https://doi.org/10.3011/ESARDA.IJNSNP.2019.12

ESARDA BULLETIN, No. 59, December 2019

Production of particle reference and quality control materials

Timothy R. Pope[1], Bruce W. Arey[1], Mindy M. Zimmer[1], Michael DeVore II[2], Michael G. Bronikowski[2], Wendy Kuhne[2], Aaron T. Baldwin[2], Cristina Padilla-Cintron[1], Norman C. Anheier[1], Marvin G. Warner[1], Matthew S. Wellons[2], and Christopher A. Barrett[1]

[1]Pacific Northwest National Laboratory, Richland, WA 99354, USA
[2]Savannah River National Laboratory, Aiken, SC 29808, USA
E-mail: Chris.Barrett@pnnl.gov

Abstract:

Maintaining the superior performance of new analytical instrumentation and pushing the boundaries of ever-smaller particle analysis by methods such as secondary ion mass spectrometry (SIMS) has become limited by the availability of certified particle standards for calibration, quality control, and validation. To meet this growing demand for a reliable and universal approach to the generation of uranium particle reference material, the Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) are collaborating on a joint venture that establishes a number of chemical pathways to the fabrication, purification, and stabilization of uranium particle material to within a fixed particle size range, and well-characterized isotopics. PNNL particle standards are designed and tailored to meet the criteria essential to the calibration and benchmarking of instruments used in both the non-destructive and destructive assay of particulate material, typically collected from environmental swipe sampling. Previous testing and optimization of this colloidal approach to particulate material has centred on tight size distributions, singular composition and density, uniform morphology, and tailored isotopic abundances. Extensive validation of this material has since been performed, both at the National Institute of Standards and Technology (NIST) and the International Atomic Energy Agency (IAEA), demonstrating its suitability for quality control needs of large geometry (LG)-SIMS analysis. Building on this momentum, the production of low-enriched uranium particle reference material, with specially tailored isotopics, has moved from development to full operation. Herein, various aspects of the production cycle will be discussed, including detailed accounts of the technical methodologies being employed, as well as insights into the sample characterization and acceptance testing requirements.

Keywords: particle; standards; uranium; safeguards, synthesis

1. Introduction

Trace analysis of particulate material collected on environmental swipe samples has long been a cornerstone in the IAEA's process of verifying member state compliancy as part of the Non-Proliferation Treaty (NPT).[1] The swipe samples collected by inspectors are taken from the surrounding environment within a nuclear site and then subjected to two common forms of measurement, namely bulk and discrete analysis. In the first case, the entire cotton swipe is digested and analysed with respect to U, Pu, and other elements present at ultra-low concentration levels. The latter approach takes aim at the precise isotopic analysis of individual U- or Pu-containing particles, with sizes ranging from 1-10 µm typically observed. Discrete analysis of individual particles generally entails the use of both scanning electron microscopy (SEM) and SIMS, both of which are regarded as non-destructive for swipe samples, as the swipe is not destroyed as part of the sample preparation process. By contrast, a swipe is completely consumed by bulk analysis using a combination of high-temperature ashing and acid digestion. While many different isotopic standards, commonly referred to as certified reference material (CRM), are available for destructive forms of assay, notably thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS), particle standards for SIMS analysis are far less common and more difficult to produce.[2]

In recent years, the IAEA has had limited success in maintaining a steady supply of particle-based standards from the European Commission - Joint Research Centre, Directorate G – Nuclear Safety and Security, Unit G.2 for Standards for Nuclear Safety, Security and Safeguards (JRC-Geel, formerly IRMM), mainly due to the fact that certified particle standards are atypical products for both IRMM, and the New Brunswick Laboratory (NBL) in the US. Because the IAEA requires a longer-term strategy for particle standards supply, production methods have been pursued at the Forschungszentrum Jülich (FZJ),[3] as well as by several other member states partnered to the Network of Analytical Laboratories (NWAL).[4-6] While many different technical approaches are being developed, all are constrained by the same stringent requirements necessary for useful particle standards for SIMS analysis. As an example, techniques for the generation of uranium-bearing particles should provide uniform particle morphology and density, narrow particle size distributions (~1 µm), singular chemical composition (oxides preferable), tailorable isotopic profiles, and a demonstrated shelf-life of 1 year or more. Additional factors to be considered range from the relative structural

Pope, T.R., Arey, B.W., Zimmer, M.M., DeVore II, M., Bronikowski, M.G., Kuhne, W., Baldwin, A.T., Padilla-Cintron, C., Anheier, N.C., Warner, M.G., Wellons, M.S., & Barrett, C.A. (2019). Production of particle reference and quality control materials. *ESARDA Bulletin - The International Journal of Nuclear Safeguards and Non-proliferation*, 59, 29-38. https://doi.org/10.3011/ESARDA.IJNSNP.2019.12

integrity of the particles subjected to mechanical forces such as sonication or micro-manipulation, to estimates on the rate of U leaching in different storage media.[7] Of paramount importance is the ability of any proposed technique to continually produce unbiased, isotopic uniformity in each batch of material. By their very nature, particles can easily migrate through an environment and deposit across surfaces, which is the premise behind environmental swipe sampling. Consequently, steps to mitigate particle cross-talk must be fully integrated with the design and production of particle reference materials.

To this end, a new method and system of producing UO_2 particle reference material of a prescribed isotopic profile is described herein. This work is the culmination of collaborative efforts between PNNL and SRNL, under the support of the National Nuclear Security Association and the United States Support Program to the IAEA. The systematic approach laid out in this paper begins with the detailed formulation and blending of CRM to generate uranium material of a desired isotopic composition, followed by chemically transforming it into a suitable precursor form for colloidal synthesis. A tailored synthesis protocol for the generation of UO_2 particulate is then introduced, including parameters to optimize the technique for specific IAEA requirements. Finally, a thorough characterization of particle properties, including crystallinity, size, shape, and density, is reported. Further, an isotopic evaluation is performed by LG-SIMS, the mass spectrometry technique for which the particles were originally designed. It is hoped that the combined efforts of PNNL and SRNL reported herein demonstrate the viability of this new production process and its potential for delivering uranium oxide particles sourced from current CRM and tailored to the stringent criteria necessary for particle reference materials.

