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Production and Characterization of Monodisperse Plutonium, Uranium, and Mixed Uranium–Plutonium Particles for Nuclear Safeguard Applications

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In order to prevent nuclear proliferation, the isotopic analysis of uranium and plutonium microparticles has strengthened the means in international safeguards for detecting undeclared nuclear activities. In order to ensure accuracy and precision in the analytical methodologies used, the instrumental techniques need to be calibrated. The objective of this study was to produce and characterize particles consisting of U, Pu, and mixed U–Pu, suitable for such reliability verifications. A TSI vibrating orifice aerosol generator in connection with a furnace system was used to produce micrometer sized, monodispersed particles from reference U and Pu materials in solution. The particle masses (in the range of 3–6 pg) and sizes ($\sim 1.5 \mu\text{m}$) were controlled by the experimental conditions and the parameters for the aerosol generator. Size distributions were obtained from scanning electron microscopy, and energy-dispersive X-ray analysis confirmed that the particle composition agreed with the starting material used. A secondary ion mass spectrometer (SIMS) was used to characterize the isotopic composition of the particles. Isobaric and polyatomic interference in the SIMS spectra was identified. In order to obtain accurate estimates of the interference, a batch of Pu particles were produced of mainly ^{242}Pu . These were used for SIMS analysis to characterize the relative ionization of Pu and U hydride ions and to determine the SIMS useful yields of U and Pu. It was found that U had a higher propensity to form the hydride than Pu. Useful yields were determined at a mass resolution of 450 for U–Pu particles: $(1.71 \pm 0.15) \%$ for Pu and $(0.72 \pm 0.06) \%$ for U. For Pu particles: $(1.65 \pm 0.14) \%$ for Pu. This gave a relative sensitivity factor between U and Pu ($\text{RSF}_{\text{U:Pu}}$) of 2.4 ± 0.2 . However, the $\text{RSF}_{\text{U:Pu}}$ showed large fluctuations during the sputtering time for each analyses of the mixed U–Pu particles, in the range of 1.9–3.4.

It is necessary to validate all methods used in analytical investigations. This is especially true when the conclusions drawn from the measurements may have political consequences, for example, in the case of nuclear safeguards. Methods of analysis are calibrated by the use of known quantities of relevant materials. The material used should be as closely related as possible to that of the sample to be analyzed. International nuclear safeguard programs evolved from the need to verify the declared nuclear activities of certain countries after the discovery of Iraq's nuclear weapons program to a more investigative approach with the aim to determine any clandestine activities. New sampling procedures were introduced where most samples are collected by swiping surfaces inside a nuclear facility, to collect traces of nuclear material.^{1,2} The composition of the samples serves as a fingerprint of the ongoing and past activities at the facility. The source and intended use of the material can be identified from the analysis of traces of uranium (U) and plutonium (Pu) and compared with the declared use.^{3–5}

These methods are also applied in the area of nuclear forensics to detect and prevent the illicit trafficking of nuclear material,^{6,7} as well as for monitoring and risk assessment of radioactively polluted sites. In the latter case, particle analysis has been introduced and used during the past decade as it has been shown that most of the activity released is carried by particles.^{8–13} These

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studies underline the importance of characterizing particulate effluents as the impacts on health and the environment ultimately depend on the chemical and physical composition of the particles.

Two techniques that have been used extensively in particle analysis are secondary ion mass spectrometry (SIMS) and scanning electron microscopy (SEM), together with microprobe analysis methods such as energy dispersive X-ray (EDX) and wavelength dispersive X-ray analysis (WDX).^{13–15} In all studies it is necessary to calibrate the method using standards containing known amounts of known materials. Uranium particles have previously been used to study the instrumental response of SIMS in safeguard investigations⁵ and in an interlaboratory round robin investigation of SIMS sensitivity.¹⁶ Calibration samples of U are already available,¹⁷ and the International Atomic Energy Agency (IAEA) has called upon its Network of Analytical Laboratories to produce similar reference materials for Pu and mixtures of U and Pu. The work presented here has been a contribution to the European Commission Safeguards support program to IAEA. When the sample to be analyzed consists of minute amounts of Pu and/or U, a reference material with a well-defined size and elemental composition is required. This article describes the production of such materials and presents the results of the characterization of three types of particle material: U, Pu, and mixed U–Pu particles. The morphology, elemental composition, and size distribution were characterized using SEM-EDX and the isotopic composition by SIMS. We also present the results of the initial optimization tests of the particle generator, where cerium (Ce) was used to simulate the behavior of Pu in the particle generation process.

INSTRUMENTS AND METHODS

Description of Particle Production System. A vibrating orifice aerosol generator system (VOAG, model 3450, TSI Inc.) was employed together with a furnace system for the production of monodisperse U, Pu, and mixed U–Pu particles. The VOAG generates particles of a specific composition with a precise and uniform size.¹⁸ This system has been used previously for the production of uranium at our laboratory¹⁷ but has since been assembled inside a glovebox to prevent the release of Pu into the workplace and upgraded (with an aerosol neutralizer).

Prior to each production run, the system was rinsed with propan-2-ol in order to avoid precipitation leading to clogging of the system. Fresh solutions were prepared before each particle production run for the same reason. The solution was passed through syringe filters prior to injection into the VOAG. The droplets were produced using a 20 μm -diameter orifice and then

dried in a drying column using an air flow of 55 L/min at 45 °C. A ⁸⁵Kr aerosol neutralizer (model 3054, TSI Inc.) was installed inside the drying column in order to minimize electrostatic charge. After the drying column, the particles continue to travel with an air flow of 8 L/min into three furnaces. The droplets are calcined into particles in the three furnaces which have temperatures sequence of 150, 300, and 800 °C. The length of the flight path in the furnace system is 1.65 m. After cooling, the particles formed are collected on a filter (Millipore, Nucleopore 0.6 μm).

