Micro Particle Suspensions for Preparation of Reference Materials for Particle Analysis Methods in Safeguards

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Abstract:

In order to produce micro particle reference materials for nuclear safeguards particle analysis, a dedicated facility has been established at Forschungszentrum Jülich. This includes an aerosol-based particle production setup which is capable of producing uranium micro particles with consistent isotopic compositions and uranium contents. While the produced particles could be used as reference materials as obtained after production, further options for packaging the particles are being considered to simplify handling of the particles and to open new possibilities, such as the preparation of particle mixtures.

The transfer of the collected particles into a suspension has several advantages. For example, particles in suspension stored in a bottle would be amenable to extraction of an aliquot, which could be dried on a substrate of interest, such as silicon wafers, glass-like carbon disks or cotton-swipes, to obtain test samples. Also, various suspensions could be mixed in different ratios followed by drying on the desired substrates to obtained particle mixtures of two or more different particle types. However, while the particles are dispersed in suspension, various reactions could have an influence on the stability of the micro particle property values. In order to assess the stability of uranium micro particles in a suspension, experiments have been conducted using synthetic powders and uranium micro particles. Our results from dissolution and uranium isotope exchange studies show that ethanol is a suitable medium for the storage of particles over a period of a few months. Using particles produced with the particle production setup at Forschungszentrum Jülich, particle suspensions have been produced by transfer of collected particles into ethanol and distribution on silicon wafers and cotton-swipes produced consistent results. It was demonstrated that the production of particle mixtures is feasible. It was also shown that particles in suspension could represent a suitable packaging for a particle reference material which permits a quick and flexible preparation of various types of test samples.

Keywords: Particle Analysis; Environmental Sampling; Reference Material; NWAL; Suspensions

1. Introduction

The destructive analysis of samples collected during inspections of nuclear facilities is one of the verification measures applied by the International Atomic Energy Agency (IAEA) to derive safeguards conclusions. One of the employed methods is particle analysis, which is based on the release of small amounts of microparticulate matter during all material handling processes. Such particles are collected via swipe samples taken during inspections of the nuclear facilities. The collected samples are sent to the IAEA Network of Analytical Laboratories (NWAL) for analysis, which is typically performed using high accuracy micro-analytical tools, such as large geometry – secondary ion mass spectrometry (LG-SIMS). These methods are capable of measuring the isotopic composition of single microparticles. The measured isotopic composition of individual microparticles could act as a tool to detect undeclared activities in the inspected facility.

Over recent years, great progress was achieved in the improvement of the measurement accuracy of the isotopic composition of fissile nuclides within micrometer sized particles [1]. The analysis of individual particles has progressed beyond the analysis of the major isotopes (e.g. ^{235}U and ^{238}U) towards the minor isotopes (e.g. ^{234}U and ^{236}U) which provide additional information, e.g. on the facility operations history.

Due to the improved measurement accuracy, quality assurance (QA) has become more stringent and members of the IAEA's NWAL need to fulfill a set of criteria set by the IAEA. Generally, the QA require various quality control (QC) measurements to be performed for the analytical method [2]:

1) Calibration;
2) Validation;
3) Quality control;
4) Proficiency testing.

Each of these measures requires a dedicated test material of high homogeneity and stability, which are generally described as reference materials (RMs) [3]. For calibration and validation, not only the stability and homogeneity of

the material is of importance, the material is also characterized with respect to one or more property values to quantify the *true* value; i.e. the absolute value of the property with given uncertainty and traceability. Such materials are classified as certified reference materials (CRMs) and have strict requirements, as described in ISO 17034 [4].

Various attempts were undertaken to produce micrometer sized particles containing uranium and/or plutonium with well-defined isotopic compositions [5-10]. Over recent years, a setup has been established at Forschungszentrum Jülich [11-13] to produce micrometer sized uranium oxide microspheres, which are intended to be used for the various quality control measurements and are to be certified as CRM (in cooperation with EC-JRC) with respect to the uranium isotopic composition and uranium elemental content. The setup consists of an aerosol generator, after which the aerosol droplets are carried through an aerosol heater in which spherical particles are formed with a homogeneous size and shape. The obtained particles have been investigated in detail [13] and were shown to consist of triuranium octoxide (U_3O_8).

