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Synthesis and Characterization of a U/Pu Mixed-Actinide Microparticulate Reference Material

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International nuclear safeguards require microparticle reference materials (RMs) with complex uranium (U) and plutonium (Pu) compositions. RMs are needed for quality control within the international nuclear safeguard community governed by the International Atomic Energy Agency, and as qualification specimens for new microanalytical methods. Prior to this effort, no combined U/Pu microparticle specimens existed with sufficient characterization and corresponding qualified analytical measurands for U and Pu isotopic and elemental composition to meet this need. Savannah River National Laboratory (SRNL) produced homogeneous mixed U/Pu, monodisperse, micrometer-scale particles (denoted RM UPu-100A) using the SRNL THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) particle production platform._The targeted attributes for RM UPu-100A were a monodisperse, spherical particle size distribution centered at 1 µm diameter, n(^{238}U)/n(^{239}Pu) = 100; n(^{240}Pu)/n(^{239}Pu) = 0.30, and n(^{235}U)/n(^{238}U) = 0.05. After identifying, purifying, and mixing three uranium and two plutonium endmembers, monodisperse U/Pu microparticulate of the desired elemental and isotopic distributions was produced and electrostatically collected onto silicon planchets. Characterization of the produced microparticulate at SRNL and Los Alamos National Laboratory (LANL) used large geometry secondary ion mass spectrometry (LG-SIMS), multicollector—inductively coupled plasma—mass spectrometry (MC-ICP-MS), scanning electron microscopy (SEM), and alpha spectroscopy. Analysis results demonstrate that a compositionally homogeneous particle population was achieved. Key characteristics of RM UPu-100A include an approximate particle diameter of 1.08 µm and n(^{238}U)/n(^{239}Pu) = 103.3 ± 2.8; n(^{240}Pu)/n(^{239}Pu) = 0.2838 ± 0.0032; and n(^{235}U)/n(^{238}U) = 0.05221 ± 0.00024. A SIMS relative sensitivity factor, $RSF_{Pu:U}$, was calculated from n(^{238}U)/n(^{239}Pu); $RSF_{Pu:U} = 2.282 \pm 0.064$, and n(^{235}U+^{238}U)/n(^{239}Pu+^{240}Pu); $RSF_{Pu:U} = 2.242 \pm 0.063$.

Introduction

Environmental sampling of nuclear facilities is routinely conducted by the International Atomic Energy Agency under the auspices of the Treaty on the Non-Proliferation of Nuclear Weapons (NPT) to verify the absence of operations outside of safeguards declarations. These verification activities are often sample limited and of necessity characterize individual nuclear material particles generated within the course of facility operations using microanalytical techniques such as large geometry secondary ion mass spectrometry (LG-SIMS).[1-4] Suitable reference materials (RMs) for the necessary operational QA/QC and related R&D in microparticle analysis have historically been extremely lacking.[5, 6] Emulation of these analytes necessitates microparticles with picogram mass, complex elemental and isotopic compositions, special nuclear material composition, matrix-matched chemistries, and other parameters. These microparticles are exceedingly difficult to manufacture and then qualify as RMs.

Recently, significant technical maturation has occurred within the international LG-SIMS microanalytical community,[7, 8] with single particle analysis of actinide mono-elemental systems via the new availability of bulk single-element uranium (U) and plutonium (Pu) RMs distributed by the U.S. New Brunswick Laboratory Program Office (NBL-PO). However, high-fidelity LG-SIMS characterization of mono and multi-element actinide systems on the microscale has been limited by a marked paucity of well characterized, metrologically traceable, mixed-actinide RMs at the micrometre size scale. Moreover, between nuclear fission augmentation of pristine single-element nuclear fuels and increasing interest in mixed oxide fuels,[9, 10] the need for high quality, multi-element calibrants has increased. Prior to the effort reported herein, no viable microparticle mixed U/Pu RM has been available to the international nuclear safeguards community.

Two main categories describe the current methods used for producing high-fidelity microparticles: hydrothermal chemical synthesis and aerosolization droplet-to-particle methods. A substantial body of work describes the development and demonstration of these methods for the synthesis of uranium

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oxide particles;[11-13] however, studies of the synthesis of mixed uranium and plutonium-bearing materials are scarce. This scarcity of plutonium-bearing microparticulate production is attributed to several key factors: 1) the high radiotoxicity of plutonium and safety infrastructure necessary for its handling, 2) the need for pertinent expertise in the proposed microparticulate manufacturing processes, and 3) characterization facilities with the capability and capacity to support bulk and single-particle measurements of radioactive materials on a continuing basis. While several facilities possess a subset of these attributes, it is uncommon for a single institution to harbour all three. As such, multi-element particle standards certified for U and Pu isotopic composition have not been produced for decades.

Recently, Savannah River National Laboratory (SRNL) has matured a production process for the synthesis of micrometre-scale actinide particles using integrated aerosolization, in-flight calcination, and electrostatic collection tools. The SRNL instrument used in this process is the SRNL THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) system.[14] Initial production campaigns on this platform targeted mono-element uranium oxide microparticles.[15] These efforts benefited from significant advancements made by the international community in the furtherance of aerosol-based synthesis methods for actinide microparticle RMs.[16-18] Subsequent attempts to produce multi-element microparticle systems began with mono-element CeO_2 particle production[19] prior to exploring mixed element U/Ce[20] and U/Th[21] enroute to the generation of U/Pu microparticulates.[22] In each case, optimization of the desired operational parameters yielded particles of the desired size distribution, isotopic content, elemental content, and morphology. The critical uranium or surrogate particle production efforts by SRNL and others ultimately enabled the U/Pu microparticle manufacturing described herein.