2. Uranium Feedstock Formulation

2.1 Isotopic Mixing

New QA/QC particulate reference materials may require the formulation of a unique uranium isotopic composition with a specific composition of four U isotopes (i.e. ^{234}U, ^{235}U, ^{236}U, and ^{238}U). For example, new reference materials may be designed to validate specific environmental sampling scenarios representative of typical nuclear operations, such as uranium enrichment and spent fuel reprocessing, among others. Manufacture of the desired uranium isotopic composition requires the mixing of uranium starting material with precisely known isotopic content, such as CRMs. CRMs are available commercially from multiple international organizations, both in Europe and the US, and have well-documented and published values for each uranium isotope. Development of the specific mixing recipe for a new QA/QC material involves the reconciliation of available CRM feedstock, their respective expense of procurement, and a desire to minimize the number of CRMs used in a formulation.

Choosing a combination of isotopic standards to incorporate under the specified constraints can be categorized as a convex optimization problem,[8] which can be solved in a variety of ways. In the optimization of isotopic standard mixing, we seek the best way to combine a set of *n* reference materials to meet a set of conditions set by the QA/QC material end user (i.e. the IAEA). These constraints are concerned with the content of ^{234}U, ^{235}U, and ^{236}U and the balance of ^{238}U. Note that minimizing the computational power necessary to solve the problem is an important consideration, as well as reducing the number of standards used within the mix. Additionally, a range of ratios must be considered for all possible CRM combinations. To date, several methods have been used to generate permutations of all possible mixes of uranium certified reference materials. Described below is the method utilized by initial work in this topic.

The primary method used was a brute force R-based program that created arrays to represent each standard. These were combined into matrices that were multiplied by a content matrix. The content matrix contained four columns that matched an isotopic composition value to each standard in the array. This multiplication generated a list of possible solutions, and such multiplications were performed over the entire problem space. Certain constraints were applied to the problem to generate a set of solutions. Figure 1 provides a visual representation of the possible combinations of all US commercially available uranium CRMs limited to combinations of ≤3. For convenience, this plot is labelled in terms of the ^{235}U enrichment, the ^{236}U concentration, and the $^{235}U/^{234}U$ ratio. The data points represent $>10^6$ individual CRM combinations varied in both CRM selection and their ratios. In practice, we have found the 3D representation to be valuable in rapidly determining potentially impossible U isotopic composition targets. The solutions were manually screened, and <10 viable recipe candidates were selected based on factors mentioned previously. This method did not take advantage of programmatic methods to reduce problem complexity and improve computational efficiency. The selected CRM mixing recipes were always checked against two separate independent review calculations to verify the numerically accuracy. We found that a subsequent iterative discussion between the various stakeholders was invaluable to validate and down select the proposed recipes (plus their respective isotopic composition) to a single mixture.

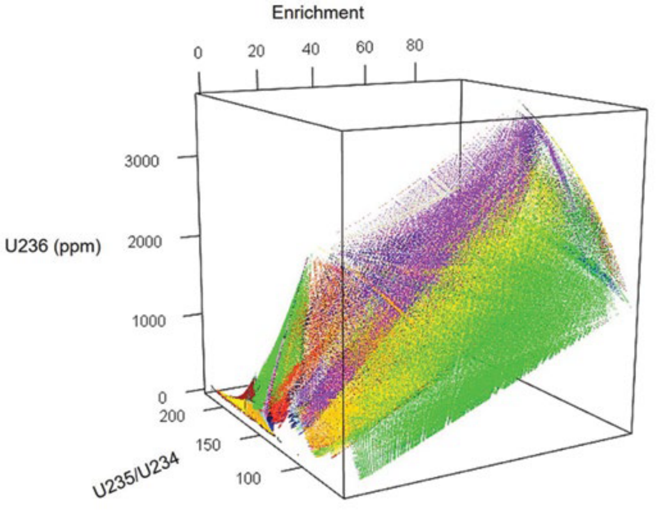

Figure 1: 3D plot of approximately 10^6 data points representing potential combinations of ≤3 CRM mixture isotopic compositions in terms of ^{235}U enrichment, ^{236}U concentration in ppm, and the ^{235}U/^{234}U ratio. Colours are for 3D illustrative purposes only.

Note that due to the proprietary nature of new QA/QC specimens for nuclear safeguards proficiency testing, feedstock and micrometre particle syntheses are discussed in a manner agnostic to specific isotopic compositions.

2.2 Chemical Manipulation

CRMs were obtained from the US Department of Energy, NBL Program Office. The mixing ratio and identity of specific CRM combinations was determined by the calculation method detailed earlier in this publication. The overall synthesis scheme is shown in Figure 2, which demonstrates the generic formulation of metal and/or oxide CRM feedstocks into a uranyl acetate product with tailored uranium isotopic content. Mixing of CRMs and subsequent synthesis of uranyl acetate were typically done on the gram scale to ease physical laboratory manipulations and minimize routine sources of measurement errors, such as with balances, pipettes, etc.

A typical uranyl acetate feedstock preparation starts with the dissolution of the CRMs, which are either uranium oxide or metal. Uranium metal rods are broken into pieces and placed in 8 mol/L HNO_3 to remove the oxide layer. After 30 minutes, the pieces are removed, rinsed with water and acetone, dried, and weighed.[9] The pieces are then put into a fresh solution of 8 mol/L HNO_3 to dissolve and form uranyl nitrate ($UO_2(NO_3)_2 \cdot xH_2O$). The U_3O_8 CRMs are heated at 400 °C for 2 hours to drive off water in accordance with recommended practices. After cooling, the U_3O_8 was weighed and dissolved in 8 mol/L HNO_3 with heating at 60 °C to generate a second uranyl nitrate solution.

