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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

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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 monodisperse 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 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 within average particle diameter of one micrometer, and a constrained particle deposition on microanalytical substrates resulting in particulate loadings of < 2500 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 isotope 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 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 assessed their respectively viability for Pu/U reference particles manufacturing routes. 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 U-Pu 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 distribution of the material used in the manufacture of this feedstock has been previously reported[5] and plutonium isotope ratios were characterized by both 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 afford 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 afford 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 100:1 U:Pu 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 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.
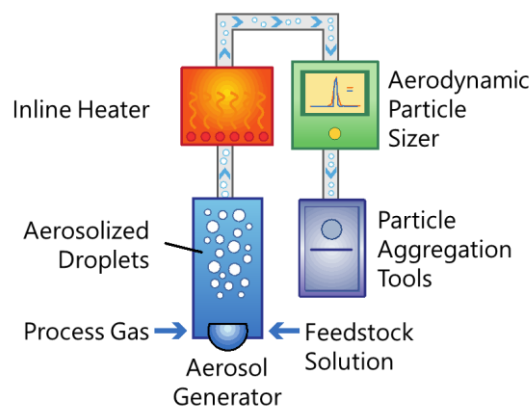

Figure 1. Cartoon diagram of the THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) production platform used in the development of U/Pu particulates.

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.
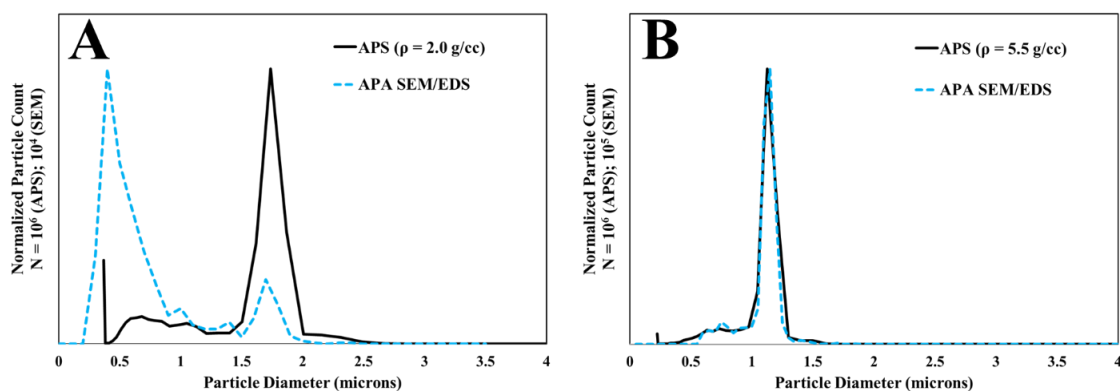