At present, the produced microparticles are collected using single-stage inertial impactors, which allow for the production of ca. 50 samples within a single run. The usage of such impactors does, however, have a number of limitations; the number of particles collected may differ between various production runs, the particles are deposited unevenly over the substrate and the production of particles mixtures under controlled conditions is not easily possible. Also, some applications require the production of more than 50 samples, which would require production of particles over multiple batches/days, which could lead to an expanded between-sample inhomogeneity.

This paper describes a method to transfer collected particles into particle suspensions. Such particle suspensions could then be mixed with similar suspensions containing different types of particles, for example different isotopic composition, which could then be distributed and dried over various substrates to prepare the final test samples. However, while in suspension, interaction of the particles with the solution could alter the properties of the particles. Therefore, a number of investigations were performed to determine whether and to what extend such interactions occur.

2. Particle Production at Forschungszentrum Jülich

The production of monodisperse uranium oxide microspheres with a nominal diameter around 1 µm at Forschungszentrum Jülich has been described elsewhere in detail [13]. The production is based on the formation of an aerosol from a dilute uranyl nitrate solution with the desired isotopic composition. The usage of uranyl nitrate was found to yield particles with minimal preparation [13], which would minimize the risk of cross-contamination. The diluted solution is fed using a syringe pump through a vibrating orifice aerosol generator, where a monodisperse aerosol is formed. The volume of a single droplet can be calculated by dividing the volume flow rate Q by the oscillating frequency f applied to the generator. When the uranium content w and the density ρ of the feed solution are known, the amount of uranium contained in a single droplet m can be calculated by multiplication of the droplet volume with the content and density.

The formed droplets are then guided with an air flow through an aerosol heater set to 500 °C; at 500 °C particles were found to be fully decomposed into uranium oxide whereas a further increase of the temperature causes the particles to deform, and a lower degree of monodispersity was obtained [13]. After cooling, the particles are collected using single-stage inertial impactors [14] onto glass-like carbon substrates. The collected particles were investigated by µ-X-ray diffraction (µ-XRD), µ-X-ray absorption near-edge structure (µ-XANES) and µ-Raman spectroscopy to identify the obtained chemical phase, all of these techniques resulted in an orthorhombic triuranium octoxide (U_3O_8) phase [13].

By using the single-stage inertial impactor, the produced particles can be collected on glass-like carbon substrates which, in turn, can be analyzed by SIMS without further handling, minimizing the risk of introducing any cross-contaminations. The usage of the inertial impactor does, however, cause a non-uniform deposition pattern of the particles on the substrate. An area with a diameter of 12 mm is deposited with particles where the particle loading density increases towards the outer rim of this deposition area and only few particles can be found at the center of the substrate (Figure 1).

The number of particles collected can be controlled in a limited manner by varying the particle collection time; with an increasing collection time, the total number of particles increases. However, due to the intricacies of aerosol transport, the particle concentration of the air flow through the impactors may vary between different production runs and even between collections within a single production run.

3. Particle Suspensions

The previously described problems with a single-stage inertial impactor can be overcome by using a suspension. When particles are dispersed in a solution, aliquots of this suspension can be distributed for analysis, where each aliquot contains approximately the same number of particles. Such suspensions also increase the maximum number of samples which can be produced during a single batch. During normal operation, the number of samples which can be collected is limited by the liquid feed input reservoir, and is sufficient for approximately 50 samples. Once the reservoir is empty, the system needs to be