Portions of the two uranyl nitrate solutions were mixed based on a previously calculated recipe to generate a uranyl nitrate solution with the desired isotopic composition. The product was subsampled and analysed by TIMS to verify the isotopic composition. The uranyl nitrate solution was heated at between 80 °C and 100 °C until dryness to form a nitrate solid salt of the isotopically mixed crystalline hydrate. Next, uranyl nitrate was heated at first at 120 °C to remove water and then at 400 °C for 2.5 hours to generate the gamma phase of UO_3.[10] The UO_3 was allowed to cool before being weighed and then a solution of dilute acetic acid was added and heated to 50 °C. The material dissolves and upon evaporation precipitates as uranyl acetate, which was filtered and washed first with cold dilute acetic acid and then with water.[11]

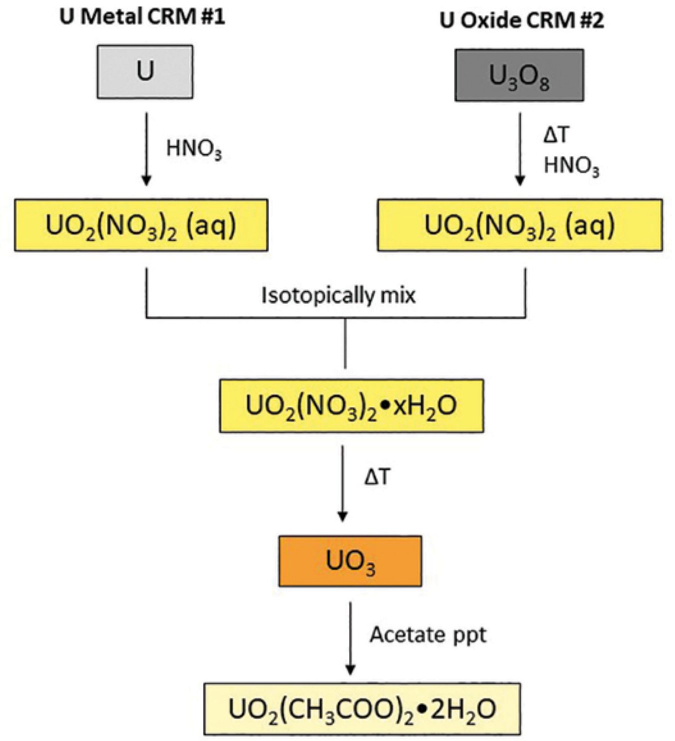

Figure 2: Prototypical chemical reaction and manipulation pathway for the dissolution of various CRMs, their mixing, and subsequent synthesis of uranyl acetate with predefined isotopic composition.

The isotopically mixed uranyl acetate product was characterized by Raman spectroscopy, fluorescence spectroscopy, and powder X-ray diffraction (PXRD) to verify the material phase and identify any other potentially undesirable chemical phases (e.g. schoepite, uranyl carbonate, etc.). Once the acetate material phase was confirmed, the product was subsampled again and analysed with TIMS to confirm isotopic content. Uranyl acetate slowly degrades in ambient conditions by reaction with atmospheric moisture, and therefore, all product was stored in nitrogen-purged containers within double mylar containers that included desiccating capsules. All laboratory workspaces were rigorously cleaned between before and after synthesis of the CRM mixed uranyl acetate product to avoid contamination between batches.

3. Production & Processing of UO_2 Particle Standards

3.1 Reaction Procedure

A facile hydrothermal route for the phase-controlled synthesis of highly crystalline UO_2 particles was developed and tailored to meet the desired characteristics needed for the milligram synthesis of particle standards. The technique can be described as a scalable batch reaction, which offers greater batch-to-batch repeatability and can be easily tuned to vary the material yield within the order of a few milligrams, all the way up to 200 mg. Hydrothermal synthesis is a well-established method of synthesizing colloid particles using a combination of high temperature and pressure.[12] In this way, reaction mechanisms not achievable at standard temperature and pressure can be performed within the confinement of a Teflon-lined pressure vessel, as shown in Figure 3. The specific method described herein uses organic amines as both reducing agents and structure-directing ligands, further simplifying the synthetic procedure. In its acetate form, uranyl ions are found to readily complex with ethylenediamine, which then undergo a thermolysis reaction that triggers the nucleation and growth of UO_2 crystals. In using a sealed reaction vessel during heating and synthesis, considerations for safe operation and handling of radioactive material are streamlined, adding multiple layers of containment and providing a simple means of mitigating any batch-to-batch "cross-talk" between particles of different isotopic profiles.

For this study, UO_2 particles were synthesized by the following protocol: 0.05 mmol (20 mg) of uranyl acetate ($UO_2(CH_3COO)_2{\cdot}2H_2O$) and deionized water (15 mL, 0.833 mol) are mixed to form a homogeneous solution under vigorous stirring. Once the uranyl acetate is completely dissolved, 8.5 mL of glacial acetic acid (CH_3CO_2H, 0.15 mol) is added and stirred for 20 minutes. To this yellow solution, 5 mL of ethylenediamine ($C_2H_4(NH_2)_2$, 75 mmol) is added dropwise under continuous stirring for 20 minutes. After the potential of hydrogen (pH) equilibrates, a surfactant can be added to the solution as an additional growth-directing agent. The resulting solution is then sealed in a 25 mL Teflon-lined, stainless-steel autoclave and heated at 160 °C for 48 hours. After the heating step, the reaction vessel is cooled to ambient temperature, and the final product is washed with deionized water and isopropanol several times using bath sonication and centrifugation (4250 rpm) before being stored over isopropanol. A minimum of 5-7 washing steps are required to remove trace amounts of organic residue on the surface of the particles. Prior to washing with isopropanol, a 15-minute dilute acetic acid (0.1 mol/L) wash under bath sonication is performed to ensure the removal of any trace amounts of schoepite (discussed below).