Materials and Solution Preparation for Particle Production. Certified reference materials, obtained from the National Institute of Standards and Technology (NIST), were used for particle production: CRM U020-A uranium oxide at 2% ²³⁵U enrichment and NBS 949d Pu metal assay standard with a ²³⁹Pu abundance of about 97 atom %. In addition, isotopically pure ²⁴²Pu oxide powder was obtained from Argonne National Laboratory.

Fresh solutions of each particle production were prepared by the dilution of an aliquot of a mother solution. The mother solutions were prepared from each material according to the following procedures. The CRM U020-A was dissolved in 1 M HNO₃ to a concentration of 36.3 mg U/g, measured by isotope dilution mass spectrometry with thermal ionization mass spectrometry (IDMS-TIMS). A weighed amount of the NBS 949d Pu metal was dissolved in *aqua regia* and evaporated and then converted into a 1 M HNO₃ matrix with a concentration of 41 mg Pu/g. An aliquot of the ²⁴²Pu oxide powder was weighed and dissolved in 14.4 M HNO₃/0.01 M HF. After evaporation, it was again dissolved in 1 M HNO₃ to a concentration of 22.9 mg Pu/g. As Ce is a well-known analogue for Pu,¹⁹ and because of its nonradioactive nature, it was initially used to simulate the Pu behavior in the particle generation process to prevent Pu contamination of the system. Specifically, the dissolution behavior of Pu was of special interest as it was crucial that no precipitation occurred that could block the generator orifice. For this, a Ce standard (SPEX CertiPrep Inc.) with a concentration of 1 mg/mL in 2% HNO₃ was used as the mother solution.

For the production of U, Pu, and U–Pu particles, 50–250 μL of mother solution was diluted in a mixture of 50 mL of distilled water and 50 mL of propan-2-ol as solvent, as this mixture is recommended for optimal drying speed of the particles (TSI VOAG Instruction Manual). In the case of U–Ce particle production, 156 μL of the U mother solution and 625 μL of the Ce mother solution were used. Table 1 gives data on the materials used and solution concentrations. The mass and size of the particles depends on the solution concentration and the operating conditions of the VOAG, which were set to produce a final particle size of ~ 1 μm in diameter in this study. However, according to the instruction manual it is possible to produce particles up to ~ 15 μm when using a 20 μm -diameter orifice and higher solution concentrations.

Calculations of Particle Mass. The diameter of a droplet produced in the VOAG is given by¹⁸ $D_d = \{(6Q)/(\pi f)\}^{1/3}$, where D_d is the diameter of the droplet, where Q is the liquid feed rate from the syringe pump assembly, and f is the frequency

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Table 1. Material and Solution Concentrations Used for Different Particle Production Batches and Their Mass Inventory

particle batch ID	material	concn of mother solution	concn with solvent	mass per particle
U020-35	CRM U020-A	37.4 ± 0.1 mg U/mL ^a	37 ± 3 µg U/mL	2.6 ± 0.2 pg U ^{a,5}
U020-84	CRM U020-A	37.4 ± 0.1 mg U/mL ^a	62 ± 5 µg U/mL	5.7 ± 0.5 pg U
	Ce standard	1.0 (±5%) mg Ce/mL	6.5 ± 0.5 µg Ce/mL	0.6 ± 0.05 pg Ce
				total: 6.3 ± 0.5 pg
U-Pu:1	CRM U020-A	37.4 ± 0.1 mg U/mL ^a	32 ± 3 µg U/mL	3.0 ± 0.3 pg U
	NBS 949d	41 ± 2 mg Pu/g	35 ± 3 µg Pu/mL	3.2 ± 0.3 pg Pu
				total: 6.4 ± 0.4 pg
Pu 3:4	NBS 949d	41 ± 2 mg Pu/g	68 ± 7 µg Pu/mL	6.3 ± 0.7 pg Pu
U-Pu-242:A	CRM U020-A	37.4 ± 0.1 mg U/mL ^a	34.45 ± 0.04 µg U/mL ^a	3.2 ± 0.2 pg U
	Pu oxide (99.7% ²⁴² Pu)	22.9 ± 0.7 mg Pu/g	32.56 ± 0.03 µg Pu/mL ^a	3.0 ± 0.2 pg Pu
				total: 6.2 ± 0.3 pg
Pu-242:B	Pu oxide (99.7% ²⁴² Pu)	22.9 ± 0.7 mg Pu/g	62.6 ± 0.2 µg Pu/mL ^a	5.8 ± 0.3 pg Pu

^a Concentration measured by IDMS-TIMS.

of droplet generation. The VOAG was operated at a liquid feed rate of 6.3×10^{-9} m³/s and at a droplet generation frequency of 68 kHz, resulting in a droplet diameter of 56 µm. The concentration of the nonvolatile fraction in the solvent and the droplet dimensions determine the mass of each particle. The concentration was calculated from weight measurements during solution preparation, and for some batches, the concentration was measured by IDMS-TIMS for greater precision.

