



Shelf-life of uranium oxide microparticle reference materials and possible implications for the identification of optimal storage conditions

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Abstract

During their inspections of nuclear facilities, inspectors of the International Atomic Energy Agency (IAEA) collect environmental swipe samples containing uranium dust particles. As reference materials, well-characterized uranium microparticles are required that are suitable for quality control, analytical refinement and method development tasks. At Forschungszentrum Jülich (FZJ), uranium oxide reference microparticles are produced using an aerosol-based process. A core requirement for distribution of a potential reference material is to guarantee a practical shelf-life. Previous studies of structure and shape of uranium oxide microparticles demonstrated possible alteration leading to the formation of uranium hydroxides such as schoepite. A systematic shelf-life study exploring storage under different environmental conditions was launched in late 2021. Uranium microparticles were stored in three environments simulating potential long-term storage conditions, whereas a fourth experiment used an unrealistically harsh environment to assess the effects of accelerated alteration. At the time of writing, only the uranium microparticles intentionally stored under these extreme conditions have shown significant signs of alteration. This implies that synthetic uranium oxide microparticles under common storage conditions have minimal shelf-lives of at least 1 year, and likely much longer.

Introduction

One of the IAEA's main tasks is the verification of solely peaceful use of nuclear materials in member states that have subscribed to a monitoring program in agreement with IAEA. Therefore, IAEA implemented numerous measures—the IAEA safeguards—to ensure the peaceful use of nuclear materials. Among other safeguards measures, the analysis of microparticulate environmental dust samples collected by IAEA inspectors during on-site inspections provides the IAEA with valuable information for its task. Using modern Large Geometry-Secondary Ion Mass Spectrometry (LG-SIMS) analysis techniques, isotopic and elemental

compositions of single particles with a size of $\sim 1 \mu\text{m}$ can be determined by the IAEA Safeguards Analytical Service-Environmental Sampling Laboratory (SGAS-ESL) and its worldwide partners in the Network of Analytical Laboratories (NWAL) [1]. To conduct these measurements in acceptable quality, the analyzing laboratories must be provided with suitable reference materials (RMs) in microparticulate form. The IAEA listed some specifications such as adjustable isotopic composition for Nuclear Forensics purposes, monodisperse size distribution for analysis technique development and sample-to-sample homogeneity. Further information can be found in Inn et al. [2].

The safeguards laboratories of FZJ developed an aerosol-based process to produce well-defined uranium microparticles using a Vibrating Orifice Aerosol Generator (VOAG) [3]. These microparticles were characterized as U_3O_8 -particles with a spherical diameter of $\sim 1\text{--}1.2 \mu\text{m}$ [4]. In 2020, FZJ's safeguards laboratories were certified as first particle-providing laboratory in the NWAL. To this day, two particle production batches (IRMM-2329P and IRMM-2331P) [5] were certified as reference materials and new batches are currently requested by the IAEA.

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An essential requirement for a potential microparticle reference material—among certified isotopic and elemental compositions and well-characterized particle size and morphology—is structural and chemical stability over the intended duration of use. Kegler et al. [6] and Potts et al. [7] reported evidence of surficial alteration of VOAG-produced uranium oxide particles stored under different storage conditions (atmospheric and alcoholic environment, respectively) leading to the surficial formation of uranium hydroxides such as schoepite or (meta-)studtite. While the oxidation state of U in pure uranium hydroxide is + VI, the U in the particles was described as a mixture of + IV, + V, and + VI [6]. However, they mention that this alteration process is not consistent for the entirety of the particles and highly depends on the age. Particles stored 4–10 months in laboratory air were characterized as U_3O_8 , while Raman spectra of particles stored for 2 years pointed towards the formation of an additional, hydrated secondary phase, in this case schoepite. This indicates that the presence of water plays a key role in particle alteration. This alteration may affect the reliability of LG-SIMS microparticle analysis. One approach to mitigate alteration is storage under controlled, structure-preserving atmospheric conditions. To identify these conditions, uranium microparticles stored in different conditions were systematically investigated in a time-series experiment.

Materials and methods

Uranium microparticle production

In the aerosol-based particle production process as used at FZJ, a uranyl nitrate solution with known and certified uranium isotopic composition is fed into the VOAG (Model 3450, TSI Inc., USA) with a defined and stable volume flow. On top of the VOAG, a silicon orifice is vibrating with an adjustable frequency creating monodisperse droplets out of the liquid jet. The concentration of the feeding solution, the feeding rate and the vibration frequency determine the average size of the particles. The droplets pass through a drying column and subsequently an aerosol heater at 500 °C where they decompose to uranium oxide microparticles. Thereupon the particles are cooled down and deposited on substrates such as glass-like carbon disks (GCDs) or Si-wafers placed in a vacuum impactor. To achieve a more homogeneous particle distribution on the substrate, the particles can be transferred into an ethanol suspension and then re-dispersed onto a sample planchet. Additional information about particle production can be found in Neumeier et al. [3] and Middendorp et al. [4].