3.2 Hydrothermal Synthesis

Under ordinary circumstances, UO_2 production for nuclear fuel comprises a series of chemical modifications followed by high-temperature annealing (>700 °C) of UO_3 under hydrogen atmosphere. While efficient, the process takes considerable effort and no small degree of risk when dealing with explosive gases. A hydrothermal synthesis, on the other hand, is a simple water-based approach that exploits the reduced nucleation threshold of crystalline UO_2 material when under pressurized conditions. By carefully controlling the starting conditions of the hydrothermal synthesis, it is possible to optimize the reaction further. One such optimization involves the reduction of schoepite, a hydroxide species that typically forms under basic conditions, in a range of pH 8-12. Schoepite has a characteristic two-dimensional morphology—distinct from the spherical shape of UO_2 particles—, which is correlated to its layered crystal structure that is comprised of alternating layers of uranium oxide and a hydrated hydroxide species of uranyl oxide. This phase of uranium has an undesired geometry, poor stability in ambient conditions, and a lower density than pure oxides of uranium (e.g. UO_2). While schoepite can be removed by bath sonicating dispersions in dilute acetic

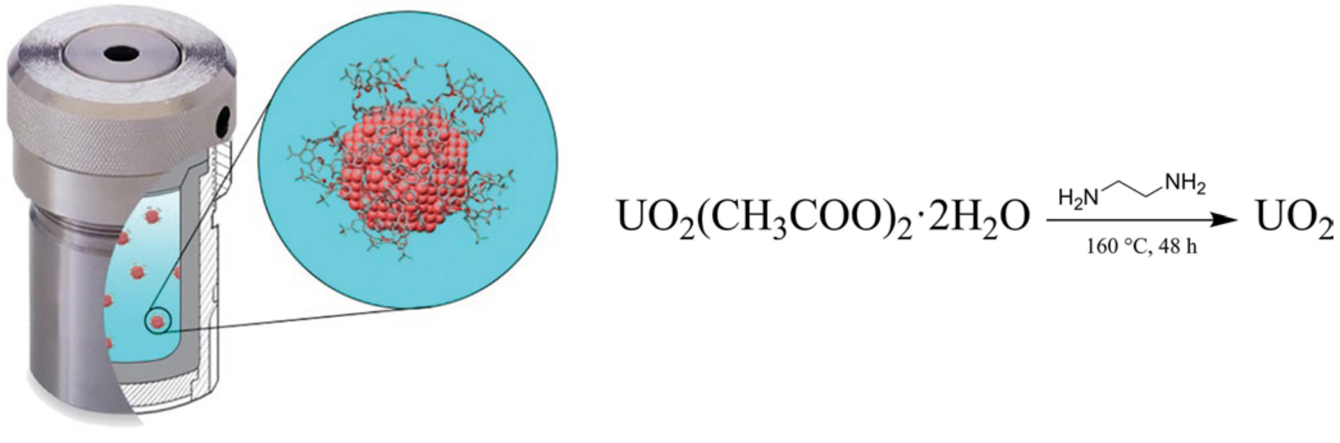

Figure 3: Hydrothermal reaction vessel comprised of a Teflon insert encased in a stainless-steel housing and the prototypical chemical reaction scheme for the synthesis of UO_2 particles.

acid, the UO_2 fraction is inadvertently damaged by surface etching. In a less-invasive attempt of mitigating schoepite, the pH of the starting solution can be systematically reduced by controlling the amount of acetic acid added to the initial solution. In this way, the production of UO_2 spheres increases to near 100% as the pH decreases to 7.5. Conversely, observations of any schoepite crystals rapidly diminished, with only trace amounts detected on rare occasion. It should also be noted that the schoepite reduces in size as the pH is decreased, visually indicating the unfavourable schoepite growth conditions in the lower, close to neutral, pH range. As the pH is adjusted to neutral and further to the acidic range (pH 6), neither schoepite nor UO_2 is produced, which is expected, as these phases are both oxide-based and are not stable under acidic conditions.

3.3 Crystal Growth & Post-Processing

During synthesis development, batches of UO_2 particles are screened using transmission electron microscopy (TEM) to evaluate the size, shape, and crystallinity of individual particles. Figure 4(A) and 4(B) show representative images of particles synthesized from a large-batch (200 mg), hydrothermal reaction. Most particles were found to have a spherical morphology, with size distributions shifting to larger diameters (1-3 µm) for reactions on the scale of hundreds of milligrams to lower diameters (0.5-1.5 µm) for smaller batches of material (10-20 mg). This level of size control was demonstrated by simply changing the starting precursor concentration while keeping reactor, solution, and reagent volumes constant. In this way, monomer supply to evolving nuclei is far less abundant, which slows the crystal growth and reduces the average diameter of the resulting UO_2 particles. The corresponding selected area electron diffraction (SAED) pattern shown in Figure 4(B) seems to indicate that the particles are close to single crystal. However, as the diffraction spots are slightly skewed along a specific d-spacing, it is more likely that the particles are pseudo-polycrystalline. Such characteristic would suggest an orientated-attachment mechanism for crystal growth, which would follow that smaller nanosized crystals are first nucleated during the reaction and then agglomerate to further crystallize into larger micrometre-sized particles. In such an instance, nanocrystalline grains assume a preferred orientation that energetically favours attachment. Under tighter ligand and precursor control, it would be possible to synthesize single-crystal UO_2 particles with ideal density characteristics.

Given that the primary end use for these materials is directed towards particle standards for LG-SIMS, removal of all organic residue from as-synthesized UO_2 particles was another primary focus of this work. Many colloidal approaches use high concentrations of surfactant ligands and structure-directing agents, all of which lead to heavy deposits of carbon contamination and poor mass spectrometry measurements. While TEM has proved to be the workhorse instrument for particle screening, helium ion microscopy (HeIM) can be employed for its surface-sensitive imaging capability and capacity to identify any residual organic material. TEM is a transmission-based technique, and so lighter element materials are transparent when imaged by this