Isotope Dilution Mass Spectrometry with Thermal Ionization. A U–Pu solution, used for the production of batch U-Pu-242:A, and a Pu solution, used for the Pu-242:B batch, were assayed by IDMS-TIMS. In the U assay, the chosen reference material was rich in ²³³U, and in the Pu assay, a reference material containing ²³⁹Pu as the dominant isotope was employed.

During the first step, the isotopic compositions of the U and/or Pu of both the sample and the reference material were determined. The total evaporation technique of TIMS, pioneered by the Institute for Transuranium Elements in 1986 was used as it gives an isotopic composition that is virtually free from mass bias effects.²⁰ In the second step, an accurately weighed portion of the sample and the reference solutions were homogenized, for each sample. Measurement of the ²⁴²Pu/²³⁹Pu and/or ²³⁸U/²³³U atom ratios of the mixtures by total evaporation-TIMS provided the information required to determine the number of ²⁴²Pu and/or ²³⁸U atoms in the sample in terms of the known amount of ²³⁹Pu and/or ²³³U atoms in the reference material. The TIMS instrument used was a Finnigan MAT262 for these analyses. The number of ²⁴²Pu and/or ²³⁸U atoms in the sample, determined using the measured isotopic composition of the Pu and/or U in the sample, was then converted to the total number of atoms and, thereafter, to a mass.

Because of the high reliability of mass spectrometry using the total evaporation technique, as is routinely demonstrated by measurements on certified isotopic reference materials, IDMS has the potential of high accuracy and, provided that accurately certified reference materials are used, elemental contents with a precision of typically 0.1% or better can be determined.

Extraction of Particles for SEM and SIMS Analysis. For SEM measurements, part of the particle filter was attached to a carbon tape on a SEM sample holder. Only part of the filter

containing particles was used in order to save the rest of the sample for further analysis.

The samples for SIMS measurements were prepared using two methods. (1) The pure U particles were removed from the filter by placing it in a glass container with a propan-2-ol solution and thereafter placing the container in an ultrasonic bath. Several drops of the suspension containing particles were then deposited on a polished pyrolytic graphite planchet (grade A no. 17680, E. F. Fullam Inc.) for SIMS and the solvent was evaporated. (2) For the Pu particles, a vacuum impactor²¹ was used to impact particles from the filter onto a conductive carbon tape attached to a SIMS graphite planchet. The use of conductive carbon tape should have reduced Pu particle bounce-off effects.

Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry. Samples were coated with a thin film of gold (~10 nm) using a sputter coater (SCD 005, BAL-TEC AG, Liechtenstein) in order to obtain high-resolution images. SEM measurements were performed to determine particle morphology and size distribution using three different instruments, and the elemental composition was determined by EDX analysis. The instruments used were (1) a SEM (Personal SEM, ASPEX Instruments, formerly RJ Lee Instruments Ltd.). The operating voltage was 20 kV, and the X-ray spectra were detected using a 10 mm² liquid-nitrogen-cooled silicon crystal detector. The working distance between the probe and the sample was 16 mm. Automated feature analysis (AFA) software, Zeppelin, (ASPEX Instruments), was used for automatic analysis of the particle size distribution. The operating conditions of the SEM were optimized with respect to AFA analysis by varying the SEM settings iteratively to obtain the best spot size, magnification, contrast, and brightness. The detection/measurement thresholds were optimized regarding accuracy and precision of the size measurements, as well as the speed of analysis. (2) A Philips SEM XL40 equipped with an EDAX EDX spectrometer, designed for the analysis of nuclear materials, placed inside a glovebox. This SEM was operated at a voltage of 25 kV with a sample–probe distance of 10 mm, and an X-ray collection time of 100 s. Imaging and elemental analysis of higher activity pure Pu and mixed U–Pu particle samples (batches U-Pu:1, Pu 3:4, U-Pu-242:A, and Pu-242:B) were

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performed on this system. The elemental analyses of the X-ray spectra were performed using a conventional standardless ZAF correction method. The ZAF correction compensates for the difference in X-ray generation during the “new” conditions of the sample (identified by the detected elemental composition), which includes corrections for the mean atomic number (Z) dependent electron scattering, absorption (A) and fluorescence (F).²² (3) A Tescan Vega 5130 LS scanning electron microscope, equipped with an EDX system with a 10 mm² liquid-nitrogen-cooled silicon crystal detector, coupled to a multi-channel analyzer. The acceleration voltage was 30 kV, and the working distance between the probe and sample was 15 mm. X-ray spectra were collected for 100 s. The system was utilized for imaging and elemental analysis of the low-activity samples U020-35 and U020-84. The X-ray spectra were processed using ZAF corrections quantified using standards.

Secondary Ion Mass Spectrometry. The SIMS analyses were performed using a double focusing CAMECA IMS 6f. A primary beam of O_2^+ ions, accelerated at +15 kV (sample impact energy, 10 keV) with currents from 1 to 10 nA, was used to sputter the sample. The mass spectrometer was tuned for positively charged secondary ions with an acceleration voltage of 5 kV. The mechanical settings and transfer lens optics were set for maximum transmission in the secondary part by using an 1800 μm field aperture, a 400 μm contrast aperture, and an 80 μm image field.⁵ The entrance and exit slits were adjusted to 150 and 300 μm , respectively, resulting in a mass resolution of 450. The energy bandwidth was set to 35–40 eV. Secondary ions were detected by an electron multiplier (dead time of 25 ns), and count rates were thus kept below 10⁶ cps for all masses. When more than one mass was to be detected, the isotopes were selected by peak jumping the magnet. Recording times were 1 s for major isotopes and 4 s for minor isotopes, with a settling time of 0.1 s for the magnet.