Figure 2: Overlays of APS and APA SEM/EDS particle sizing data acquired during or post synthesis, respectively, for 100:1 U:Pu particles synthesized with uranium nitrate (A), or oxalate (B) feedstock. Shown APS data was density-scaled to fit signal patterns and enable assessment of any correlation between data sets.
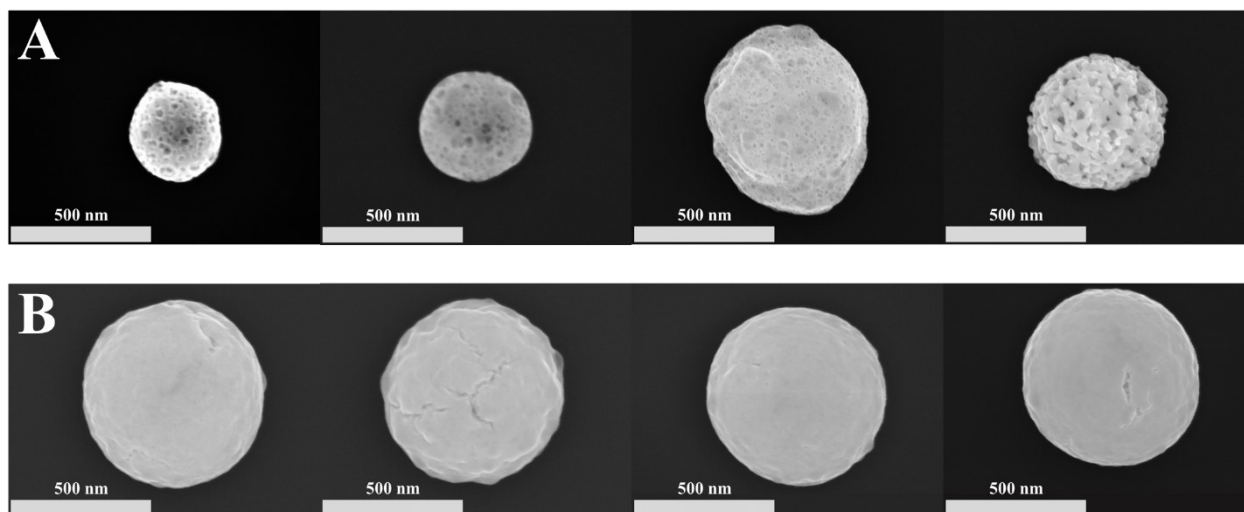
Figure 3: Representative high resolution secondary electron images of 100:1 U:Pu particles synthesized with uranyl nitrate (A), or oxalate (B) feedstock. All images captured via the Zeiss InLens detector with magnification of 65 kX, working distance of 13 mm, probe current of 500 mA, and electron high tension of 20 kV.

Particles generated via the uranyl nitrate and plutonium nitrate feedstock combination exhibited a multi-modal size distribution (Figure 2) with two aggregate histogram maxima centered at approximately 0.5 and 1.7 μm. 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 ρ = 2.2 g/cc. This low-density approximation relative to solid uranium oxides (U_3O_8 ρ = 8.3 g/cc) 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 of 1 μm. Particles generated using the uranyl oxalate and plutonium nitrate feedstock combination demonstrated mono-modal size distributions with a single histogram maximum centered at approximately 1.1 μm, consistent with the THESUES recipe target particle diameter of 1 μm (Figure 2. This particle population correlates well with the overlaid APA SEM measurements, assuming a particulate density of approximately 5.5 g/cc. This 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 large geometry secondary ion mass spectrometer (LG-SIMS) was used for isotopic ratio particle analysis using methods as previously reported.[13] Typical analyses of particles with Pu and U used four of the five multicollectors positioned to detect signal from masses 235, 238, 239, and 240 (i.e., typically the most abundant isotopes of Pu and U), 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^{1}H and ^{239}Pu, ^{239}Pu^{1}H and ^{240}Pu, ^{240}Pu^{1}H and ^{241}Pu + ^{241}Am, ^{235}U^{1}H and ^{236}U) because there are too many

unconstrained variables. However, the hydride abundance can be estimated from measurements of the substrate surrounding particles and used to correct raw data[13]. Cameca's Automated Particle Measurement (APM) software was used to initially locate Pu/U containing particles of interest. The data presented herein is high-precision single particle analysis using a small primary ion beam raster (5 μm^2 to 10 μm^2)[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 relatively higher averaged Pu/U ratios and smaller uncertainties than those from the traditional method for single particle analyses. In addition, plotting the average data points demonstrates the relationships between the depth profiles and the single particle measurement data. 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 comparatively higher Pu/U values over the first 1000 seconds. This suggests that the oxalate feedstock allows incorporation of more Pu into the particulate. Numerical representation of this phenomenon is presented below in Table 1.
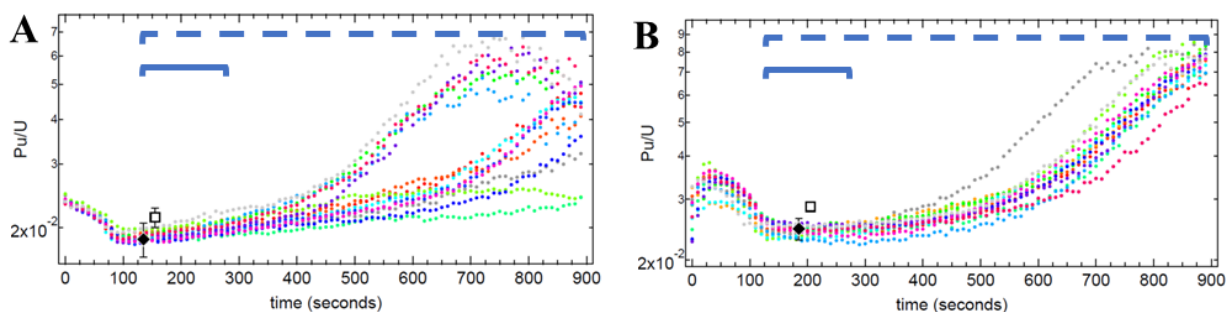