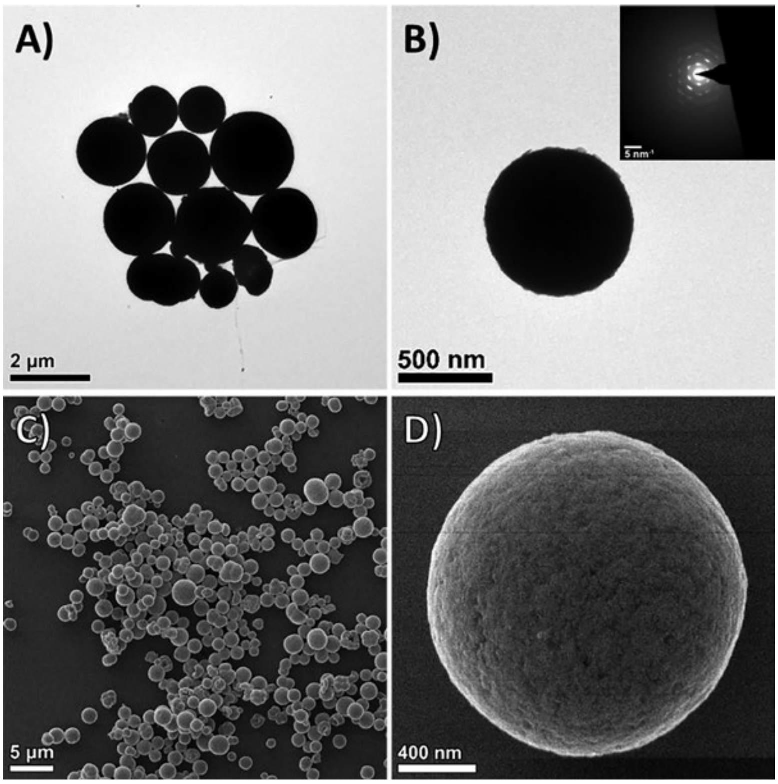

Figure 4: (A, B) TEM and (C, D) HeIM images of UO_2 particles post-processed with solvent washing.

approach. Electron-based microscopy, both the scanning and transmission variants, typically suffers from what is referred to as a high-interaction volume. This phenomenon arises because of the elevated accelerating voltage and current used to image a sample with electrons, which can reach up to 300 keV in the case of transmission systems. Consequently, the volume of sample releasing secondary electrons increases, and the resulting image can appear transparent and less representative of the surface topography. In the case of high-Z contrast material, the effect is suppressed; however, the low-Z organic residue, often encountered with colloidal synthesis, can be difficult if not impossible to fully observe. To gauge the level of "cleanliness" of our UO_2 particles, HeIM is used to thoroughly evaluate samples washed with repeated amounts of isopropyl alcohol and deionized water. The end result, as portrayed in Figure 4(C) and 4(D), is well-defined particles in which the surface topography is clearly resolved, with no trace of organic residue detected.

4. Material Characterization & Validation

4.1 Particle Crystallinity and Size Distribution

Pure oxide of uranium, including UO_2, UO_3, and U_3O_8, have extend storage times in both solution and powder form such that particulate materials meet the requirement to maintain a shelf-life of 1 year or more. PXRD analysis is employed to evaluate the chemical composition and crystal structure from the bulk product of each hydrothermal synthesis. In all cases, peak analysis of collected data matched to that of a fluorite crystal structure, indicative of UO_2 material. Over the course of many different variations of hydrothermal synthesis, only UO_2 and schoepite were observed from the reaction of uranyl acetate and ethylenediamine. As can be seen in Figure 5(A), precisely tuning the pH of the starting mixture to 7.5 gives a single composition of UO_2 material. The sharp peak intensities of the observed diffraction pattern are typical of highly crystalline material and provide a useful means of estimating the average density of the particles.

Aliquots taken from milligram-sized (~20 mg) reactions of as-synthesized UO_2 particles are used to prepare a silicon planchet with concentrated areas of particles for imaging and size analysis. Multiple images are then collected at a consistent field of view (100 µm) so that a large population of particles can be measured for a representative estimate of the size distribution. Figure 5(B) summarizes the results from this analysis; however, it should be noted that a circularity filter was used during image processing to isolate particle agglomerations and instead focus on the measurement of discrete, individual particles. This commonly employed practice of size analysis mitigates the addition of spurious measurements to the overall distribution that might otherwise skew the results in one direction or the other. As can be seen from the plotted size distribution, the largest fraction of UO_2 particles (27%) are found to have a diameter in the range of 1-1.25 µm. In addition, approximately 55% of particles analysed fell within a size range of 0.5-1.25 µm, a metric mandated by the IAEA in their request for QC particle materials. Roughly 77% of the sample falls within the size range of 0.5-1.5 µm, which gives a corresponding mean diameter of 1.26 µm. However, the median diameter, measured at 1.19 µm, is likely a better reflection of the sample, given the slight downshift in the mean diameter due to