The search for U, Pu, and U–Pu particles was performed in ion microprobe mode, with the mass set to 238, 242, and 242, respectively, and with a raster size of 500 \times 500 μm^2 . The actual analyses were performed with an analytical area (raster size) of 10 \times 10 μm^2 covering the secondary ions emitted from the particle. A time correction was applied to the isotopic ratios,²³ with additional error propagation for the uncertainty in the mass bias. Isotopic ratios were corrected for a mass bias of (0.64 \pm 0.08)% per atomic mass unit determined using U standards. A CRM U010 standard (U_3O_8) of 1% ²³⁵U enrichment, obtained from NIST, was used for SIMS mass bias determinations and mass calibration. The reference material was prepared for SIMS analysis by transferring it in particulate form to a propan-2-ol suspension and then depositing it on a polished pyrolytic graphite planchet.

Because of varying efficiency of the SIMS ionization process for different elements, relative sensitivity factors (RSFs) are used to quantify SIMS data. The RSF relates secondary ion intensities to those of another element in the sample or to the concentration of the element in the sample, and is defined as (c_A/c_B) =

(I_A/I_B)RSF_{A:B}, where A and B represent elements A and B, c denotes the elemental concentration, and I are the recorded secondary ion currents.²⁵ The RSF is matrix dependent and should be obtained from standards with specific elemental compositions applied to related matrixes. The RSF_{U:Pu} was calculated in this work from the measured relative U and Pu efficiency of the produced particles. The efficiency was measured in terms of “useful yield” that equals the amount of ions collected in the detector versus the amount of sputtered atoms. The particles produced by the VOAG are well suited to this application as they have a specified mass content and mono-disperse distribution. The main component affecting the useful yield is the transmission of the system. The SIMS measurements were performed with settings corresponding to standard settings for U:Pu analysis, as described above.

Isotopically pure ²⁴²Pu material is advantageous for the analysis of the useful yield of Pu due to that ²⁴²Pu is insignificantly influenced by any interference (compare with the discussion below regarding the hydride study), and particles from batches U-Pu-242:A, Pu-242:B, and U020-35 were employed. The SIMS measurements were performed in depth profile mode, where ²³⁸U and/or ²⁴²Pu was recorded for 10–15 min until the particle was fully consumed. The useful yield was obtained from the ratio of the total integrated signal to the number of atoms in the particle, obtained from the data presented in Table 1. The RSF_{U:Pu} was then computed by the ratio of the useful yields of Pu to U, resulting in an averaged RSF_{U:Pu} for the complete particle analyses and not taking into account any fluctuations during the sputtering. Only single-droplet particles were taken into account in the analysis; all others were removed based on their significantly higher ion intensities and longer times for complete particle consumption.

Peaks in the SIMS mass spectra arising from U and Pu hydrides interfere to different degrees with the analysis, and when it is possible to quantify them, the isotopic ratios can be corrected accordingly. The interference depends on the operating conditions (e.g., vacuum level) and on the hydrogen and water contents of the sample. In the analysis of U, ²³⁵UH interferes with ²³⁶U and is corrected by a peak-stripping method specific for each sample.²⁴ However, this method cannot be applied in Pu analysis. The most common isotope in materials containing Pu is ²³⁹Pu and consequently interference from peaks representing the hydrides of all Pu isotopes with higher mass (²⁴⁰, ²⁴¹, ²⁴²Pu) will be present in the SIMS mass spectra. Furthermore, the peak-stripping method cannot be used to obtain the ²³⁶U component in U–Pu mixtures because of the ²³⁹Pu interference on ²³⁸UH. In order to obtain an estimate of the degree of Pu hydride formation in the particles during SIMS measurements, hydride formation was studied by measurements of the produced Pu particles with ²⁴²Pu as the main component. Isotopically pure ²⁴²Pu was specifically chosen for the purpose as the dominant nuclide in the spectrum is insignificantly influenced by ²⁴¹MH (M = metal). The ²⁴²PuH:²⁴²Pu was directly measured in particles from the batches Pu-242:B and U-Pu-242:A while the ²³⁸UH:²³⁸U ratio was estimated from the measurements of the mass ratio 239:242 in particles of batch