Figure 4: LG-SIMS single particle depth profiles for (A) 100:1 U:Pu (nitrate feedstock) and (B) 100:1 U:Pu (oxalate feedstock). Each color represents a different single particle analysis. Pu/U (y-axis) as a product of sputtering time (x-axis). Scatter in the Pu/U ratio approaching the 900 second mark is indicative of particle consumption. 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. Note: Pu/U data are not RSF corrected.

Figure 5 (uranyl nitrate feedstock) and Figure 6 (uranyl oxalate feedstock) show single particle intra- and inter-elemental isotopic ratios for the analyzed 100:1 U:Pu particulates. The figures include data from both traditional and consumption method single particle LG-SIMS measurements. All data are summarized in Table 1, which also includes nominal laboratory referenced values. Regardless of LG-SIMS analytical protocol demonstrated the $^{235}U/^{238}U$ ratios are consistent with particle production

feedstocks ($^{235}U/^{238}U$: 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, particle homogeneity/heterogeneity assessment includes use of a counting statistics 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 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 isotope or elemental ratio calculated averages for each of the two methods of analysis (single particle consumption and traditional single particle measurement) per sample type, 100:1 U:Pu oxalate feedstock and 100:1 U:Pu nitrate feedstock. Provided uncertainties are 2SD of the mean for the accumulated particle data. Reference data were calculated from U and Pu feedstock isotope ratio and laboratory assay values. Pu/U RSF values are calculated from the division of LG-SIMS (e.g. raw) 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	-