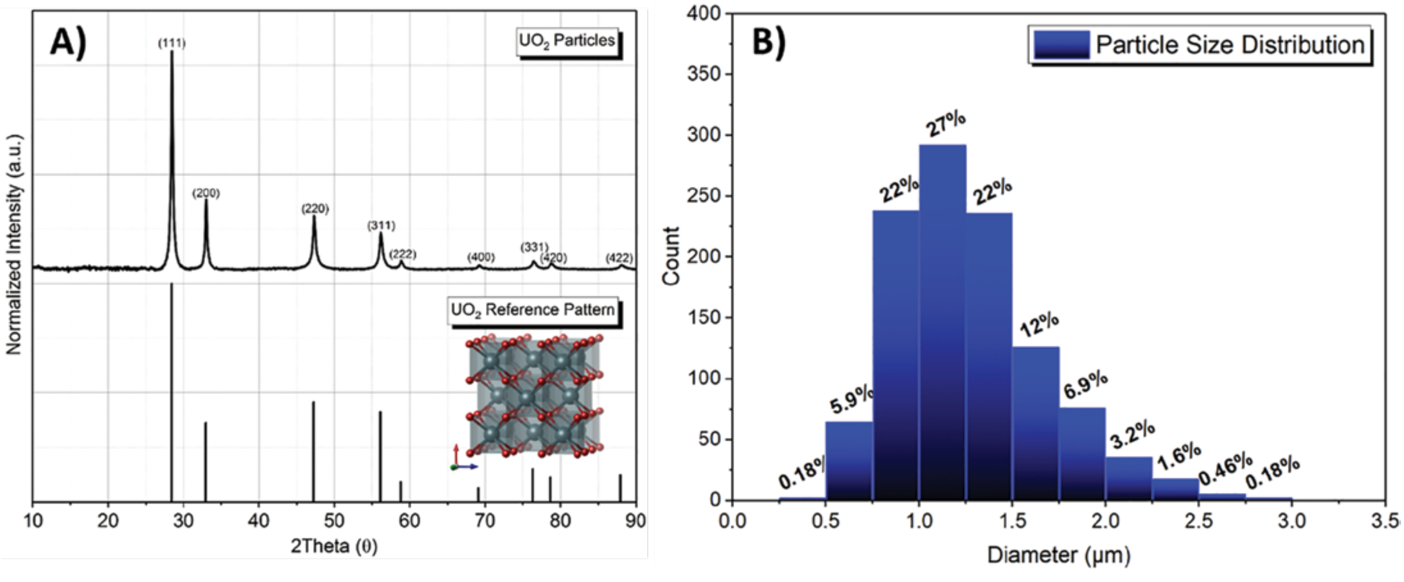

Figure 5: (A) PXRD data of the as-synthesized material, including the matching reference pattern of UO_2 (cubic/fluorite crystal structure, black droplines). (B) Size distribution of all U-containing particles.

a few larger particles in the 2.5-3 µm range, which constitute less than 1% of the total sample.

4.2 Microstructure and Density

While estimation of particle density can be qualitatively calculated from bulk PXRD, microstructural analysis of individual UO_2 particles is a more accurate means of quantifying density and other influencing factors such as porosity and void fraction. For this analysis, a method of particle encapsulation and focused-ion beam (FIB) milling is used to generate cross-sections for internal micro/nanostructural imaging. This process is accomplished by first depositing a thick layer of carbon via electron beam-induced deposition (EBID) that encompasses the entire particle. The surrounding layer of carbon encapsulates the particle, providing support during the FIB milling process and manipulation of the thin particle cross-section. Cross-sections are extracted from individual UO_2 particles and then mounted such that the inner surface of the particle can be imaged from a side-on perspective using SEM and STEM (Figure 6).

A representative set of images taken of a 1 µm particle is given in Figure 6. The results highlight near-uniform density expected for crystalline particles, with small amounts of porosity on the order of 4-6%. Cross-sectional images in Figure 6, captured with several different imaging modes, resolved only a minute number of nanosized pores, likely arising from the postulated crystal growth mechanism of orientated-attachment. Estimates for the measured particle void fraction and density were calculated using the theoretical density of single-crystal UO_2 (10.97 g/cm^3) and the volume of a particle calculated from the diameter observed during SEM imaging. Calculations for the particle shown in Figure 6 were based on a measured diameter of 1.1 µm and a relative porosity of 4.5%, giving an estimated density of 9.23 g of U/cm^3 (1.8×10^{10} U atoms). A lack of severe porosity of the synthesized particles is an important result, as the theoretical density of the particles presented in this work is higher than that of other forms of uranium oxide, providing more uranium atoms per particle volume for mass spectroscopy applications.

4.3 Isotopic Profile

To facilitate end-user analysis and develop a capability for the selection of specific particles of interest, a technique akin to fission track TIMS can be used to prepare UO_2 particles on a specialized substrate.[13] As a means of expediting the search routine normally employed to find uranium-bearing particles, a 500×500 µm grid (with letter and number reference markings) is etched into the surface of a vitreous-carbon planchet for particle placement at marked locations. Under SEM imaging, shown in Figure 7A, a nanomanipulator is then used to pick and place particles of interest to the patterned grid. The manipulator, housing a FIB-sharpened tungsten needle, can extract particles from the surface using localized carbon adhesion focused at a point of contact and then places them onto designated regions of a secondary substrate. Once deposited, the particle is held to the substrate via weak forces and can be analysed immediately or, alternatively, held in place via a small amount of deposited platinum (Figure 7B) for long-term storage or shipment. The patterned, vitreous-carbon planchet provides a referenceable grid location (Figure 7C) of each particle placed on the substrate, negating the need to run Automatic Particle Measurement software and expediting the overall measurement time. Additionally, this method provides the opportunity to directly image particles prior to and directly after SIMS analysis. Figure 7D shows a representative sample prepared on a laser-etched carbon planchet.

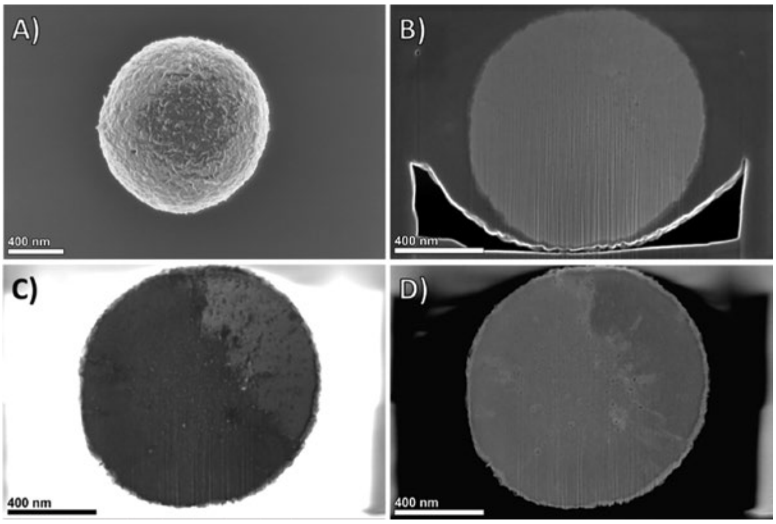

Figure 6: SEM images of (A) a 1 µm particle and (B) a FIB-milled cross-section of a carbon encapsulated UO_2 particle. (C) Annular bright-field and (D) annular dark-field images of the same cross-section.