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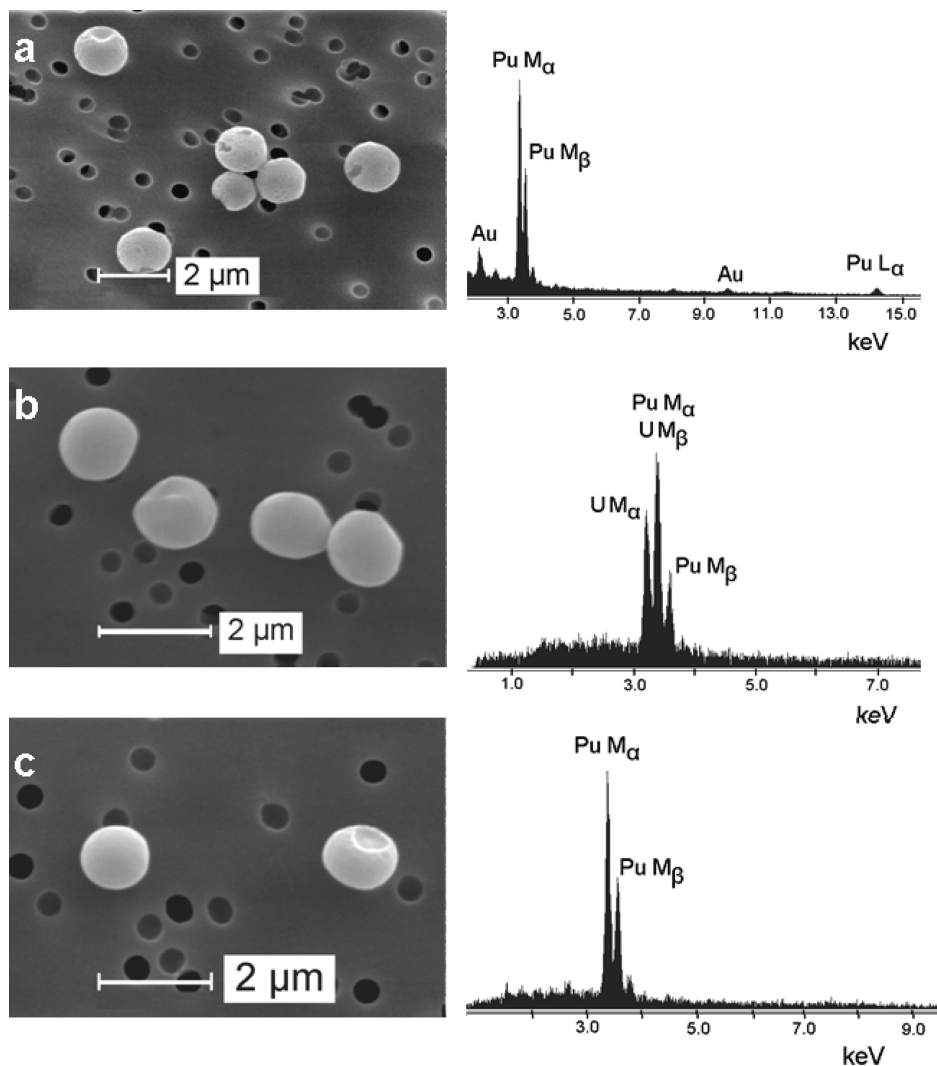


Figure 1. SEM images and X-ray spectra from the three batches: (a) Pu 3:4, (b) U-Pu-242:A, and (c) Pu-242:B.

U-Pu-242:A. The $^{238}\text{U}/^{238}\text{U}$ ratio was here extracted from the relation: $(^{239}/^{242}) = (^{238}\text{U}/^{238}\text{U})(^{238}\text{U}/^{242}\text{Pu}) + (^{239}\text{Pu}/^{242}\text{Pu})$, where the $^{238}\text{U}/^{242}\text{Pu}$ and $^{239}\text{Pu}/^{242}\text{Pu}$ were attained from the IDMS-TIMS measurements (taking into account the $\text{RSF}_{\text{U-Pu}}$ obtained in this study).

RESULTS AND DISCUSSION

Particle Elemental Composition and Size Distribution.

Examples of SEM images and spectra from EDX analysis for different particle batches are shown in Figure 1. The Pu particles, the mixed U–Pu particles, and mixed U–Ce particles showed similar morphology, consistent with our previous findings in the production of U particles. The EDX elemental analysis confirmed that the particle compositions were the same as that of the materials used for their production. The ZAF analysis of batch U-Pu:1 gave nominal weight concentrations of U and Pu of 47.0% and 53.0%, respectively, which agree well with values in Table 1: 47.7% U and 52.3% Pu. However, the elemental values predicted by ZAF for batch U020-84 were 87.3% U and 12.7% Ce, which deviate somewhat from the data in Table 1: 90.5% U and 9.5% Ce. The instrument typically performs under an accuracy of 1%; however, as ZAF corrections are developed for infinitely flat polished samples, the effects become more severe in the case of

particles and when the composition is U–Ce. The greater difference in Z (U, 92, versus Ce, 58, and Pu, 94) and greater energy difference in U and Ce X-rays (U, $M_{\alpha} = 3.17$ keV versus Ce, $L_{\alpha} = 4.84$ keV) compared with U–Pu particles (U, $L_{\alpha} = 13.60$ keV versus Pu, $L_{\alpha} = 14.26$ keV) could explain the observed deviation.

The size distribution of U particles obtained from measurements using automatic SEM (Personal SEM) analysis is presented in Figure 2a. The first population, due to one-droplet particles, was found at 1.24 ± 0.12 (2σ) μm . (Stated standard deviations (σ) were obtained for each single droplet peak.) The second population, at 1.60 ± 0.14 (2σ) μm , derived from particles formed by the combination of two droplets and agrees with the theoretically expected value of $(2)^{1/3}$ times the one droplet particle diameter. A third distribution could be expected at $\sim 1.8 \mu\text{m}$ (equivalent to three droplet particles), but this could not be seen, implying that the formation of such particles was rare. A total of 90% of the distribution was found to derive from one droplet particles. The distribution is typical for U particles produced by the system at our laboratory.