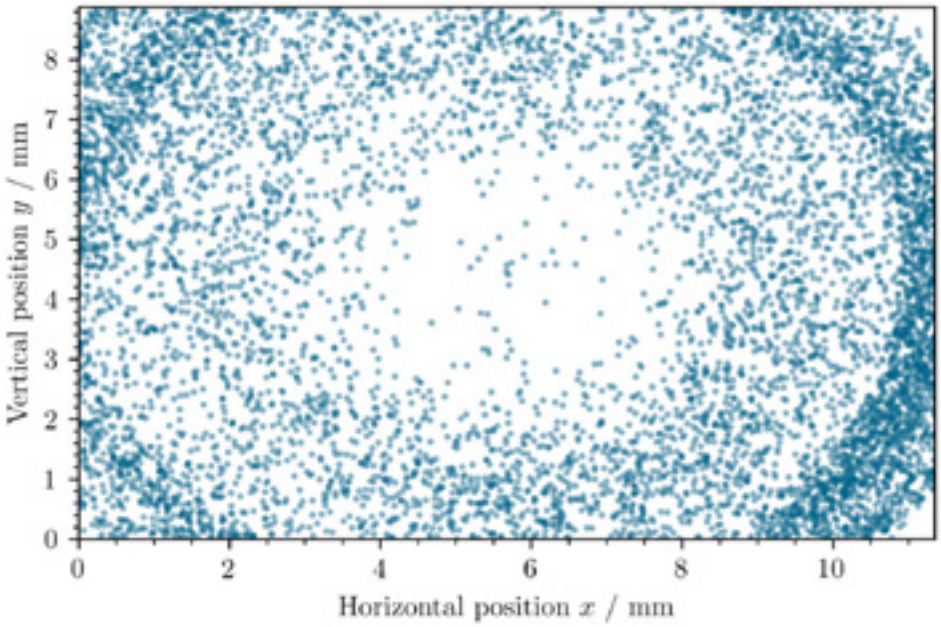

Figure 1: Spatial particle distribution of microparticles collected on a glass-like carbon disk using a single-stage inertial impactor, obtained from low-magnification SEM scans.

interrupted to refill the reservoir before continuing. The particles properties between two such runs could therefore be different. Although similar limitations would be present when using suspensions, particles collected during multiple production runs could be homogenized, eliminating the between-sample inhomogeneity.

Particle suspensions could be produced by two methods; either the particles can be collected in a suspension directly or particles are collected using an inertial impactor and are subsequently transferred into a suspension. The former method has proven to be unsuccessful as the air flow causes evaporation of the solvent during longer operation. Therefore, particles are collected using the single-stage impactors, typically onto silicon wafers due to the high degree of cleanliness and affordability. The silicon wafers can then be placed into a vessel filled with the selected medium and placed in an ultrasonic bath for a few minutes. The ultrasonic bath causes the detachment of particles from the surface into the medium, after which the silicon wafer can be removed.

The selection of the liquid medium has proven to be a critical factor in the production of particle suspensions. The medium should:

1. Be of high purity to prevent significant cross-contaminations,
2. Not cause dissolution of particles within the required processing time,
3. Be suitable to detach the particles from the substrate and,
4. Not cause agglomeration of particles.

Previous investigations [15] have shown that ethanol is most suitable as liquid medium, as water and dimethyl formamide cause dissolution of the particles, n-hexane and n-decane prevent the detachment of particles from the substrate and 2-propanol causes increased agglomeration of particles.

In order to demonstrate the suitability of particle suspensions using ethanol as liquid medium, particles produced during the same run as the particles shown in Figure 1 were transferred into ethanol and were subsequently dried onto a glass-like carbon substrate. The temperature at which the samples were dried proven to be a critical parameter, as with an increasing temperature agglomeration of particles was observed. The prepared samples were therefore placed in a glass Petri dish onto a heating plate set to 50 °C, the actual temperature at the surface of the substrate is, however, unknown. The prepared substrate was investigated by scanning electron microscopy (SEM), the obtained particle distribution is shown in Figure 2. The figure shows a much higher uniformity compared to Figure 1 and shows the value of homogenizing the particles using a suspension. Although not yet quantified, the homogeneity between samples is also expected to be much higher compared to the direct collection.

The prepared suspension also opens a number of new possibilities, such as the production of mixtures containing various types of particles. In order to demonstrate the possibility to produce particle mixtures, cerium particles were produced, which were subsequently transferred into an ethanol suspension. Cerium particles were generated as surrogate for uranium particles, due to the relative comparable chemistry of both elements and the simplified