An early report details the production and characterization of plutonium-bearing microparticulate in the form of aluminosilicate microparticles charged with actinides as calibration specimens for mixed actinide SIMS.[23] More recent efforts, including the authors', have focused on oxide microparticulate which better emulate analytes collected by environmental sampling.[24-26] Förthmann and Blass described the synthesis of mixed $(U/Pu)O_2$ and PuO_2 microparticulate using a hydrothermal process, wherein an actinide solution was sprayed through a vibrating nozzle into a hot silicon oil, allowing the aqueous droplets produced thereby to solidify and be collected for analysis.[24] More recently, Ranebo et al. (2010) used a vibrating orifice aerosol generator to generate mixed $(U/Pu)O_2$ and $^{242}PuO_2$ microparticles.[26] Other studies detail the synthesis of a polydisperse collection of U/Pu particles through successive evaporation/dissolution cycles and manual pulverization to generate particles.[27, 28] These manually generated particles have been demonstrated to be amenable to thermal ionization mass spectrometry (TIMS) analysis method wherein U/Pu and minor isotope ratios were measured.[29, 30] In a subsequent work, similar manually-pulverized materials were used for plutonium chronometry measurements by inductively coupled plasma—mass spectrometry (ICP-MS).[25, 31-33] In addition to these mixed U/Pu examples, polydisperse PuO_2 particles were prepared by dissolving plutonium nitrate in water, nebulizing, and calcining droplets in-flight, yielding polydisperse PuO_2 particulate then collected by impaction.[34]

Since the work of Ranebo et al. in 2010[26], there has been no openly published production of monodisperse, mixed U/Pu single particles with verified isotopic compositions for the nuclear safeguards microanalysis community. In fact, the production of U/Pu monodisperse microparticles that have been characterized for size, isotope amount ratios, and elemental and isotope amount homogeneity has never been published in the open literature. To fill this gap, SRNL synthesized a tailored U/Pu microparticulate material, RM UPu-100A, for use as a "gold standard" reference material across the nuclear safeguards microanalytical communities. From the outset, a synthesis goal for this material was interparticle elemental and isotopic homogeneity (i.e., each particle is identical within nominal measurement variance).

The target parameters for uranium and plutonium composition were driven by a need for the RM to possess, 1) significant Pu content relative to U to enable meaningful characterization of LG-SIMS ionization relative sensitivity factors and related measurement artifacts, 2) enable the exploration of mass spectra hydride interference phenomena common in mixed actinide materials, and 3) measurable concentrations across the mass range of most U and Pu isotopes. Other synthesis targets included particle size at ca. 1 micrometre in diameter with high monodispersity to ease reproducible particle to particle analysis, limited and well-characterized particle concentrations per sample, less than 5,000 particles, to address radiological safety requirements, and nominal oxide chemistry to better represent sample materials collected during nuclear safeguards environmental sampling. Details of the material preparation, feedstock mixing, particle production, and characterization are described successively herein.

Synthesis Details

CAUTION! *Plutonium and uranium are radioactive and toxic elements. All manipulations of these materials were performed inside of negative pressure radiological gloveboxes or radiological fume hoods which permit the safe handling of these materials.*

Note: Unless specified otherwise, all glassware used for manipulations described in this report was leached with nitric acid prior to use to remove trace contaminants from the wettable surfaces of the glass.

Feedstock Solution Calculation/Planning

The targeted isotope amount ratios for RM UPu-100A were $n(^{238}U)/n(^{239}Pu) = 100$; $n(^{240}Pu)/n(^{239}Pu) = 0.30$, $n(^{235}U)/n(^{238}U) = 0.05$, and $n(^{236}U)/n(U) = 17$ ppm. Since no individual U or Pu standards fit all these requirements, multiple materials were used to make the RM UPu-100A feedstock. Uranium and plutonium endmembers for feedstock solution preparation were identified using the SRNL Actinide Mixing Optimization

Solver (AMOS) MATLAB script.[35] This algorithm inputs available endmember isotopic information and calculates optimized endmember mixing ratios which will achieve a specified isotopic composition and minimizes the number of endmembers. The AMOS algorithm returned five endmembers for use in RM UPu-100A feedstock mixing: NBL-PO uranium certified reference materials (CRMs): C112A, U930D, U970, and two SRNL plutonium stock materials which were made and purified in-house at SRNL. The details of the preparation of these materials are described below and in the supporting information (SI).

Plutonium Purification and Binary Mixing

Two quantities of unique, legacy plutonium materials sourced from SRNL were purified for use in the synthesis of RM UPu-100A. The first was an approximately 5 gram quantity of reactor-grade plutonium dioxide (~79% ^{239}Pu; ~19% ^{240}Pu) which had been spiked with ^{241}Am and ^{238}Pu to increase the specific activity of the material for use in 3013 container corrosion studies.[36] The last known purification date of this material was ca. 2010 and significant radiogenic ingrowth of daughter isotopes made this material unsuitable for use in RM UPu-100A manufacturing if not chemically purified. To remove ^{241}Am and other radiogenic impurities, the entire 5-gram quantity was purified by anion exchange chromatography. Following chromatographic separation, the purified Pu-bearing solution was characterized by ICP-OES, Q-ICP-MS, and gamma spectroscopy.

The second source material purified for this effort was a quantity of plutonium, >97% ^{240}Pu, that was separated from a ^{244}Cm source ca. 1980. This material was also dissolved and purified by anion exchange chromatography. Full experimental details of both purification processes including dissolution, valence adjustment, column parameters, in-line analysis techniques, and final characterization information, are in the SI.

Aliquots of the reactor grade plutonium (800 µL; 0.10 mmol Pu) and ^{240}Pu (41 µL; 0.0046 mmol Pu) endmembers were combined into a 5 mL polypropylene centrifuge tube and stored for use in particle manufacturing.

Uranium Endmember Preparation, Mixing, Characterization, and Ternary Mixing

The three uranium endmember CRMs identified by the AMOS mixing algorithm were prepared for use in feedstock mixing in accordance with certificate instructions when available. C112A and U970 were prepared as nitric acid solutions while U930D (~5 mg U in a nitric acid solution) was used as received. A binary mixture of U970 and U930D was prepared first, and an aliquot of this binary uranium solution was removed for analysis by MC-ICP-MS to ensure that the targeted uranium isotopic composition was achieved before continuing, as U970 and U930D are not certified for U assay. To complete the ternary mixture, an aliquot of the C112A uranyl nitrate solution was transferred into a scintillation vial and was then quantitatively transferred into the binary U970/U930D solution to yield the ternary uranyl nitrate solution for RM UPu-100A manufacturing. The uranium isotopic composition of the final, ternary solution was measured by MC-ICP-MS prior to the precipitation of uranium from the solution as uranyl oxalate. The uranyl oxalate trihydrate solids were stored in an amber vial in a desiccator over CaSO$_4$. Details on preparation of uranium CRMs for dissolution, quantities of materials used, and the oxalate precipitation methodology are available in the SI.