For the size distribution for batch U-Pu-242:A, Figure 2b, the main population was positioned at 1.37 ± 0.24 (2σ) μm and the

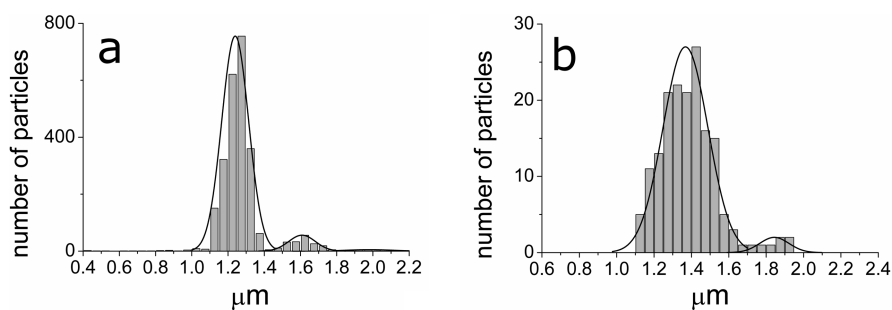


Figure 2. Size distribution with superimposed Gaussian fits for (a) U particles, batch U020-35 (automatic analysis of 2500 particles and (b) U–Pu particles, batch U–Pu-242:A (manual analysis of 170 particles).

second at 1.84 ± 0.12 (2σ) μm . One droplet particles constituted 90% of the distribution here as well. The sizes of the Pu-containing particles were measured using the glovebox SEM setup (Philips XL40), and automated particle size analysis was therefore not available and only a limited amount of size data was acquired. The distribution for a larger sample size is expected to be narrower ($\sigma \propto (n - 1)^{-1/2}$, n = number of measurements), as in the case of the U particles.

Particle Mass. Table 1 summarizes the data used for particle mass calculations and masses obtained. For batches U–Pu-242:A and Pu-242:B, the mass concentration of the starting solution was measured by IDMS-TIMS. The mass in each particle has been measured previously for batch U020-35 using IDMS-TIMS and found to be 2.57 ± 0.17 pg of U,⁵ which is included in Table 1 for comparison. Because of laboratory regulations, a similar procedure to confirm mass calculations could not be applied to the Pu containing batches, as it would have required equipment outside of the restricted area containing Pu handling facilities.

Mass calculations were not performed based on particle size because the efficiency of the calcination process has not been determined, and the density varies considerably with uranium stoichiometry. In addition, the formation process of the particles can vary due to different operating settings, resulting in different interior structures, from solid particles to those containing voids. For example, on the basis of mass values and size measurements, the mass density (of U) in batch U020-35 was 2.6 ± 0.2 g/cm³ per particle, while for batch U–Pu-242:A, the mass density (of U and Pu) was 4.6 ± 0.4 g/cm³ per particle, even though particles from U020-35 had similar sizes to those in other batches. This indicated that the U020-35 particles contained more voids. Their difference in density was due to the lower mass concentration of the solvent mixture used for the production of batch U020-35, generating equal droplet sizes containing less nonvolatile material.

Isotopic Measurements by SIMS. SIMS mass spectra recorded from particles from batches U020-35, U–Pu-242:A, and Pu-242:B are presented in Figure 3, and the isotopic ratios obtained from SIMS and IDMS-TIMS are given in Table 2. Because of the complexity of the SIMS U–Pu mass spectra, which contain unresolved elemental and hydride interference, there was some discrepancy between the SIMS values and the IDMS-TIMS values. The SIMS result for the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio of the U particles agreed well with the certified value of the material used for their production. However, for the U–Pu particles, a negative bias against the IDMS-TIMS values of 3.7% was found, most probably due to interference from ^{238}Pu but could also suggest

a contamination scenario where the bias was due to excess of ^{238}U . However, the latter suggestion is unlikely since memory effects have never been observed in the VOAG instrumentation even when large variations in the U enrichment have been used between different particle productions.¹⁷ The discrepancy for the $^{240}\text{Pu}/^{242}\text{Pu}$ ratio was considered acceptable taking the low recorded ^{240}Pu ion intensities into account. The ^{242}Pu in the Pu spectrum (Figure 3b,c) was considered interference free and was used to study the relative ionization of Pu hydride ions and Pu efficiency (in terms of useful yield) with SIMS, as described below.

Useful Yield and Relative Sensitivity Factor for U and Pu Determined Using SIMS. The results regarding useful yield, determined on single droplet particles of U, Pu, and mixed U–Pu are presented in Table 3. The interference of ^{241}MH on ^{242}Pu and the interference of ^{238}Pu on ^{238}U in the case of mixed U–Pu particles were regarded as insignificant (as observed in SIMS analysis of pure Pu particles, Table 2, 238:242, –4%). The $\text{RSF}_{\text{U:Pu}}$ obtained from mixed particles (2.30 ± 0.09) was consistent with that deduced from individual U and Pu particles (2.54 ± 0.23). $\text{RSF}_{\text{U:Pu}}$ data are few in the literature, but examples are 2.41 for a matrix of pure oxide particles and 2.34 for sulfate particles;²⁶ 2.9 for a Pu–U clay matrix (aluminosilicate);²⁷ and 3.3 for a Pu–clay matrix (aluminosilicate).²⁸ The result obtained in this work agreed with these previously reported values.

The $\text{RSF}_{\text{U:Pu}}$ showed variations with the sputtering time. This effect is displayed in Figure 4 obtained from one useful yield measurement. During the initial stage of the SIMS sputtering, the $\text{RSF}_{\text{U:Pu}}$ increased significantly during a transient region (from a value of 1.9) until reasonably stabilization was reached, and at the end of the analyses the $\text{RSF}_{\text{U:Pu}}$ increased again (to a maximum of 3.4). These effects are not considered in the data given in Table 3, as the RSF has been computed from the total amount of ions collected in the detector versus the total amount of sputtered atoms.