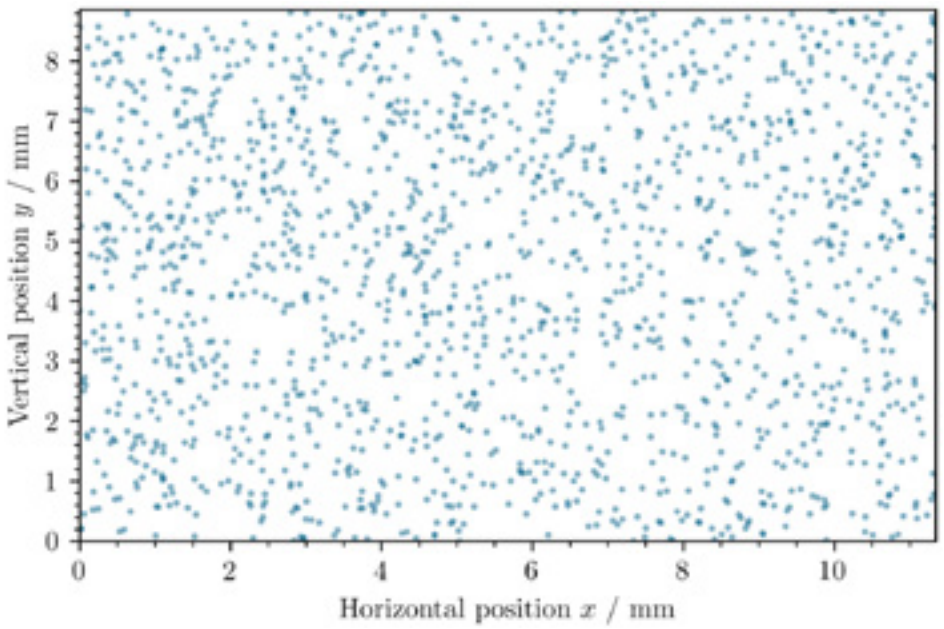

Figure 2: Spatial particle distribution of microparticles deposited on a glass-like carbon disk using an ethanol suspension, obtained from low-magnification SEM micrographs.

distinction between uranium and cerium (e.g. by SEM/EDX) compared to the distinction of uranium particles with different isotopic compositions. The cerium particle suspension was mixed with a uranium suspension, where the produced mixture was dried on a silicon wafer. The obtained wafer was then investigated by SEM/energy-dispersive X-ray spectroscopic (EDX) analysis where EDX spot measurements were performed on each identified particle to distinguish between uranium and cerium. Figure 3 shows collected EDX spectra of 12 randomly selected particles. The spectra show clear lines for either cerium (between 4.5 and 6 keV) or uranium (between 3.0 and 3.5 keV), no spectra containing both uranium and cerium were found. Of the 533 particles, 21 were identified as uranium particles and 509 were identified as cerium particles. A second sample prepared, to which less cerium suspension was added, showed a decrease of the relative amount of cerium particles in line with the first suspension, demonstrating that specific mixtures of particles could be produced, although the particle count of the initial suspensions need to be quantified before mixing.

The prepared suspensions also expand the possibilities to prepare different substrates. When using the inertial impactor, only solid, flat substrates can be used, whereas the suspensions could be distributed over any type of substrate as long

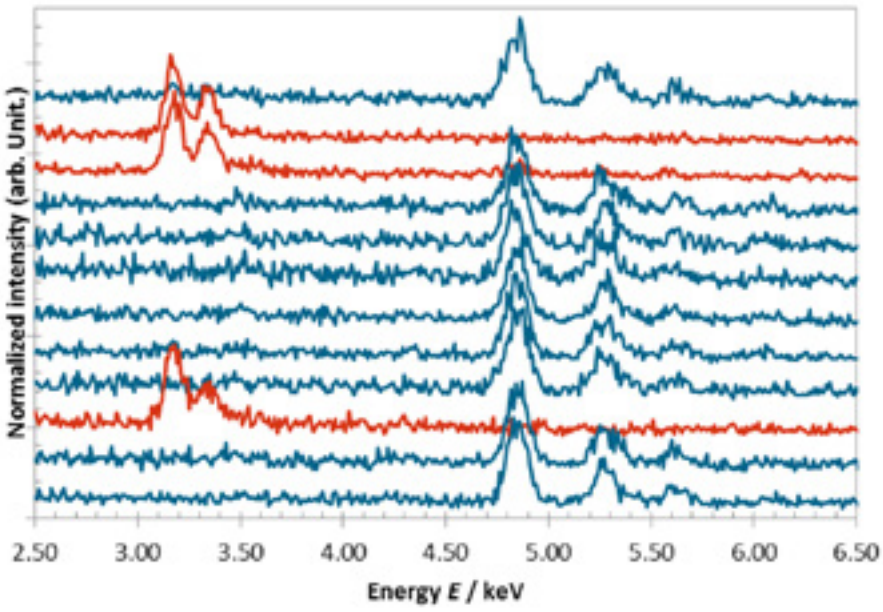

Figure 3: Measured EDX spectra of 12 randomly selected particles in a uranium/cerium mixture.