U/Pu Feedstock Mixing

The feedstock solutions, comprised of uranyl oxalate trihydrate and plutonium nitrate, were prepared fresh each day of particle production. A weighed quantity of uranyl oxalate trihydrate was dissolved in 0.1 M HNO$_3$ to create a 2.04 mM solution. An aliquot of the binary plutonium solution was diluted with 0.1 M HNO$_3$ to create a 2.04 mM solution. These solutions were then combined volumetrically to yield a feedstock containing the desired ratio of U:Pu (ca. 100:1).

THESEUS Preparation

To ensure minimal cross-contamination from previous particle production experiments, all wettable components of the THESEUS particle production platform were disassembled and either discarded or thoroughly cleaned prior to the production of mixed U/Pu microparticles. The details of the THESEUS components and operational parameters were previously reported by the SRNL team.[21] Discarded (consumable) components included: the electrostatic precipitator, the radioactive containment enclosure, exhaust HEPA filter, inline heater, diffusion drier, three capillary fluid lines of the Flow Focusing Monodisperse Aerosol Generator (FMAG) and the Luer lock syringe fitting, all conductive silicone tubing, and Swagelok® valves. The inlet of the Aerodynamic Particle Sizer (APS) was cleaned with an isopropanol wipe and the piezoelectric stage of the FMAG was cleaned with alternating rinses of isopropyl alcohol and water.

After reassembly, the THESEUS platform was tested with water for operational functionality and thereafter no other modification in the production platform was made prior to the generation of RM UPu-100A.

Initial U/Pu Feedstock Mixing and Solution Instability

As stated previously, a series of mixed U/Th particle samples were manufactured prior to RM UPu-100A to quantify mixed element particle behaviour on the THESEUS production platform. Once the optimized parameters for the U/Th system were achieved, those settings were subsequently used for RM UPu-100A without significant modification.[21] Upon transitioning to RM UPu-100A production, several test U/Pu batches with increasing Pu content were manufactured using ultrapure water as the solvent/diluent. The test batch experiments produced spherical particles which exhibited a narrow size distribution cantered at 1 µm. Upon characterization by LG-SIMS, these test materials were observed to contain compositionally heterogeneous, interparticle U/Pu ratios. A literature review yielded information regarding the precipitation of plutonium colloids upon introduction of plutonium nitrate solutions into dilute nitric acid or water.[37-40] Ultraviolet-visible spectroscopy (UV-Vis) experiments were performed to determine a feedstock acid concentration that would be high enough to stabilize plutonium nitrate in solution, yet low enough that perturbation to the feedstock matrix was minimized. The details of this UV-Vis investigation are provided in the SI. In short, UV-Vis observation of a mixed uranyl oxalate/plutonium nitrate solution (U/Pu = 100; 2.04 mM total actinide) prepared using 0.1 M HNO_3 yielded no detectable plutonium colloids over the course of 24 hours. As such, all feedstock matrices used for RM UPu-100A manufacturing were 0.1 M HNO_3.

Feedstock Mixing and Particle Production

On the day of production, the mixed U/Pu feedstock was prepared and injected into the THESEUS particle production platform. Typical FMAG parameters included a feedstock solution injection rate of 3 mL/hr, a piezoelectric orifice vibration frequency of 130 kHz, dilution air flow rate of 15.0 L/min, and a flow focusing air pressure of 2.1 psi. Aerosolized droplets were calcined in flight at a temperature of 600 °C and in-line aerodynamic particle size distribution measurements were captured using an aerodynamic particle sizer (TSI, Inc.). After calcination, the microparticles were electrostatically deposited onto silicon wafers, planchets, (University Wafer, B-doped silicon with <100> orientation, ~0.5 mm thick) in 10 s intervals.

Characterization Details

LG-SIMS

LG-SIMS characterization was performed on three RM UPu-100A doped Si wafer planchets prepared the beginning, middle, and end of the particle production campaign. Uranium and plutonium isotopic compositions of RM UPu-100A particles were measured using a Cameca IMS 1280 instrument at LANL. For all analyses, five electron multipliers (EM) were positioned to simultaneously collect signals from ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, and ^{241}Pu+^{241}Am. In addition to the inability to resolve Pu and Am at mass 241, isotopes and molecular hydrides cannot be spectrally resolved at masses 239 (^{239}Pu and $^{238}U^1H$), 240 (^{240}Pu and $^{239}Pu^1H$), and 241 (^{241}Pu and $^{240}Pu^1H$); however, it has been demonstrated that similar test material particles mounted on doped Si wafers have low hydride backgrounds (i.e., tens of ppm)[41, 42], which corresponds to negligible influences on measured isotope ratios. As such, no hydride correction was applied to data. While carbon substrates are commonly used the elevated hydride backgrounds observed when they are employed (several thousands of ppm[41]) can cause inaccuracies when characterizing particles with U and Pu due to hydride interferences that cannot be mathematically corrected. Hydride backgrounds can be independently measured to correct raw data [41], but this adds complexity to characterization. The O^- primary ion beam current was adjusted to generate an EM secondary ion signal of approximately 5×10^4 to 2×10^5 counts per second when measuring ^{238}U, the most abundant isotope for the RM UPu-100A particles. The slits and apertures of the instrument were adjusted to produce a mass resolving power greater than 2000. Two types of analyses were employed: 1) single particle analyses, used to determine isotope ratios using weighted mean values of the datasets, and 2) automated particle mapping (APM), which generates a large population of isotope ratio data and is used to evaluate the material's $n(^{235}U)/n(^{238}U)$ and $n(^{240}Pu)/n(^{239}Pu)$ interparticle homogeneity (i.e., particle-to-particle). The interparticle homogeneity of isotopic/elemental ratios was evaluated by comparing datasets to a model of expected counting-statistical variability from Tenner et al.[41]:

$$\overline{R}_{isotopes} \pm \left(\overline{R}_{Isotopes} \times n \times \sqrt{\frac{1}{\overline{N}_{counts}} + \frac{1}{\overline{D}_{counts}}}\right) \quad (1)$$