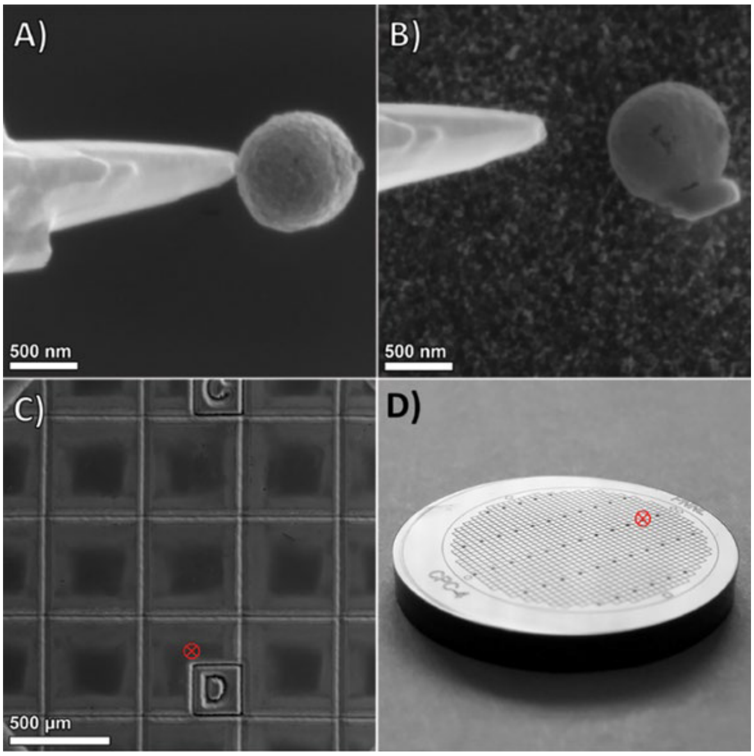

Figure 7: SEM images showing (A) the removal of a particle from a silicon wafer, followed by (B) placement on a carbon planchet at a (C) known marked location. (D) Optical image of the laser-patterned planchet.

To test the suitability of the particles to serve as standards in the environmental sampling program for IAEA Safeguards, prepared planchets are evaluated using a Cameca IMS-1280 Large Geometry SIMS. This is the same model that is used for particle measurements by most of the members of the IAEA NWAL. Analyses are performed with a focused primary ion beam of O^{2+} at an impact energy of 8 keV. The species detected are positive uranium ions at an energy of 10 keV. The primary beam current and raster-scanned area are adjusted depending on the specific analysis. Uranium-bearing particles are located by real-time scanning ion imaging over a 500x500 µm area with the mass spectrometer tuned to ^{238}U. Bright particle images are easily visible against a uniform uranium background after a period of pre-sputtering. A selected target particle is centred on the ion optical axis by translation of the sample stage, and the raster size and beam current are adjusted to 10x10 µm and 200 pA, respectively, for isotopic analysis. In this manner, isotopic measurements of all six particles picked and placed to a patterned substrate can be made, and the results processed to account for signal trending, detector dead time, isotopic mass bias, and hydride correction for ^{236}U. The results of these isotopic composition measurements are given in Table 1, along with the weighted averages and standard deviations. The measured isotopic variation among the particles is consistent with the internal measurement uncertainty for each particle, and is in good agreement with the bulk analysis of the same material analysed by multi-collector ICP-MS.

Several individual particles were subjected to depth profile measurements by SIMS. Particles were selected in a similar manner to that described above for isotopic measurements, but they were analysed by monitoring the ^{238}U signal continuously as a function of time until the signal fell to about 1% of its maximum value, and then the integrated number of ^{238}U ion counts was determined. Two different types of profiles shapes (count rate *vs.* sputter time) are observed, as illustrated in Figure 8. One type, depicted by particles D and DE, shows a short increase in signal, followed by a gradual signal fall-off, with the entire profile lasting 300-400 seconds. Based on the previous analysis, this behaviour is characteristic of particles at or near a micrometre in size. The other type of profile, illustrated by particles DC and ED, shows an almost immediate onset of a roughly exponential signal decay, and the signal persists for a little less than 200 seconds. This behaviour is characteristic of much smaller particles or of a thin film of uranium. The first profile type contains much higher ^{238}U counts than the second profile, which is consistent with the smaller particle size measured by SEM. Following SIMS analysis, particles were re-imaged by SEM, where it was found that the depth profile analysis completely consumes the UO_2, leaving behind only a small amount of platinum (from EBID) and a sputtered region of about 12 µm in diameter.

Sample	^{234}U	^{235}U	^{236}U	^{238}U	Ø (µm)
E	0.00088	0.20330	0.00287	99.79295	0.675
ED	0.00062	0.20370	0.00300	99.79268	0.525
DE	0.00067	0.20339	0.00297	99.79296	0.725
D	0.00070	0.20405	0.00295	99.79229	0.850
DC	0.00068	0.20178	0.00309	99.79444	0.600
C	0.00073	0.20099	0.00275	99.79553	0.500
SIMS Average	0.00071	0.20287	0.00294	99.79348	0.645
1σ	0.00006	0.00121	0.00015	0.00122	
ICP-MS Average	0.000695	0.1984	0.00278	99.798	
1σ	0.000043	0.0004	0.00009	0.0003	

Table 1: Uranium isotopic composition of PNNL particles in atom percent.

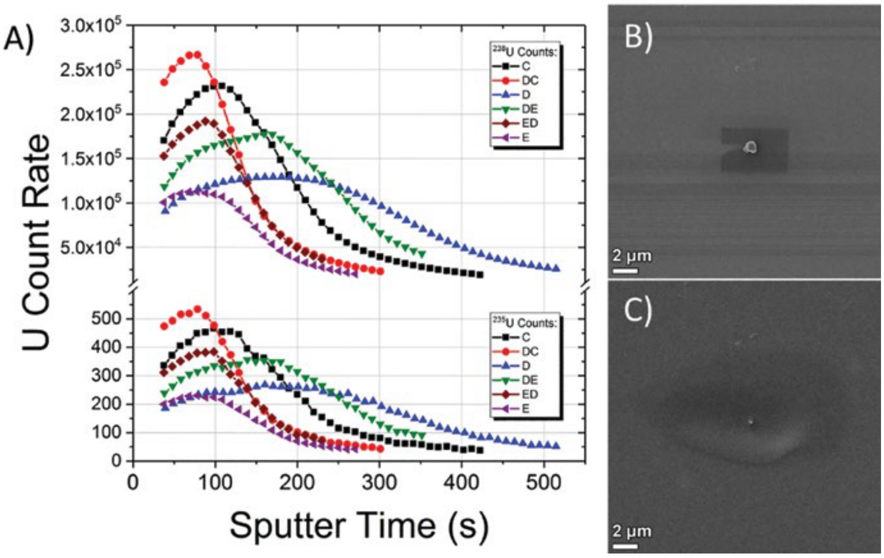

Figure 8: (A) The measured trends for count rate over sputtering time, and (B,C) SEM images of UO_2 particle (designated "DE") before and after depth profile analysis by LG-SIMS.