as the medium (ethanol) does not interact with the substrate. One such substrate would be cotton swipes, which are normally used to collect particles during inspections. To demonstrate the suitability of particle suspensions to prepare particle samples on such cotton swipes, an aliquot of the uranium/cerium mixture was dried on a small piece of cotton swipe. SEM/EDX analysis was complicated by the degradation of the swipe by the electron beam, though both uranium and cerium particles could be identified. One of the collected SEM micrographs is shown in Figure 4, in which uranium particles are marked by a yellow circle and cerium particles with a red circle. The SEM/EDX studies show the possibility to deposit microparticles onto substrates which could not be used with the inertial impactors, and open new possibilities for method optimization and quality control measurements in nuclear safeguards particle analysis.

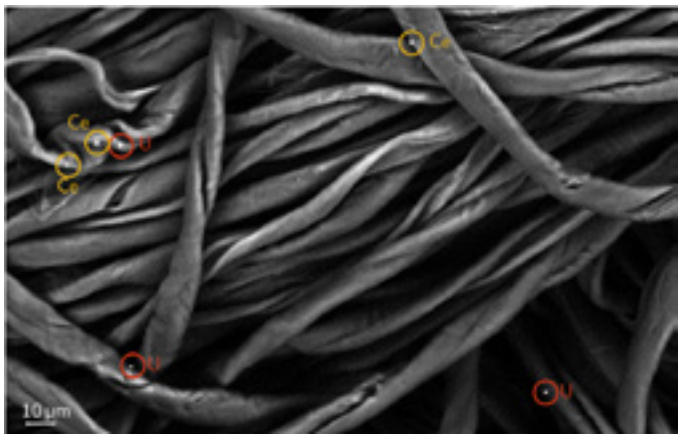

Figure 4: SEM micrographs of uranium (red) and cerium (yellow) particles transferred onto a cotton swipe from an ethanol particle suspension.

4. Stability of Particles in Suspensions

Although the previous section has shown the suitability of using particle suspensions as processing step and has shown some new possibilities with such suspensions, the suspensions could also have a negative impact on particle property values. The produced particles are intended to be certified as a reference material for both uranium isotopic composition and uranium content. Such certification does, however, not only require the property values to be quantified, but also required the determination of the expanded uncertainty, including contributions to the combined uncertainty of the assigned reference value stemming from the assessment of homogeneity and stability. During the storage of particles in a suspension, a number of effects could have an influence on the property values and/or the uncertainty of these values. For example, dissolution would decrease the uranium content, and exchange of uranium isotopes between particles and traces of natural uranium in the liquid medium would alter the composition. In order to assess these effects, various studies were undertaken.

The dissolution of particles was studied by storage of particles in an ethanol suspension for 365 days. After storage, an aliquot of the suspension was dried on a silicon wafer which was investigated by SEM. Figure 5 shows a collected micrograph of a particle compared with a micrograph collected of the sample before transfer into the suspension. Although the brightness/contrast differs slightly due to different SEM settings, no alteration of the particle could be observed. In contrast, strong signs of dissolution were observed for particles stored in water for only 16 days [15].