The mean isotope ratio, $\overline{R}_{isotopes}$, is that of the dataset to be modeled. $\overline{N}_{counts}$ and $\overline{D}_{counts}$ correspond to all possible count combinations of the numerator and denominator of the mean isotope ratio modeled. The *n* term approximates a Gaussian distribution probability where a value of 4 was applied, corresponding to ~99.99% of data falling within the model bounds if the material is isotopically homogeneous. The model is represented by the red lines in figures 5-7.

Each automated particle measurement was 300 seconds in duration, using a 250×250 µm rastered primary ion beam with an intensity of 10 nA. Prior to each APM analysis, a sputter cleaning step was applied using the same raster size, with a 25 nA primary ion beam for a duration of 60 seconds. A total of 123 APM analyses were performed on the three planchets, which generated a dataset consisting of data from 304 particles The raw APM weighted mean $n(^{235}U)/n(^{238}U)$ and $n(^{240}Pu)/n(^{239}Pu)$ ratios were bias corrected such that they are equivalent to the corresponding, metrologically traceable compositions determined by MC-ICP-MS bulk analysis (Figure 5).

Single particle measurements consisted of ten individual particle analyses performed on each planchet. Each particle measurement was 900 seconds in total duration, divided into 90 ten-second cycles. This analysis duration was selected to ensure complete particle consumption, as this method has been shown to provide the highest consistency when generating intra-element U/Pu ratio data.[41] Analyses employed a 10×10 µm rastered primary ion beam, with a current of 1 nA. Prior to each analysis, a 25 second primary ion sputter cleaning step was employed, using 1 nA beam current and a 25×25 µm raster. The $n(^{235}U)/n(^{238}U)$, $n(^{240}Pu)/n(^{239}Pu)$, and $n(^{238}U)/n(^{239}Pu)$ isotope amount ratios from these single particle analyses were used to quantify interparticle elemental and isotopic dispersion. Due to the lack of a LG-SIMS inter-element U/Pu calibration standard, the raw isotope ratios of the single particle datasets were bias corrected such that the values are equivalent to those determined by MC-ICP-MS bulk measurements for the included plots (Figures 6 and 7). A second set of single particle data was collected without total consumption, wherein the measured intra-element $^{235}U/^{238}U$ and $^{240}Pu/^{239}Pu$ isotope amount ratios were independently bias corrected with certified and working reference material particles; specifically, NBL-PO CRM U030 to calibrate for $^{235}U/^{238}U$ and Nuclear Forensics International Technical Working Group (ITWG) sixth collaborative materials exercise (CMX-6)[43, 44] to calibrate for ^{240}Pu/^{239}Pu. Additional LG-SIMS analysis details are provided in the electronic supporting information.

Note that for values in Table 1, LG-SIMS measurements were used only for the homogeneity uncertainty and relative sensitivity factor (RSF) calculations. Isotope amount ratios for RM UPu-100A were measured by MC-ICP-MS.

MC-ICP-MS Measurements

RM UPu-100A particles from two planchets prepared early and late in the production process were analysed at the bulk scale after being extracted from their silicon substrates with 8 M HNO_3. Bulk U and Pu isotopic composition and assay measurements were performed at SRNL using a Nu Plasma HR MC-ICP-MS. For U and Pu characterization, a traced (^{233}U-spiked and ^{244}Pu-spiked, respectively) and non-traced analysis was performed for each element, for a total of four analyses per planchet (non-traced U isotopic composition; traced U assay; non-traced Pu isotopic composition; traced Pu assay). All measurements employed the standard-sample bracketing method with NBL-PO CRMs U010 and C128 used for instrument calibration for U and Pu analysis, respectively. ^{235}U/^{238}U isotope amount ratios and U isotope amount values are traceable to the certified ^{235}U and ^{238}U isotope amount values of CRM U010; ^{236}U/^{238}U and ^{234}U/^{238}U isotope amount ratios are traceable to the certified ^{235}U and ^{238}U isotope amount values of CRM U500 through the revised U010 ^{236}U/^{238}U and ^{234}U/^{238}U isotope amount ratios of Richter and Goldberg.[45] CRMs U020 and U200 were analysed for uranium mass spectrometry quality control (QC). RM UPu-100A uranium analytical aliquots were each characterized by static multicollection, with ^{238}U, ^{235}U and ^{233}U collected on Faraday detectors and ^{236}U and ^{234}U on full-size secondary electron multipliers. Pu isotope amount ratios and values are traceable to the certified, decay-corrected ^{239}Pu/^{242}Pu isotope amount ratio of NBL-PO CRM C128. Half-life values and uncertainties (k=2) used for plutonium isotope decay corrections were 24,110 ± 30 years (^{239}Pu) and 375,000 ± 2,000 years (^{242}Pu). Note that RM UPu-100A contains trace ^{238}Pu; however, the isotopic contribution of ^{238}Pu to mass 238 in this material is insignificant compared to that of ^{238}U and its corresponding, traceable analytical precision.

Assay and U/Pu ratios were determined by isotope dilution mass spectrometry using a highly enriched ^{233}U Spike[46] and NBL-PO CRM C131 ^{244}Pu Spike. Prior to use and to ensure accurate Pu isotope dilution results, legacy CRM C131 solution was calibrated using an in-house, SRNL Pu assay working reference material (WRM), which was previously characterized using ISO-17025 accredited methods at SRNL for Pu assay by controlled potential coulometry (CPC) and Pu isotopic composition by Thermal Ionization Mass Spectrometry (TIMS). Analytical Pu aliquots were not elementally purified prior to MC-ICP-MS analysis, and therefore mass-241 measurements (^{241}Pu*) integrated ^{241}Pu and ^{241}Am. A separate Pu solution was analysed for plutonium mass spectrometry QC. RM UPu-100A plutonium analytical aliquots were characterized by dynamic peak-hopping, with ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu analysed sequentially on a full-size secondary electron multiplier.