Particle storage conditions for shelf-life implications

The particles used for this shelf-life study were produced with a feeding solution containing NBL CRM 129-A, a certified reference material resembling natural uranium. Four GCD sample planchets were prepared using an additional suspension step with ethanol as suspension media according to Potts et al. [7]. Considering the anticipated influence of water on alteration, the particle planchets were stored under three conditions that minimize exposure to H_2O and that can be practically implemented for long-term storage: (1) laboratory air with silica gel as desiccant, (2) laboratory air with silica gel at 90 °C, (3) commercial argon with silica gel. An additional planchet with particles was stored in a water-saturated atmosphere for comparison. Table 1 summarizes the storage conditions for the four particle planchets.

Particle analysis techniques

After certain intervals, planchets were removed from their respective storage conditions and measured using SEM, μ -Raman spectroscopy and LG-SIMS. During these analyses, the planchets were intermittently stored in a desiccator with silica gel, the counting of storage time was stopped until all measurements were completed, and the respective storage conditions were re-applied. An accelerated sample alteration by repeatedly removing samples from their storage conditions, applying vacuum for the analyses and returning them to their respective conditions cannot be excluded. However, considering the intended use as reference materials for analytical techniques such as LG-SIMS, intermittent transfer into vacuum conditions is a realistic scenario possibly influencing the particles' shelf-life.

SEM images were created using a JEOL FEG-SEM JSM-IT800 at $\sim 2 \times 10^{-4}$ Pa detecting secondary electrons for a 10–15 kV beam. The used high voltage (HV) is necessary because uranium oxide particles are poor conductors when not coated in carbon or gold. Higher HV will lead to sample charging and therefore imaging artifacts, while lower HV will reduce lateral resolution.

Structural investigations regarding the uranium microparticles were carried out with a WITec alpha 300R μ -Raman spectroscope. Single particles were analyzed with a 532 nm

Table 1 Particle planchets stored under different storage conditions

| Condition | Atmosphere | Desiccant | Temperature |
|-----------|-------------------|------------|------------------|
| 1 | Laboratory air | Silica gel | Room temperature |
| 2 | Argon | Silica gel | Room temperature |
| 3 | Laboratory air | Silica gel | 90 °C |
| 4 | H_2O -saturated | – | Room temperature |

laser and a grating of 1200 grooves/mm. The measuring duration was 60 s with a 1 mW laser power. Analysis time and laser power were carefully adjusted to mitigate particle dehydration and potential re-formation of uranium oxides.

The U isotopic composition of single particles was determined using LG-SIMS at the Heidelberg Ion Probe facility with a CAMECA ims 1280-HR. The current measurement setup is based on the suggestions of a dynamic multi-collection mode by Hedberg et al. [8] ^{234}U , ^{235}U , ^{236}U , ^{238}U and $^{238}\text{U}^1\text{H}$ are counted simultaneously on electron multipliers (EMs) with an intermediate step to determine the detector yield between the two EMs for ^{235}U and ^{238}U . The data evaluation is based on the IAEA SGAS-ESL protocol for SIMS measurements of environmental samples.

Results and discussion

Particles in this ongoing study were analyzed after 30, 117 and 218 days of storage time. Freshly produced uranium oxide particles are characterized as well-rounded with a diameter of $\sim 1.2\ \mu\text{m}$ [3, 4, 6]. Their main component is U_3O_8 .

SEM images after 30 days of storage time are indistinguishable for all storage conditions with particles retaining their original shape. However, the test sample intentionally exposed to a water-saturated atmosphere shows first evidence of alteration in the form of surface roughening. After 117 days, particles from the three practical long-term storage conditions are still well-rounded and resemble freshly produced particles. However, the particles from

the water-saturated atmosphere show additional signs of alteration that become even more evident after 218 days of storage. Particles stored in laboratory air (Fig. 1a), argon atmosphere (Fig. 1b) and laboratory air at $90\ ^\circ\text{C}$ (Fig. 1c) remain in their original shape with a smooth surface with no evidence for alteration after 218 days of storage. However, the particles in a water-saturated atmosphere significantly differ from their initial form (Fig. 1d). Although still observable, the originally spherical shape of the particle is now obscured by a microcrystalline secondary phase on the particle's surface. The formation of this layer of columnar crystallites appears to be a result of the dehydration of a surficial hydrated phase that takes place when high vacuum is applied to the sample. Therefore, the observed crystal shape is an artifact enhancing the visibility of alteration layer. Consequently, the aggregates of particle and surficial secondary crystallite phase have increased in size and volume compared to the particles from the other three storage conditions.