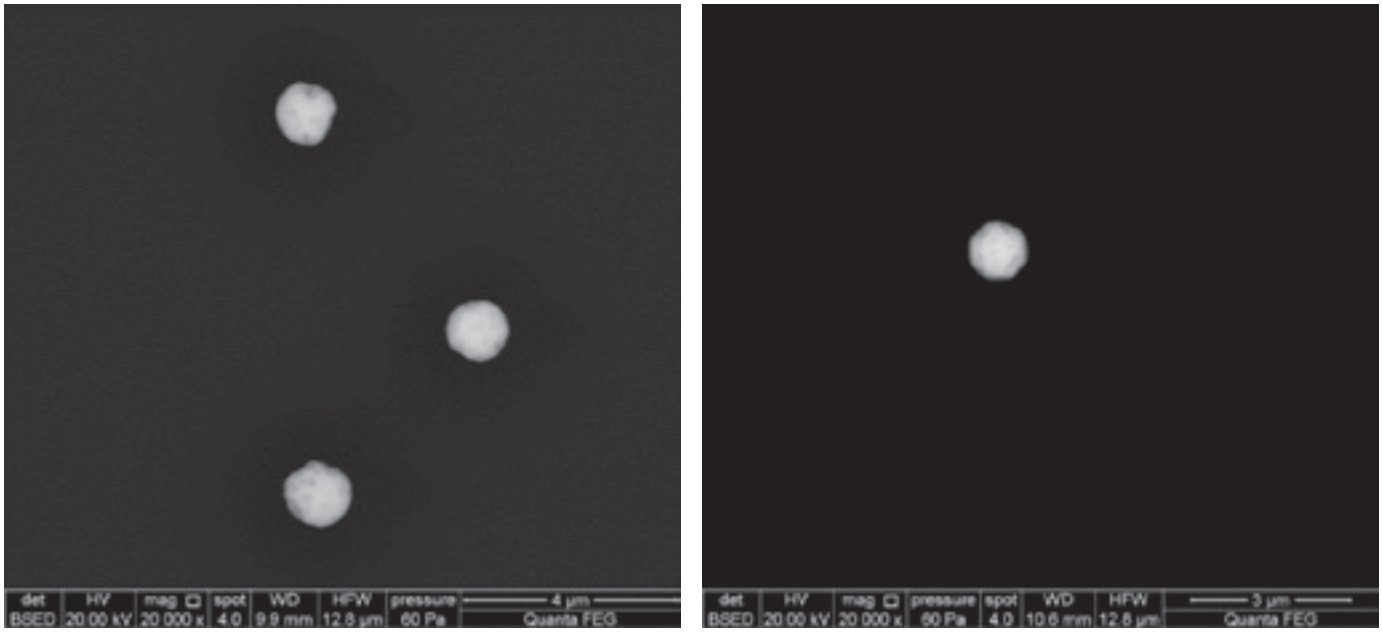

Figure 5: Microparticles (a) before and (b) after storage in ethanol for 365 days.

A second effect which might be of significance to the produced particle property values is isotope exchange. When a particle suspension is prepared consisting of two or more particle populations with different isotopic compositions, exchange of uranium between particles could alter the isotopic composition of the particles. Although no information on such exchange is currently available, Johnston et al. [16] measured the exchange of oxygen between water and various uranium oxides, including U_3O_8. In order to assess whether such exchange occurs between particles, particles consisting of depleted uranium (DU) and low-enriched uranium (LEU) were produced and subsequently transferred into suspensions. The suspensions were distributed over a number of clean silicon wafers. One wafer containing DU particles and a wafer containing LEU particles were transferred into a vial to which ethanol was added. The sample was stored for a given time, after which both wafers were removed and the uranium oxide particles separately dissolved in HNO_3 for quadruple–inductively coupled plasma–mass spectrometric (Q-ICP-MS) analysis. The particles were not suspended and remained separately attached to the respective silicon wafers during the extent of the studies. A schematic overview of the experimental setup is shown in Figure 6.

The experiment aims to investigate the stability of the isotopic composition of particle mixtures stored in ethanol. Two distinct effects could occur; exchange between particles and traces of natural uranium (NU) in the medium or exchange of uranium between particles. Figure 7 shows the measured isotope ratio of both the DU and LEU particles after storage for up to 202 days, neither of which show any significant change of the isotopic composition. Therefore, it can be concluded that no exchange occurs within the investigated timeframe.

