, M.; Bronikowski, M. G.; Kuhne, W.; Baldwin, A. T.; Padilla-Cintron, C.; Anheier, N. C.; Warner, M. G., Production of particle reference and quality control materials. *ESARDA* **2019**, 29.
3.   Neumeier, S.; Middendorp, R.; Knott, A.; Dürr, M.; Klinkenberg, M.; Pointurier, F.; Sanchez, D. F.; Samson, V.-A.; Grolimund, D.; Niemeyer, I., Microparticle production as reference materials for particle analysis methods in safeguards. *MRS Advances* **2018**, *3*, (19), 1005-1012.
4.   Kegler, P.; Pointurier, F.; Rothe, J.; Dardenne, K.; Vitova, T.; Beck, A.; Hammerich, S.; Potts, S.; Faure, A.-L.; Klinkenberg, M., Chemical and structural investigations on uranium oxide-based microparticles as reference materials for analytical measurements. *MRS advances* **2021**, *6*, 125-130.
5.   Scott, S. M.; Baldwin, A. T.; Bronikowski, M. G.; II, M. A. D.; Inabinet, L. A.; Kuhne, W. W.; Naes, B. E.; Smith, R. J.; Villa-Aleman, E.; Tenner, T. J. *Scale-up And Production Of Uranium-bearing QC Reference Particulates By An Aerosol Synthesis Method*; Savannah River Site (SRS), Aiken, SC (United States). Savannah River …: 2021.
6.   IAEA, Research and Development Plan: STR-385. In Safeguards, I., Ed. IAEA: Vienna AU, January 2018.
7.   Diacre, A.; Fauré, A.-L.; Cornaton, M.; Pointurier, F.; Evrard, O., 240Pu/239Pu isotopic ratio measurements in micrometric Pu and MOX particles using Secondary Ion Mass Spectrometry. *Talanta* **2023**, *252*, 123848.
8.   Konegger-Kappel, S.; Prohaska, T., Spatially resolved analysis of plutonium isotopic signatures in environmental particle samples by laser ablation-MC-ICP-MS. *Analytical and bioanalytical chemistry* **2016**, *408*, 431-440.
9.   Stoffel, J.; Briant, J.; Simons, D., A particulate isotopic standard of uranium and plutonium in an aluminosilicate matrix. *Journal of the American Society for Mass Spectrometry* **1994**, *5*, (9), 852-858.
10.   Potts, S. K.; Kegler, P.; Modolo, G.; Hammerich, S.; Niemeyer, I.; Bosbach, D.; Neumeier, S., Structural incorporation of lanthanides (La, Eu, and Lu) into U3O8 as a function of the ionic radius. *MRS Advances* **2022**, *7*, (7-8), 128-133.
11.   Asplanato, P.; Zannouh, W.; Fauré, A.; Imbert, P.; Lautru, J.; Cornaton, M.; Dacheux, N.; Pointurier, F.; Clavier, N., Hydrothermal synthesis of homogenous and size-controlled uranium-thorium oxide micro-particles for nuclear safeguards. *Journal of Nuclear Materials* **2023**, *573*, 154142.
12.   Beck, C. L.; Arnold, E. S.; Warzecha, E. J.; Koh, K.; Stene, R. E.; Pope, T. R.; Henson, N. J.; Vogt, S. K.; Wellons, M. S.; Barrett, C. A., Separation of thorium from uranium in support of particle reference material production. *Journal of Radioanalytical and Nuclear Chemistry* **2022**, 1-4.

13.   Tenner, T. J.; Naes, B. E.; Wurth, K. N.; Meininger, D.; Wellons, M. S.; Pope, T. R., New Particle Working Standards for NWAL Particle Laboratory Calibration and Quality Control – LANL LG-SIMS Characterization and Evaluation. *Proceedings of the INMM & ESARDA Joint Annual Meeting* **2023**.

14.   Louis-Jean, J.; Bergin, R.; Bronikowski, M.; Kuhne, W.; Lawson, S.; Waldron, A.; Wellons, M.; Scott, S. M., Synthesis of Metal Oxide Microparticles for Use as Carriers of Intentional Forensic Signatures. *Proceedings of the INMM & ESARDA Joint Annual Meeting* **2023**.

15.   Bronikowski, M. *Technical Basis for Safe Operations with Pu-239 in NMS and S Facilities (F and H Areas)*; Savannah River Site (SRS), Aiken, SC (United States): 1999.

16.   Costanzo, D.; Biggers, R.; Bell, J., Plutonium polymerization—IA spectrophotometric study of the polymerization of plutonium (IV). *Journal of inorganic and nuclear chemistry* **1973,** *35*, (2), 609-622.

17.   Wallenius, M., Origin determination of reactor produced plutonium by mass spectrometric techniques: application to nuclear forensic science and safeguards. **2001**.

18.   Tamborini, G.; Wallenius, M.; Bildstein, O.; Pajo, L.; Betti, M., Development of a SIMS method for isotopic measurements in nuclear forensic applications. *Microchimica Acta* **2002,** *139*, 185-188.