Raman spectra after 30 days of storage are indistinguishable for particles stored in room-temperature laboratory air (Fig. 2a), argon atmosphere (Fig. 2b) and in laboratory air at $90\ ^\circ\text{C}$ (Fig. 2c). Although the intensity of the single Raman bands varies between the different storage conditions, the same effect can be observed between particles on the same sample planchet and is therefore independent of different storage conditions. The spectra for storage conditions 1–3 verify the presence of U_3O_8 as indicated by the triplet between 300 and $500\ \text{cm}^{-1}$, and peaks at $\sim 240\ \text{cm}^{-1}$ and $\sim 750\ \text{cm}^{-1}$ [9]. However, there is also evidence for the presence of UO_3 indicated by the strong band at $\sim 767\ \text{cm}^{-1}$ [10, 11] and the absence of a band at $\sim 800\ \text{cm}^{-1}$ that would

Fig. 1 Representative SEM images of particles stored for 218 days in laboratory air (a), argon (b), laboratory air at $90\ ^\circ\text{C}$ (c) and in H_2O -saturated atmosphere (d)

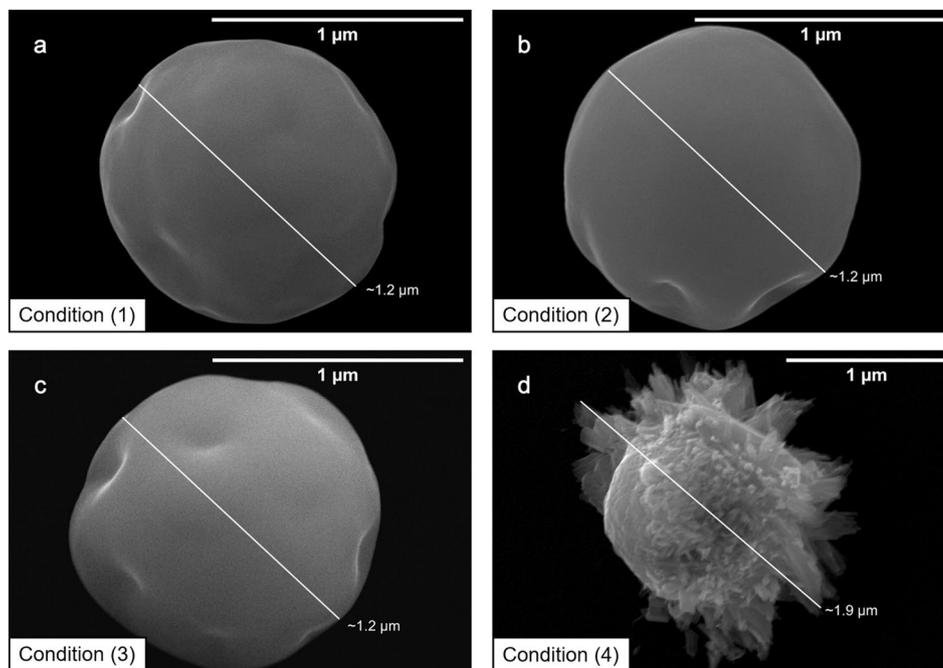
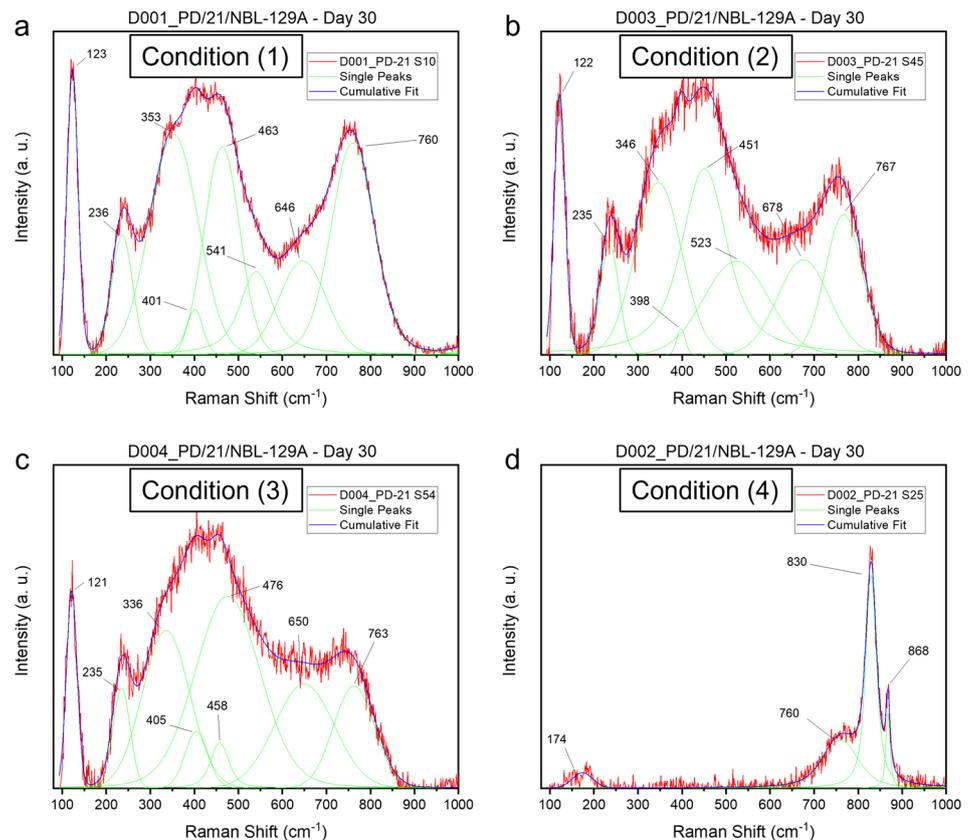