Quantitative blank and baseline corrections were applied to all analyses, and uncertainty propagation of all uncertainties was performed by the Monte Carlo method in the R statistical programming environment.[47] Uranium and Pu analytical results were integrated to produce bulk particle isotopic composition values.

Measurement Uncertainty (LG-SIMS and MC-ICP-MS).

RM UPu-100A presented challenges to developing a scheme for measurement uncertainty due to the lack of a mixed U/Pu standard for LG-SIMS measurements. Therefore, two separate uncertainty treatments were used in the results. The first, MC-ICP-MS bulk measurements, employed Monte Carlo data reduction algorithms to establish metrological traceability of RM UPu-100A analyses and corresponding uncertainties (u_{MC}) to the above-described reference material framework.[48] The second used LG-SIMS single particle measurements to determine the homogeneity uncertainty, u_{hom}. When assessing the uncertainty of the homogeneity of a bulk material, ISO 33405:2024 recommends performing an ANOVA using measurements from multiple aliquots (particles) of multiple batches (planchets).[49] An ANOVA was performed on uncorrected measurements made by LG-SIMS single particle analysis of ten particles on each of three planchets taken from the beginning, middle, and end of the RM UPu-100A production process. Using the within- and between-group mean squares (MS_w and MS_b, respectively), the uncertainty of the homogeneity was calculated as $u_{hom}^2 = u_w^2 + u_b^2$, where $u_w^2 = MS_w$ and $u_b^2 = (MS_b - MS_w)/n$.

Scanning Electron Microscopy

Scanning electron microscopy automated particle mapping (SEM APM) was performed at SRNL using an FEI ASPEX Explorer (ASPEX) to measure particle sizes, map particle positions, and qualitatively investigate elemental composition of RM UPu-100A microparticles. Particles were detected by adjusting brightness and contrast to provide particle edge discrimination using backscattered electron (BSE) signal intensity and measured using a rotating chord algorithm (RCA) to characterize morphology and provide an individual aspect ratio for each particle. Compositional analysis by energy dispersive X-ray spectroscopy (EDS) was used to qualitatively distinguish between actinide bearing microparticles and other features such as surface contaminants or laser-scribed fiducial markings. To ensure proper instrument calibration and prevent drift in the automated particle sizing algorithm on the ASPEX, an SRNL-produced WRM of uranium oxide particles on a silicon planchet was employed. Particle sizes of U_3O_8 particles on this planchet were characterized using an TESCAN MIRA 4 with NIST Certified pitch distances and a Metro Chip Microscope Calibration Target. This WRM was used as a measurement standard for the ASPEX before and after each RM UPu-100A planchet analysis. Using the known particle size characteristics of the U_3O_8 WRM, a correction factor was determined and applied to all measurement values for the RM UPu-100A.

High-resolution SEM images, Figure 2, were acquired using a Zeiss Crossbeam 550 Scanning Electron Microscope-Focused

Ion Beam (SEM-FIB), used as a traditional SEM with accelerating voltages from 20 to 30,000 V and currents from 10 pA to 40 nA. Typical measurements were taken at a working distance of 13 mm, probe current of 500 pA and magnifications between 40-60 K. EDS measurements consisted of an average of one million counts collected at 20 kV.

Alpha Spectroscopy

Alpha spectra were acquired using a vacuum-assisted (1 mTorr) Alpha Duo® (ORTEC) spectrometer equipped with passivated ion-implanted planar Si (PIPS) detectors with a thickness of 275-315 μm. The RM UPu-100A planchets had an active measurement diameter of nominally 24 mm (note that the particles are centred in a 9 mm region of the planchet). Routine background measurements (>72-hour duration) were collected between planchet measurements to account for potential background contributions to the total alpha spectrum (i.e., detector contamination from α-recoil sputtering). An electrodeposited, NIST-traceable standard containing equal activities of ^{230}Th, ^{239}Pu, and ^{241}Am was used to calibrate the emission spectrum energies in the range of 3-8 MeV. Measurements of this electroplated standard were also used to estimate the efficiency of alpha emission detection for each detector and assess detector efficiency stability.

For alpha measurements, the sample tray was placed into the highest indexed location in the detector chamber, directly below the PIPS detector. Spectra were acquired for 24 to 48 hours to ensure a relative standard deviation (RSD) of the integrated total peak area of <5% for each of the primary alpha spectral peaks (^{238}Pu and ^{239}Pu+^{240}Pu). To verify the absence of energy shift within the collected spectral data, an internal pulser was applied before and after the measurement at a fixed energy near 3 MeV, where no associated U or Pu alpha peaks would be observed (Note: the observed counts from the pulser were subtracted from the final calculation of total alpha activity).

Results and Discussion

Baseline Characterization

Throughout the particle production process, in-flight aerodynamic particle size measurements were made before and after planchet batches. These data were compared to particle size distributions of the particles on seven planchets from throughout the production process that were measured by SEM APM (correlation shown in Figure 1). The aerodynamic particle size distributions are related to the density of the particulate and APS distribution corrected to the SEM APM size distribution gives an estimated average density of the particle population of approximately 6.0 g/cm^3.

The average geometric standard deviation (GSD), used due to the log normal properties of aerosol particle size distributions measured via APS, obtained from all APS Measurements (calculated using the formulae found in TSI Application Note PR-001[50]) during the production of RM UPu-100A was 1.11 μm. The GSD of the particles from the seven planchets analysed by SEM APM was 1.11 μm. While the exact GSD value at which a particle population can be considered monodisperse is not well defined, TSI, Inc. recommends ≤1.25 μm, which correlates well with the recommendations of "practical monodispersity" presented by Fuchs and Sutugin (≤1.22 μm).[51] While the GSD of RM UPu100-A is consistent with monodispersity and the primary particle population consists of individual particles near 1 μm average diameter, features outside the anticipated monomodal distribution were observed in the APS and APM size distribution (Figure 1). The primary deviation from monodispersity was a small population, approximately 7% of total particles, of "doublet" particles which occur as the result of liquid droplet combination during generation. Given this, while RM UPu-100A is monodisperse on average, there is a non-trivial population of "doublet" particles of slightly larger diameter.