5. Summary

To tackle the shortfall in particle reference material for nuclear safeguards activities, PNNL and SRNL have devised a multi-step production process to meet the stringent requirements mandated for uranium particle standards. SRNL have developed a unique means of generating tailored isotopic profiles derived from a computational matrix of different blending options available from current CRM inventories. It was also shown that a method of re-crystallising blended material into different chemical forms, more conducive to particle synthesis, could be used following the CRM mixing process. In this way, precursor material of a desired isotopic profile could be prepared at SRNL and shipped in a form compatible with a given synthetic procedure. In the case of this study, uranyl acetate precursor was outlined for PNNL's synthesis of uranium oxide (UO_2) particle standards, realised by a hydrothermal reaction technique. The colloidal chemistry approach developed at PNNL is tailored for the primary production of UO_2, and the minimization of other uranium products—namely, schoepite—and other morphologies. Optimization was accomplished through acid-base equilibrium chemistry (pH control), and control of reactant stoichiometry.

The bulk composition of the produced particles was examined by PXRD and SAED, with both analytical techniques confirming the particles to be highly crystalline and of a single fluorite structural phase. Additionally, particle size analysis from TEM, SEM, and HeIM images showed that the isolated spherical particles had a size range of 0.5-1.25 µm for a typical synthesis of 20 mg batches. If particles could also be produced with much tighter control of particle size and in different size ranges, they could be suitable for other applications such as interlaboratory comparisons and improvement of mass spectrometry measurement techniques. Using FIB and STEM analysis, observations were made of the internal structure of individual UO_2 particles, with measurements for the void fraction confirming low-levels of porosity (4-6%), and densities reaching near theoretical levels for UO_2 (9.23 g of U/cm^3). UO_2 particle standards generated by hydrothermal synthesis afford much greater uranium densities compared with other oxide compositions, making them ideal candidates for particle standards analysis. Throughout each phase of the production process, a rigorous handling and cleaning protocol was continually maintained to ensure that batches of particles remained free of cross-contaminants.

Finally, a technique to select particles of specific size and morphology and place them on a laser-patterned grid of a vitreous carbon planchet for SIMS analysis was reported. This approach was then used in conjunction with a SIMS analysis to assess particle proficiency. Findings from the evaluation study of UO_2 particles suggests that in their present form they could be quite useful as QC samples that the IAEA could introduce to the NWAL as blind samples on cloth. The micrometre size range is typical of the samples that the IAEA collects, and for this purpose, they do not need to be monodispersed. To be useful on a continuing basis, they would need to be produced in batches of various enrichment levels with avoidance of cross-contamination and validation of the isotopic composition after production. It is advantageous that they are not bound to a medium during production and instead can be supplied in a vial for the IAEA to use as it sees fit.

6. Acknowledgements

The authors wish to thank the team at the IAEA Safeguards Analytical Laboratory for their expert advice and critical feedback throughout this work. The Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830. This work was sponsored by the U.S. Department of Energy, National Nuclear Security Administration, Office of Nonproliferation and Arms Control, International Nuclear Safeguards program.

7. References

[1] Boulyga, S.; Konegger-Kappel, S.; Richter, S.; Sangely, L. *J. Anal. At. Spectrom.* 2015, 30, 1469-1489.

[2] Mathew, K. J.; Stanley, F. E.; Thomas, M. R.; Spencer, K. J.; Colletti L. P.; Tandon, L. *Anal. Methods*, 2016,8, 7289-7305

[3] Middendorp, R.; Dürr, M.; Knott, A.; Pointurier, F.; Ferreira Sanchez, D.; Samson, V.; Grolimund D. *Anal. Chem.* 2017 89 (8), 4721-4728.

[4] Stoffel, J. J.; Briant, J. K.; Simons, D. S. *J. Am. Soc. Mass Spectrom.* 1994, 5, 852-858.

[5] Erdmann, N.; Betti, M.; Stetzer, O.; Tamborini, G.; Kratz, J. et al. J. *Spectrochim. Acta, Part B* 2000, 55, 1565-1575.

[6] Kips, R.; Pidduck, A. J.; Houlton, M. R.; Leenaers, A.; Mace, J. D.; Marie, O.; et al. *Spectrochim. Acta, Part B* 2009, 64, 199– 207.

[7] Middendorp, R.; Dürr, M.; Niemeyer, I.; Bosbach D. *ESARDA BULLETIN*, No. 54, June 2017

[8] Boyd, S.; Boyd, S. P.; Vandenberghe, L.; Press, C. U., *Convex Optimization. Cambridge University Press:* 2004.

[9] Lacher, J. R.; Salzman, J. D.; Park, J. D., *Dissolving Uranium in Nitric Acid. Industrial & Engineering Chemistry.* 1961, 53, 282-284.

[10] Herrmann, W. A., *Synthetic Methods of Organometallic and Inorganic Chemistry Georg Thieme Verlag:* 1996.

[11] Bagnall, K. W., *The actinide elements. Elsevier Publishing Company:* 1973.

[12] Nkou Bouala, G. I.; Clavier, N.; Podor, R.; Cambedouzou, J.; Mesbah, A.; Brau, H. P.; Léchelle J.; Dacheux N. *CrystEngComm*, 2014, 16, 6944-6954.

[13] Admon, U.; Donohue, D.; Aigner, H.; Tamborini, G.; Bildstein, O.; Betti M. *Microsc. Microanal.* 2005, 11, 354–362.