Fig. 2 Raman spectra of particles stored for 30 days in laboratory air (a), argon (b), laboratory air at 90 °C (c) and in H₂O-saturated atmosphere



be typical for U₃O₈. There is also the possibility of the presence of a minor U₄O₉ phase, indicated by the broad band between 640 and 670 cm⁻¹ [12]. Regardless, Raman spectra of uranium oxides are very complex and there may be additional bands that could be assigned to U₃O₈ [9]. In contrast to the particles investigated by Kegler et al. [6], there is no strong Raman band at ~830–840 cm⁻¹, indicating the absence of uranium hydroxides in the particles stored under conditions 1–3 [11, 13].

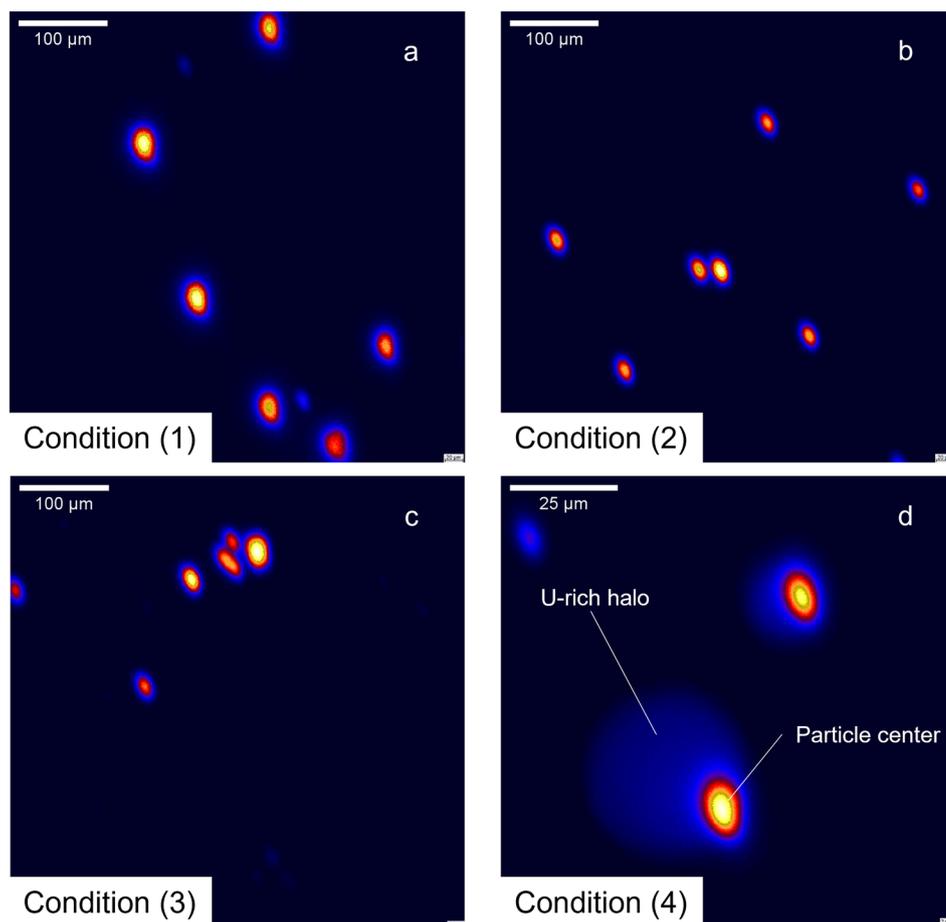
The Raman spectrum of microparticles stored in a water-saturated atmosphere (Fig. 1d) is clearly different from the other ones. Even after 30 days of storage, the particle's surface underwent a phase transition, which is consistent with the observed increase in surface roughness of the particles. Although the formation of schoepite with a typical single Raman band at ~840–845 cm⁻¹ was expected, the significant two Raman bands at ~830 cm⁻¹ (U–O vibration) and ~868 cm⁻¹ (O–O vibration) point towards the formation of (meta-)studtite, a form of uranyl hydroperoxide [14–17].