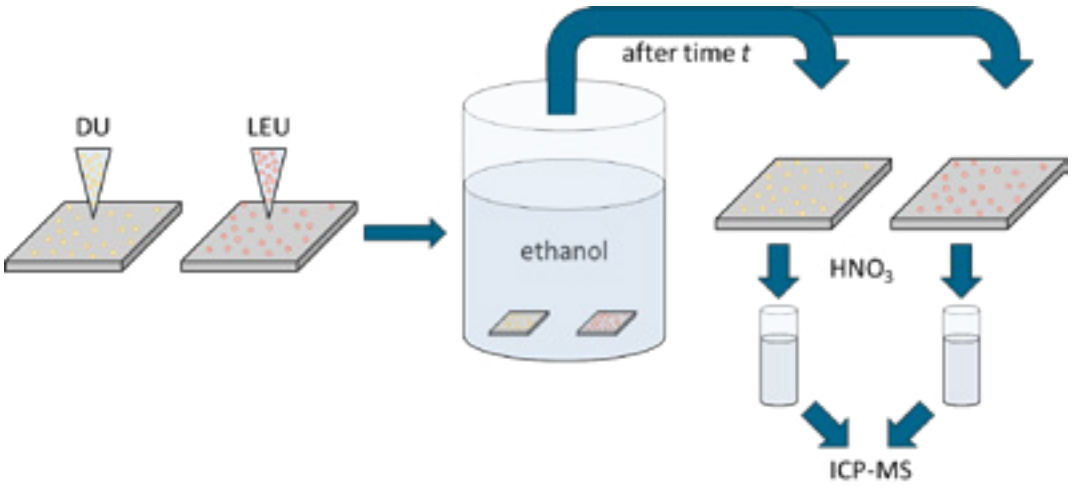

Figure 6: Schematic procedure to investigate the exchange of uranium between particles stored in an ethanol suspension.

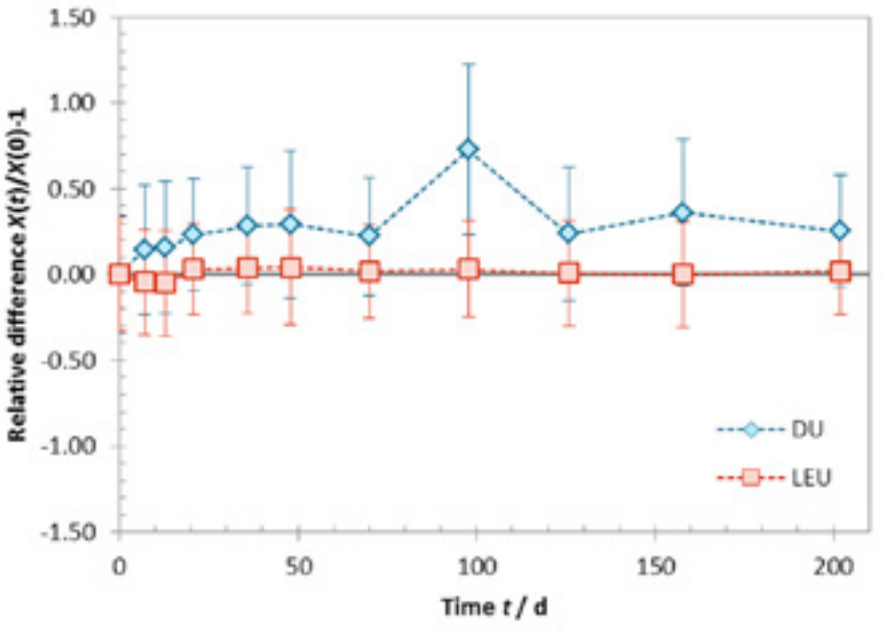

Figure 7: Measured change of the $m(^{235}U)/m(^{238}U)$ (X) isotope ratio after storage in ethanol.

5. Summary and Outlook

This paper proposes a method to transfer produced uranium microparticles into an ethanol suspension, which could then be divided into multiple samples. The proposed method greatly increases the uniformity of the particle distribution over the substrate. Also, the method reduces the spread of the total number of particles on different samples and allows the preparation of a larger number of samples, either from a single batch or combining multiple production runs. The particle suspensions also open new possibilities towards quality control materials for nuclear safeguards particle analysis. Mixtures of different particles could be prepared, as demonstrated with uranium and cerium particles, and mixtures of particles with different uranium isotopic compositions would also be feasible. The suspensions also allow for a wider choice of substrates, such as cotton swipes, or a multitude of substrates with a single batch of particles.