Pu and U Hydride Formation during SIMS Analysis. The $^{238}\text{UH}/^{238}\text{U}$ ratio was estimated to $(8.77 \pm 0.37) \times 10^{-3}$ from the measurements of the mass ratio 239:242 in particles of batch U–Pu-242:A (using an $\text{RSF}_{\text{U:Pu}}$ of 2.4 obtained from Table 3 on the $^{238}\text{U}/^{242}\text{Pu}$). This is slightly higher than the values for PuH/

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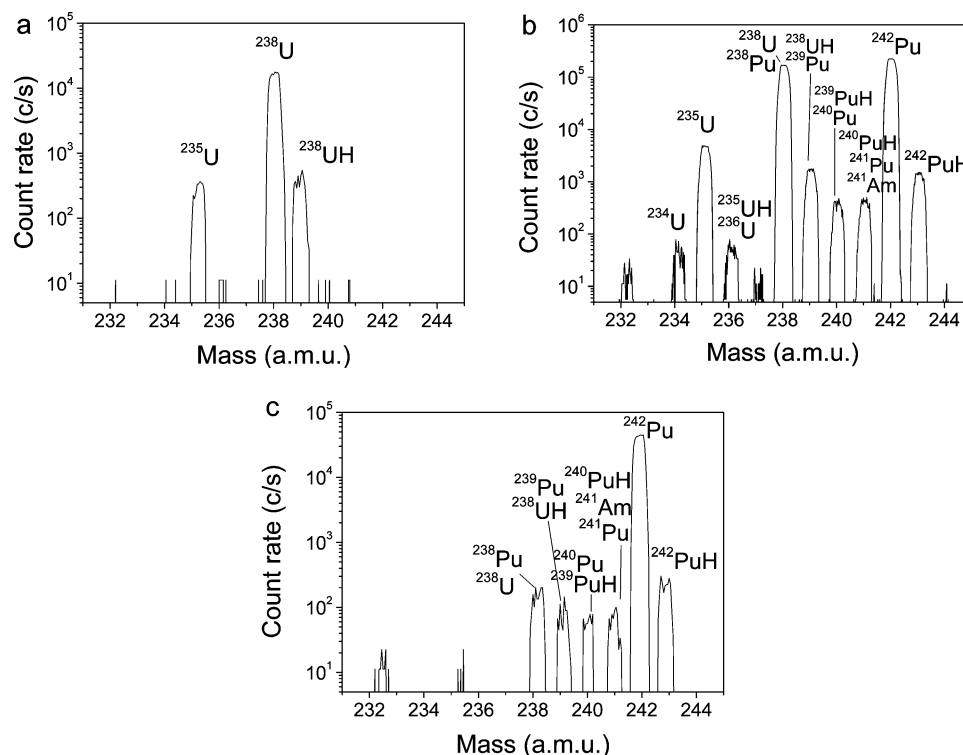


Figure 3. SIMS mass spectra showing the isotopes present in (a) a U particle, batch U020-35, (b) a U–Pu particle, batch U–Pu-242:A, and (c) a Pu particle, batch Pu-242:B.

Table 2. SIMS Isotopic Ratios of U Particles (U020-35),⁵ U–Pu Particles (U–Pu-242:A), and Pu Particles (Pu-242:B), Compared with Values Obtained from IDMS-TIMS Analysis and Certified Values

mass ratio		U020-35 ⁵	U–Pu-242:A	Pu-242:B
235:238	SIMS $^{235}\text{U}/^{238}\text{U}$ certified value relative bias	$(2.0692 \pm 0.0056) \times 10^{-2}$ 2.0687×10^{-2} 0.000 24	$(1.991 \pm 0.030) \times 10^{-2}$ 2.0687×10^{-2} –0.037	
239:238	SIMS $^{239}\text{UH}/^{238}\text{U}$	$(2.046 \pm 0.021) \times 10^{-3}$		
238:242	SIMS $(^{238}\text{U} + ^{238}\text{Pu})/^{242}\text{Pu}$ IDMS-TIMS $^{238}\text{Pu}/^{242}\text{Pu}$ relative bias		$(4.538 \pm 0.098) \times 10^{-1}$ $(4.55 \pm 0.20) \times 10^{-5}$ 10 000	$(4.04 \pm 0.52) \times 10^{-3}$ $(5.06 \pm 0.10) \times 10^{-5}$ 79
239:242	SIMS $(^{239}\text{UH} + ^{239}\text{Pu})/^{242}\text{Pu}$ IDMS-TIMS $^{239}\text{Pu}/^{242}\text{Pu}$ relative bias		$(5.15 \pm 0.16) \times 10^{-3}$ $(1.2478 \pm 0.0034) \times 10^{-3}$ 3.1	$(1.835 \pm 0.030) \times 10^{-3}$ $(1.2390 \pm 0.0031) \times 10^{-3}$ 0.48
240:242	SIMS $(^{239}\text{PuH} + ^{240}\text{Pu})/^{242}\text{Pu}$ IDMS-TIMS $^{240}\text{Pu}/^{242}\text{Pu}$ relative bias		$(1.304 \pm 0.013) \times 10^{-3}$ $(1.2704 \pm 0.0013) \times 10^{-3}$ 0.025	$(1.3312 \pm 0.0093) \times 10^{-3}$ $(1.2835 \pm 0.0038) \times 10^{-3}$ 0.037
241:242	SIMS $(^{240}\text{PuH} + ^{241}\text{Pu} + ^{241}\text{Am})/^{242}\text{Pu}$ IDMS-TIMS $^{241}\text{Pu}/^{242}\text{Pu}$ relative bias		$(1.668 \pm 0.034) \times 10^{-3}$ $(2.653 \pm 0.017) \times 10^{-4}$ 5.3	$(1.73 \pm 0.11) \times 10^{-3}$ $(2.635 \pm 0.038) \times 10^{-4}$ 5.6
243:242	SIMS $^{242}\text{PuH}/^{242}\text{Pu}$		$(7.10 \pm 0.20) \times 10^{-3}$	$(6.53 \pm 0.26) \times 10^{-3}$