Further Raman measurements after 117 and 218 days of storage time confirmed the results obtained after 30 days. The spectra of particles from storage conditions 1–3 point towards complex uranium oxide phases but lack any evidence for the formation of uranium hydroxide or uranium hydroperoxide. Over the same duration, particles stored under condition 4 yielded Raman spectra confirming the

surfacial formation of (meta-)studtite. It remains to be examined, why the alteration—in contrast to the observations made in previous studies [6]—leads to the formation of (meta-)studtite instead of schoepite.

Complementary to SEM and μ -Raman analyses, the particles were measured after the same 30, 117 and 218 days of storage by LG-SIMS. Particles were located using the ion microscope mode for ²³⁸U intensities with a raster of 500 × 500 μ m. After 30 days, all particles displayed sharp boundaries in the ion images, independent of storage conditions. When looking at the sample planchets after 117 days of storage time, the single particles stored in air (Fig. 3a), argon (Fig. 3b) and air at 90 °C (Fig. 3c) looked similar with clearly separated particles with sharp particle boundaries. However, ²³⁸U ion images of some of the particles stored under H₂O-saturated conditions started to display a U-rich halo, but the particle center typically remains intact (Fig. 3d). These observations were confirmed in ion images taken after 218 days of storage. Particles stored in conditions 1–3 are clearly separated, whereas uranium migration intensified for the altered particles with more particles displaying uranium halos. The formation of the uranium halo makes the particles harder to locate in ion imaging and sometimes requires a pre-sputtering of the sample surface to remove the undesired, diffuse ²³⁸U signal.

Fig. 3 ^{238}U ion images of particles stored for 117 days in laboratory air (a), argon (b), laboratory air at 90 °C (c) and in H_2O -saturated atmosphere (d)



During each SIMS measurement, a randomly chosen population of microparticles for each storage condition was measured for their uranium isotopic compositions. The results were compared to the literature values for CRM NBL 129-A. For all storage conditions, the uranium isotopic composition remained invariant up to 117 days. After 218 days of storage, minor, mass-independent deviations were detected for some particles stored under water-saturated conditions, whereas particles stored under conditions 1–3 (Table 1) match the starting composition. However, this infrequently occurring isotopic deviation is statistically insignificant and cannot be reliably quantified at this point. Future measurements after longer storage are anticipated to further explore this behavior.

Conclusions

The shelf-life of uranium oxide microparticles depends heavily on storage conditions. The presence of water triggers formation of uranyl hydroperoxides, even after a relative short duration of 30 days. Additionally, surficial particle alteration can be observed, where clearly visible changes in

the physical form of the particles compared to their original shape are recognized. Reliable SIMS measurements can still be performed, even if lateral migration of uranium occurred upon alteration. However, continued exposure to a water-saturated atmosphere could eventually make the uranium microparticles impracticable as a reference material due to extensive spread of the uranium halos until they cover most of the sample planchet, thus preventing reliable analysis of individual particles. Moreover, isotopic fractionation caused by either alteration or ion beam pre-sputtering remains to be investigated. Brief exposure to water-saturated atmospheres is of no concern for the particles' viability as a reference material. Three easily implemented storage conditions under which particles remained stable for at least 1 year are devised here. It remains to be seen by future measurements if these storage conditions are also suitable for multi-year storage. In conclusion, storage in an inert and water-free environment is strongly recommended.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interests.

Research involving human and animal participants Within this work no experiments on human and animal subjects are reported.

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