The produced microparticles characterized by SEM imaging were spheroidal with occasion particulates demonstrating irregular surface texture. Figure 2 shows four representative SEM images of the produced microparticles. Some particles exhibited a textured surface while others were smooth. The surface mottling may be a function of the acidified (nitric acid) feedstock, which has been shown to destabilize microparticle formation in aerosol production methods.[52] SRNL's previous efforts for the generation of mono-uranium oxide particulates typically did not demonstrate this level of particle surface micro texture but did not use acidic feedstock solutions.

Particle loadings on 13 planchets were determined by SEM APM, with the total number of particles per planchet ranging from 239 to 4081. For a subset of these specimens, the spacing between the particles was determined; for each particle, the distance to all other particles was calculated using a vector displacement algorithm in R and a minimum value tabulated. From this, a set of "nearest neighbour" histograms was produced (see electronic supporting information).

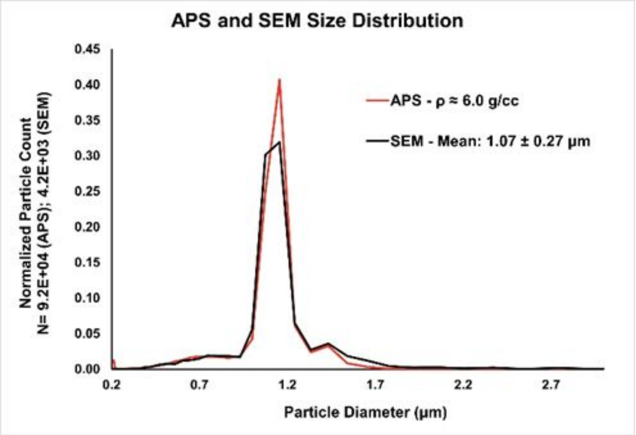

Figure 1. Overlay of in-flight aerodynamic particle size distribution (black curve) and SEM APM particle size distribution obtained from seven RM UPu100-A planchets.

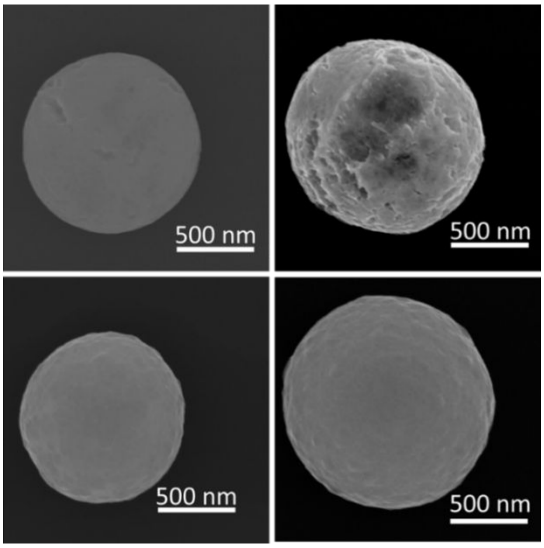

Figure 2. Representative high-resolution SEM images of RM UPu-100A microparticles.

Alpha Spectroscopy Measurements and SEM Correlation

Alpha spectroscopy measurements were performed on 90 planchets bearing the RM UPu-100A microparticles to estimate the number of RM UPu-100A particles. Thirteen of the RM UPu-100A planchets that had particle counts by SEM APM were counted by alpha. Alpha activities were correlated with U-bearing particle counts using linear regression to calculate a conversion factor used to estimate the number of particles on each planchet based on alpha spectroscopy screening results. Figure 3 shows a histogram of the number of particles on 90 planchets as estimated by the total net alpha activity. The red vertical lines give the median ± 68.3% confidence interval for the number of particles per planchet, which is 1180 +1345/-759 particles per planchet for this dataset. The relatively wide range of this distribution is due to the collection method. Particles are collected using electrostatic corona particle collection, also known as electrostatic precipitation (ESP) where the corona wire is energized briefly (~ 10 seconds) to induce the collection. The brief collection period and position of the individual planchets in the collector contribute to the dispersion seen in the particle counts between planchets.

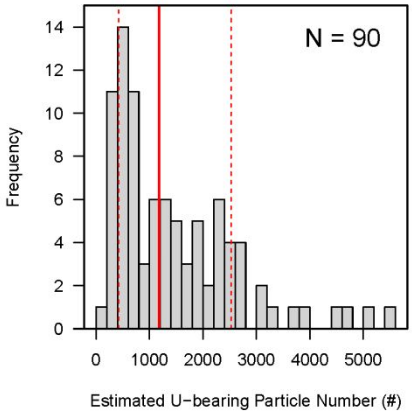

Figure 3. Histogram of the number of RM UPu-100A particles per planchet as estimated by alpha spectroscopy results.

MC-ICP-MS U and Pu Analysis

The U and Pu isotopic composition of RM UPu-100A determined by MC-ICP-MS analysis of bulk particles extracted from two planchets were integrated to obtain the final, weighted-mean compositions given in Table 1. The $^{235}U/^{238}U$ isotope amount ratio of 0.05221 ± 0.00019 (k=2) is consistent with a low-enriched uranium target composition, with a corresponding ^{236}U isotope amount of 18.73 ± 0.16 parts per million (ppm) U atoms. Measured $^{240}Pu/^{239}Pu$ and $^{238}U/^{239}Pu$ isotope amount ratios of 0.28381 ± 0.00095 and 103.3 ± 1.2, respectively, align well with the nominal target values for these quantities.