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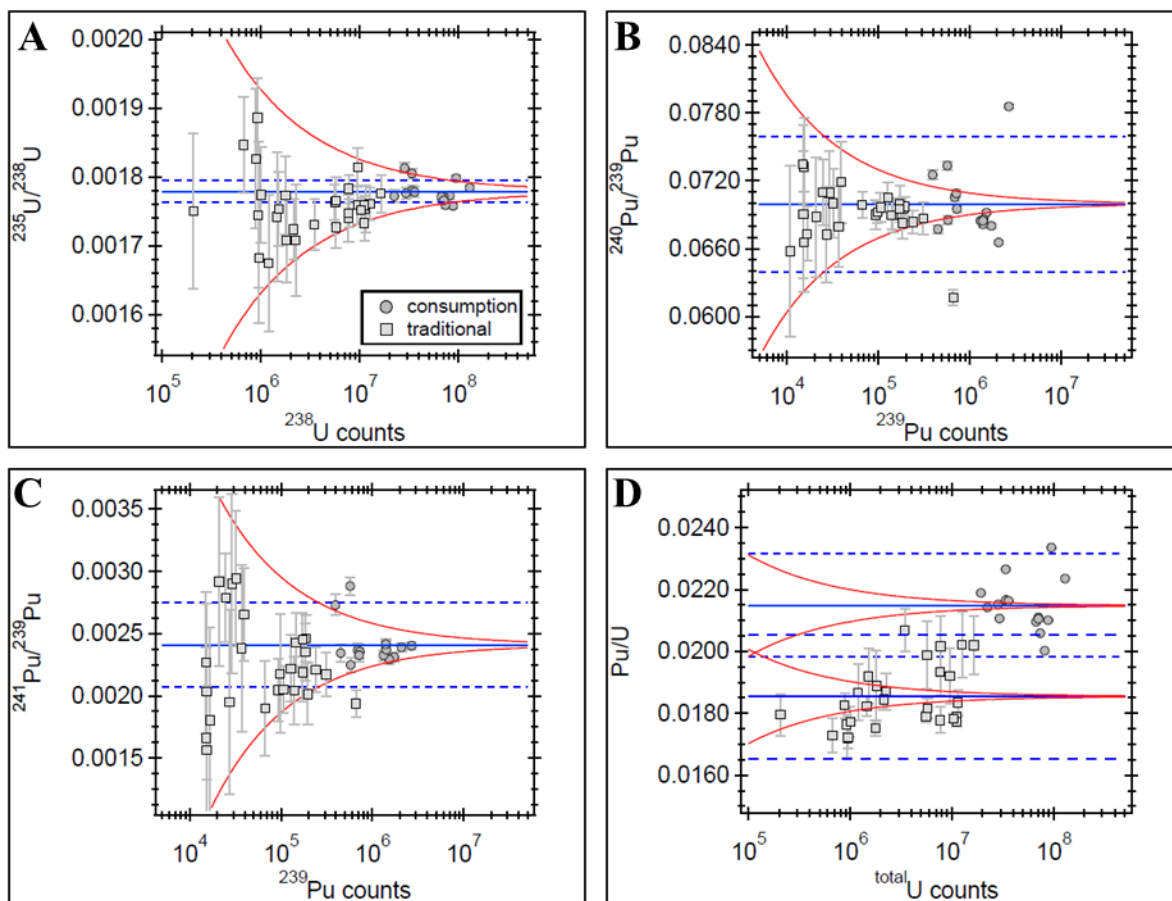
Figure 5 : LG-SIMS single particle analysis isotope ratio (particle distribution) plots for the 100:1 U:Pu (nitrate feedstock) sample. Results from the traditional and consumption methods of analysis are shown in (A) ^{235}U/^{238}U, (B) ^{240}Pu/^{239}Pu, (C) ^{241}Pu/^{239}Pu, and (D) Pu/U. Averages 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]. Error bars of individual particle data from the consumption method are based on counting statistics whereas error bars of the single particle method are 2SE of the 10 cycles of accumulated data. Note: Pu/U data are not RSF corrected.
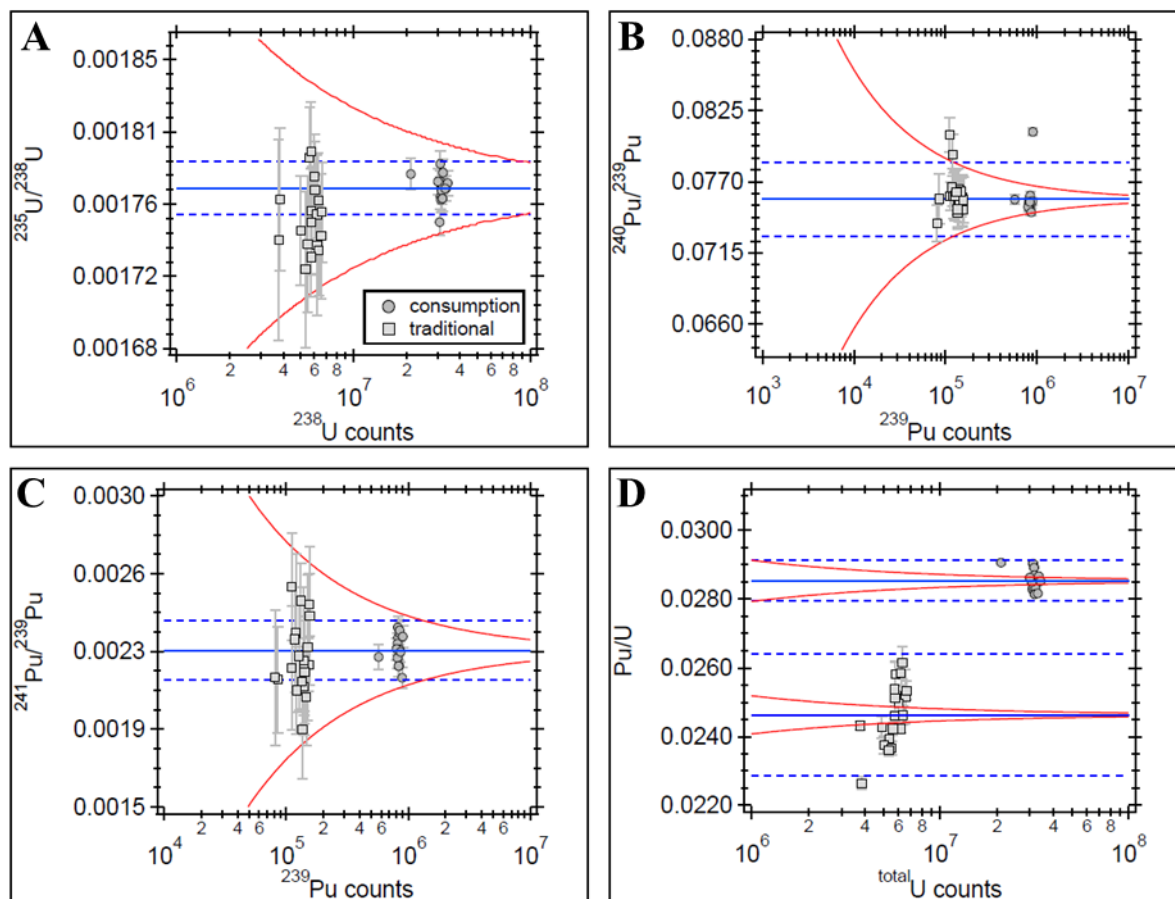
Figure 6: LG-SIMS single particle analysis isotope ratio (particle distribution) plots for the 100:1 U:Pu (oxalate feedstock) sample. Results from the traditional and consumption methods of analysis are shown in (A) $^{235}U/^{238}U$, (B) $^{240}Pu/^{239}Pu$, (C) $^{241}Pu/^{239}Pu$, and (D) Pu/U. Averages 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). Error bars of individual particle data from the consumption method are based on counting statistics whereas error bars of the single particle method are 2SE of the 10 cycles of accumulated data. Note: Pu/U data are not RSF corrected.

Without Pu/U reference materials to calibrate the instrument, raw SIMS Pu/U ratios are inherently inaccurate. This is primarily 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 have the same RSF, meaning that regardless of Pu abundance, all test material samples should have the same Pu/U RSF. In this regard, 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., 100:1 U:Pu) based on the laboratory manipulations to synthesize the feebstocks. As such, the $(Pu/U)_{known}$ can be combined with the LG-SIMS $(Pu/U)_{raw}$ values to calculate an estimated 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 identity.

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 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 collective Pu/U RSF values of the oxalate feedstock-derived samples (2.46 & 2.85) more closely match the previously determined value of 2.4 than those from the nitrate feedstock-derived samples (1.85 & 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 would require further bulk characterization of these samples, such as inductively coupled plasma mass spectrometry (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 ICP-MS and/or TIMS characterization, they can serve to calibrate the LG-SIMS instrument, which will allow for generation of accurate measurements (e.g., RSF corrected Pu/U ratios) of particle unknowns 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, utilizing 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 ICP-MC/MS. The planned activity will utilize uranium and plutonium reference spikes to unambiguously characterize aggregate particle composition and provide qualified reference information to assist both the particle synthesis and LG-SIMS data analytical method development.

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