In order to verify the stability of particles in ethanol, particles were stored for 365 days in a suspension, during which no alteration of the particle morphology was observed. Also, no exchange of uranium isotopes between different particles was measured after a period of 202 days. These studies show that even over multiple months' storage in suspension, the particles remain unaltered. As the transfer of particles into suspensions, possible mixing of different suspensions and distribution over a large number of substrates can be performed within a few days, particle suspensions offer a wide range of new possibilities to enhance the quality control measurements without affecting the property values.

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References

[1] Boulyga, S., Konegger-Kappel, S., Richter, S., Sangely, L., *Mass spectrometric analysis for nuclear safeguards*, J. Anal. At. Spectrom., **30**, 1469, 2015.

[2] ISO 17025:2005 *General requirements for the competence of testing and calibration laboratories*, 2005.

[3] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML. *International vocabulary of metrology - Basic and general concepts and associated terms*, volume 3. 2012.

[4] ISO 17034:2016 *General requirements for the competence of reference material producers*, 2016.

[5] Stoffels, J.J., Cannon, W.C., Robertson, D.M., *A particulate isotopic standard of plutonium in an aluminosilicate matrix*. Journal of the American Society for Mass Spectrometry, **2**, 81-8, 1991.

[6] Raptis, K., Ingelbrecht, C., Wellum, R., Alonso, A., Bolle, W., Perrin, R., *The preparation of uranium-doped glass reference materials for environmental measurements*. Nucl. Instrum. Meth. A **480**, 40-43, 2002.

[7] Park, Y., Lee, M., Pyo, H., Kim, H., Sohn, S., Jee, K., Kim, W., *The preparation of uranium-adsorbed silica particles as a reference material for the fission track analysis*. Nucl. Instrum. Meth. A. **545**, 493, 2005.

[8] Kips, R., Leenaers, A., Tamborini, G., Betti, M., Van den Berghe, S., Wellum, R., Taylor, P., *Characterization of Uranium Particles Produced by Hydrolysis of UF_6 Using SEM and SIMS.* Microscopy and Microanalysis, **13**, 156-164, 2007.

[9] Ranebo, Y., Niagolova, N., Erdmann, N., Eriksson, M., Tamborini, G., Betti, M., *Production and Characterization of Monodisperse Plutonium, Uranium, and Mixed Uranium-Plutonium Particles for Nuclear Safeguard Applications.* Analytical Chemistry, **82**, 4055, 2010.

[10] Shinonaga, T., Donohue, D., Aigner, H., Bürger, S., Klose, D., Kärkelä, T., Zilliacus, R., Auvinen, A., Marie, O., Pointurier, F., *Production and Characterization of Plutonium Dioxide Particles as a Quality Control Material for Safeguards Purposes*. Analytical Chemistry, **84**, 2638, 2012.

[11] Knott, A., Dürr, M., *Production of monodisperse uranium particles for nuclear safeguards applications*. ESARDA Bulletin, **49,** 40, 2013.

[12] Middendorp, R., Knott, A., Dürr, M., *Preparation of Uranium Micro-Particles as Reference Material for Nuclear Safeguards*. ESARDA 37th Annual Meeting Proceedings, 448-497, 2015.

[13] Middendorp, R., Dürr, M., Knott, A., Pointurier, F., Ferreira Sanchez, D., Samson, V., Grolimund, D., *Characterization of the Aerosol-Based Synthesis of Uranium Particles as a Potential Reference Material for Microanalytical Methods*, Analytical Chemistry **89**, 4721, 2017.

[14] Esaka, F., Watanabe, K., Fukuyama, H., Onodera, T., Esaka, K. T., Magara, M., Sakurai, S., Usuda, S., *Efficient Isotope Ratio Analysis of Uranium Particles in Swipe Samples by Total-Reflection X-ray Fluorescence Spectrometry and Secondary Ion Mass Spectrometry*, Journal of Nuclear Science and Technology, **41**, 1027, 2014.

[15] Middendorp, R., Dürr, M., Bosbach, D., *The stability of uranium microspheres for future application as reference standard in analytical measurements*, Procedia Chemistry, **21**, 285, 2016.

[16] Johnston, F., Hutchison, D., Katz, J., *Oxygen exchange between uranium oxides and water*, J. Inorg. Nucl. Chem., 7, 392, 1958.