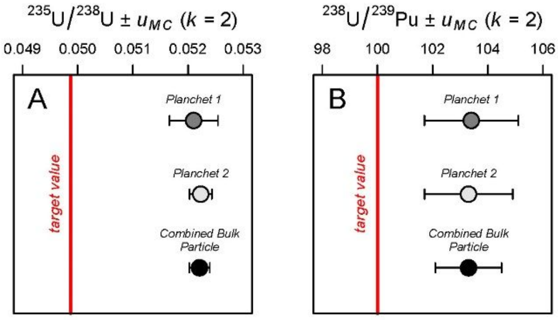

Figure 4. MC-ICP-MS results of bulk particle analysis, including $^{235}U/^{238}U$ (A) and $^{238}U/^{239}Pu$ (B) isotope amount ratios.

Table 1. RM UPu-100A isotope amount ratios and amount percentages determined by MC-ICP-MS. u_{MC}: MC-ICP-MS measurement uncertainty. u_{hom}: LG-SIMS interparticle homogeneity uncertainty. U: expanded uncertainty, $U = k\sqrt{u_{MC}^2 + u_{hom}^2}$. Reference date: 1 September 2023.

Quantity	Value	u_{MC} $(k = 2)$	u_{hom} $(k = 2)$	U $(k = 2)$	RSF$_{Pu:U}$ RSF‡	U $(k = 2)$
n(^{234}U)/n(^{238}U)	0.0006201	0.0000030	not evaluated	0.0000030	–	–
n(^{235}U)/n(^{238}U)	0.05221	0.00019	0.00015	0.00024	–	–
n(^{236}U)/ n(^{238}U)	0.00001972	0.00000017	not evaluated	0.00000017	–	–
n(^{234}U)/n(U) (%)	0.05889	0.00028	not evaluated	0.00028	–	–
n(^{235}U)/n(U) (%)	4.959	0.017	not evaluated	0.017	–	–
n(^{236}U)/n(U) (%)	0.001873	0.000016	not evaluated	0.000016	–	–
n(^{238}U)/n(U) (%)	94.980	0.017	not evaluated	0.017	–	–
n(^{240}Pu)/ n(^{239}Pu)	0.28381	0.00095	0.0030	0.0032	–	–
n(^{241}Pu+^{241}Am)/ n(^{239}Pu)	0.00447	0.00022	0.00014	0.00026	–	–
n(^{242}Pu)/ n(^{239}Pu)	0.00888	0.00014	not evaluated	0.00014	–	–
n(^{239}Pu)/n(Pu) (%)	77.091	0.058	not evaluated	0.058	–	–
n(^{240}Pu)/n(Pu) (%)	21.880	0.057	not evaluated	0.057	–	–
n(^{241}Pu+^{241}Am)/n(Pu) (%)	0.344	0.017	not evaluated	0.017	–	–
n(^{242}Pu)/n(Pu) (%)	0.685	0.011	not evaluated	0.011	–	–
n(^{238}U)/ n(^{239}Pu)	103.3	1.2	2.6	2.8	2.282	0.064
n(^{235}U+^{238}U)/ n(^{239}Pu+^{240}Pu)	84.66	0.99	2.1	2.3	2.241	0.063

‡Note that these RSFs apply to the specific measurement conditions described in the Characterization Details section of this document.

LG-SIMS Analysis

LG-SIMS isotope amount ratio datasets were evaluated against the expected data dispersion about the mean value due solely to counting statistics with a coverage factor of 4 (~99.99% confidence level). In the APM n(^{235}U)/n(^{238}U) and n(^{240}Pu)/n(^{239}Pu) datasets shown in Figure 5, all measurements fall within the predicted model bounds, indicating the material is isotopically homogeneous at the particle level within the counting statistical uncertainty of the LG-SIMS APM method. The corresponding single particle data for n(^{235}U)/n(^{238}U) and n(^{240}Pu)/n(^{239}Pu) also demonstrate that all the particles are homogeneous within uncertainty (Figure 6).

Regarding single particle n(^{238}U)/n(^{239}Pu) ratios (Figure 7), the range of measured values exceeds the respective model bounds and individual analyses are characterized by relatively large uncertainties. This is because the raw, measured ^{238}U/^{239}Pu ratio evolves significantly when profiling through particles during LG-SIMS measurements when using an O^{-} primary ion beam (producing relatively large uncertainties of individual particle data), largely due to different U and Pu sputtering behavior.[41] While this profiling behaviour was consistent from particle-to-particle, it contributes to increased variability in measured ^{238}U/^{239}Pu because of challenges in conducting measurements under identical conditions; for example, the time spent selecting and tuning prior to analysis varies slightly from particle-to-particle, which influences where profiling is initiated and consumption concluded for each analysis. When these analytical aspects are taken into account, the observed variability of the datasets in Figure 7 likely reflects challenges related to profiling effects during LG-SIMS U/Pu ratio measurements; as such, the actual interparticle U/Pu variability of RM UPu-100A is likely smaller than shown.

A complementary set of single particle measurements was performed to measure n(^{235}U)/n(^{238}U) and n(^{240}Pu)/n(^{239}Pu) isotope amount ratios that were independently bias-corrected. The values for these measurements, 0.05205 ± 0.00023 (k=2) and 0.2817 ± 0.0025 (k=2), respectively, are consistent with bulk measurement values (see supplemental information for more details).