Pu for the same batch listed in Table 2 obtained under identical analytical conditions, $(7.10 \pm 0.20) \times 10^{-3}$. Consequently, the U was found to have a higher propensity to form the hydride than Pu. This finding is also in agreement with the observations from an earlier study.²⁷ A $^{238}\text{UH}/^{238}\text{U}$ ratio of $(2.046 \pm 0.021) \times 10^{-3}$ was obtained for the pure U particles in batch U020-35, which is higher than obtained for the previous batch, reflecting the variability of hydride formation under different analytical conditions.

CONCLUSIONS AND FUTURE WORK

A method for the production of standard monodispersed particles containing Pu and U–Pu mixtures has been presented, and the characteristics of the particles produced have been

described regarding morphology and elemental and isotopic compositions. The size distribution showed the presence of two populations, originating from one droplet and two droplet particles produced in the process; however, the dominant population (90%) consisted of one droplet particles. The particle mass was around 6 pg of material between the different batches (except for batch U020-35 which had 2 times less particle mass). Mass quantities were obtained from production parameters and solution concentrations, set by the user, and can be varied for the purpose. For some batches, the solution concentration was measured using IDMS-TIMS to improve the precision in mass estimates.

The elemental composition of the particles agreed with that of the material used for their production, according to SEM-EDX

Table 3. Useful Yield and $RSF_{U:Pu}$ Values Determined on Single-Droplet U and/or Pu Particles (n is the Number of Measurements)^a

particle batch ID	useful yield (%)		$RSF_{U:Pu}$
	Pu	U	
mixed U–Pu	1.71 ± 0.15	0.72 ± 0.06	2.30 ± 0.09
U–Pu-242:A	($n = 10$)	($n = 10$)	($n = 50$)
Pu-242:B	1.65 ± 0.14		2.54 ± 0.23
	($n = 11$)		
U020-35 ⁵		0.65 ± 0.02	
		($n = 14$)	

^a Uncertainties are given as 1 standard deviation of the measurements except for the 2nd RSF value, which is an error propagated uncertainty.

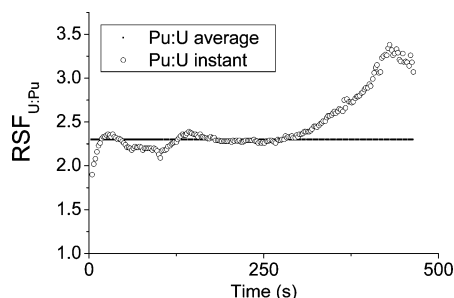


Figure 4. An example of an useful yield measurement displaying the time evolution of the $RSF_{U:Pu}$ compared with the average $RSF_{U:Pu}$ of the complete measurement.

analysis, and a good agreement was found with the original solution used for their production. The isotopic composition was measured by SIMS; however, because of isobaric interference in the U–Pu and Pu spectra, some deviation from the composition of starting material was found. This is not the case for the U particles produced, the composition of which agreed well with the material used for their production. The SIMS measurements described here serve as a starting point, but further studies are recommended for quality assurance to validate the isotopic composition by another instrument, for example, by TIMS. The relative ionization of the hydrides of U and Pu in U–Pu particles was studied using SIMS. Under identical analytical conditions, U showed a slightly higher tendency to form hydrides than Pu. The useful yield and $RSFs$ of U and Pu were determined for the particles using SIMS. The average $RSF_{U:Pu}$ was found to be 2.4 ± 0.2 , which is in good agreement with some previous results.^{26–28} No dependence of the $RSF_{U:Pu}$ on the presence of other elements in the matrix was observed; however, the

$RSF_{U:Pu}$ showed large fluctuations during the sputtering time for the mixed U–Pu particles, in the range of 1.9–3.4.

The results on U and Pu performance during SIMS and SEM-EDX measurements will support the analyses of actual samples containing U and Pu particles, for instance, swipe samples collected at nuclear safeguard inspections or samples from environmental sites contaminated with fissile material. In particular, to study the performance of SIMS when analyzing nuclear swipe samples, it is suggested that the particles be mixed with Pb or Ba. These elements are often present in nuclear swipe samples and cause severe isobaric interference. The introduction of such particles would simulate the “real” case and could contribute to improvements in the measurement techniques.

The particle material described in this study is suitable for quality assurance in safeguard applications where SIMS, SEM-EDX, and TIMS are the routine analysis techniques but may also be useful in other microanalytical techniques for similar purposes, for example, particle induced X-ray spectrometry (PIXE), transmission electron microscopy (TEM), and micro X-ray fluorescence analysis (μ -XRF). A specific advantage of the particle production method lies in the fact that it is possible to vary the isotopic composition and mass content in order to suit the application in question.

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