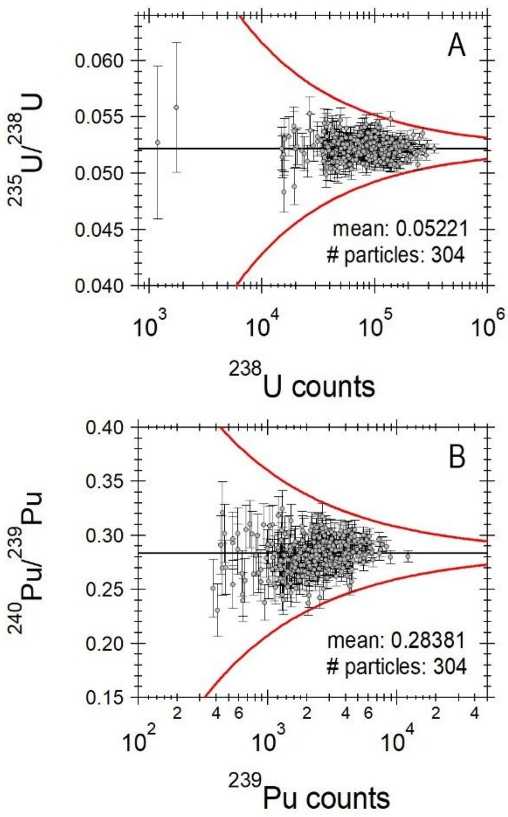

Figure 5. LG-SIMS APM data (n=304) and counting statistics models (red curves) for ^{235}U/^{238}U (A) and ^{240}Pu/^{239}Pu (B) isotope amount ratios. Error bars are counting statistics.

Also, RSFs were calculated from LG-SIMS single particle data using the Monte Carlo method with equation (2).

$$RSF_{Pu:U} = \frac{[Pu/U]_{LG-SIMS}}{[Pu/U]_{MC-ICP-MS}} = \frac{[U/Pu]_{MC-ICP-MS}}{[U/Pu]_{LG-SIMS}} \qquad (2)$$

$RSF_{Pu:U}$ was calculated for each particle and then the weighted mean of the particle RSFs was calculated, yielding $RSF_{Pu:U} = 2.282 \pm 0.064, \mathrm{k} = 2$ for n(^{238}U)/n(^{239}Pu) and $RSF_{Pu:U} = 2.242 \pm 0.063, \mathrm{k} = 2$ for n(^{235}U+^{238}U)/n(^{239}Pu+^{240}Pu). Both uncertainties include the homogeneity uncertainty component. Note that these RSFs apply specifically to the measurement conditions described in the Characterization Details section of this document.

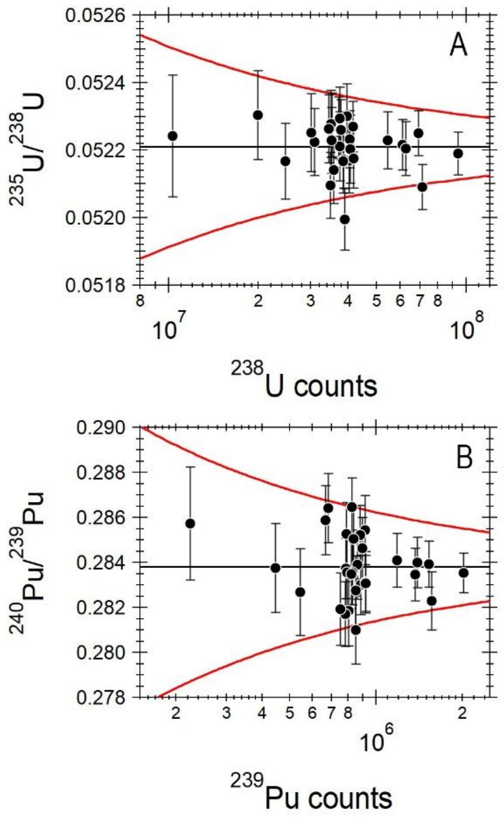

Figure 6. LG-SIMS single particle total consumption data (n=30) and models of homogeneity (red curves) for ^{235}U/^{238}U (A) and ^{240}Pu/^{239}Pu (B) isotope amount ratios. Error bars are twice the standard error of the individual measurements from the 90 ten-second cycles.

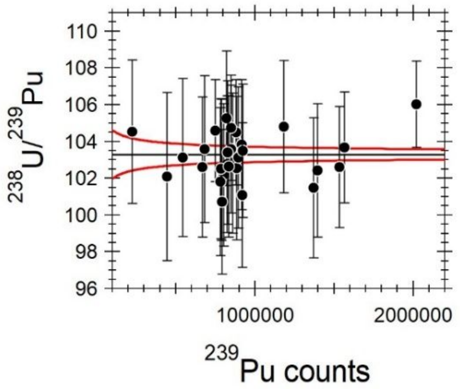

Figure 7. LG-SIMS single particle total consumption data (n=30) and counting statistics model (red curve) for ^{238}U/^{239}Pu isotope amount ratio. Error bars are twice the standard error of the individual measurements from the 90 ten-second cycles.

Conclusion

Well-characterized, mixed-actinide particle reference materials are critically needed for mass spectrometry applied to support international nuclear safeguards. SRNL's THESEUS particle production platform was used to synthesize RM UPu-100A, a novel U/Pu microparticle specimen with ideal physical and compositional properties for analytical calibration and quality control assessment. Comprehensive bulk and particle-scale characterization conducted at SRNL and LANL included APS, alpha spectroscopy, SEM, MC-ICP-MS, and LG-SIMS, permitting quantification and confirmation of key RM UPu-100A target attributes (monodispersity, homogeneity, metrologically traceable U/Pu isotopic and elemental composition). Successful manufacture of RM UPu-100A represents the first dedicated U/Pu microparticulate production effort in decades and directly addresses a longstanding void in microanalytical measurement traceability. Distribution of this material amongst the global community will bolster the international nuclear safeguards regime and facilitate research and development of next-generation analytical methods and technologies. Finally, this work underscores the capability of the SRNL THESEUS platform to generate precisely controlled, compositionally complex microparticles, establishing a foundation for production of ever more exotic and as-yet unexplored particle formulations. It is also noted that this technology may benefit other sample limited particulate characterization methods such as particle analysis for engine wear, contaminants within a microelectronics fabrication facility, or environmental particulate matter studies.[53-55]

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data availability is subject to US Department of Energy information release rules.

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Notes and references

Note: RM UPu-100A was produced using guidance from ASTM C1128, ISO 33405:2024, and ISO 17034:2016. SRNL is not accredited to ISO 17034:2016; however, SRNL is qualified by the IAEA as a Network of Analytical Laboratories (NWAL) particle reference material producer.

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Data availability

Data availability is subject to US Department of Energy information release rules.