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Production of Uranium Oxide-based Reference Microparticles at FZJ – Current Status and New Developments

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Abstract

In 2020, the safeguards laboratories at Forschungszentrum Jülich GmbH (FZJ) were officially qualified as the first member for the provision of microparticulate reference materials to the IAEA's (International Atomic Energy Agency's) worldwide NWAL (Network of qualified Analytical Laboratories). These reference particles are applied to strengthen the IAEA's quality control system for particle analyses including, e.g. the application in interlaboratory exercises as well as to support the pressing demand to build-up new NWAL capabilities. Very recently the first available batches of highly enriched uranium (HEU) particles with 50% and 90% ^{235}U enrichment were produced in the NWAL laboratories at FZJ using an aerosol-based particle production process and thoroughly analysed using advanced mass spectrometric methods. This paper will discuss – exemplarily for the 90% ^{235}U enriched material - several steps towards the provision of these HEU reference microparticles. They include (1) the preparation and certification of starting solutions conducted at Joint Research Centre (JRC) in Geel (Belgium), (2) the production of the particles at FZJ and particularly (3) the required analyses of process control measurements as well as the verification measurements via MC-ICP-MS (Multicollector - Inductively Coupled Plasma Mass Spectrometry) and LG-SIMS (Large Geometry - Secondary Ion Mass Spectrometry) conducted at FZJ, Oak Ridge National Laboratory and Heidelberg University, respectively. The results of these measurements demonstrate the high quality of the HEU reference particles, and the reliability of the particle production process established at FZJ. Additionally, a preview on recent activities related to the development of microparticulate reference materials for age-dating applications will be addressed. Therefore, a co-precipitation method was adopted to produce Th-doped bulk-scale materials as a kind of "internal reference materials". These materials allow for investigations with state-of-the-art analytical techniques to unravel the structural incorporation mechanism of Th into uranium oxide crystal structures (UO_3 and U_3O_8) in dependence of the amount of Th-doping. Regarding the transferability of the results to the particle production process, the phase transformation from UO_3 to U_3O_8 is of particular interest. Thus, the pristine materials (Th-doped ammonium diuranate) were investigated with TG-DSC (Thermogravimetry - Differential Scanning Calorimetry) to identify the temperature at which the phase transformation of UO_3 to U_3O_8 for the doped materials occurs. Subsequently, the materials were calcined at the identified temperatures and structurally characterised with XRD (X-ray Diffractometry). The results indicate to an incorporation of Th-dopant into the UO_3 and U_3O_8 crystal structure which is an important material property of reference particles for reliable age_dating measurements. They help to identify relevant process parameter such as the aerosol heating temperature to produce high quality microparticulate reference materials to the IAEA's NWAL.

Introduction

In 2022 the IAEA conducted around 3,000 in-field verifications and collected *inter alia* almost 520 environmental samples during their in-field inspections. For the measurements of these environmental samples containing micro-sized U-oxide based particles advanced mass spectrometric methods were used allowing for high resolution determination of isotopic ratios combined with a high level of spatial resolution, e.g. LG-SIMS. This progress goes hand in hand with the need of microparticulate reference materials (RM) as a fundamental part of the Quality Assurance and Control (QA/QC) system of analytical measurements, e.g. for the development of new analytical methods and for the verification of the absence of undeclared nuclear materials and activities in nuclear facilities [1, 2].

Since 2020 the safeguards laboratories at FZJ are officially qualified members of the worldwide dedicated NWAL for the provision of microparticulate uranium-oxide based reference materials. The reference microparticles are produced using a reliable aerosol-based process which was established and optimised in the safeguards laboratories at FZJ [3, 4] leading to the provision of certified U_3O_8 microparticles reference materials [5-7] suitable to be used as reference material in an international comparison exercise NUSIMEP-9 [8, 9]. Recently, highly enriched uranium-oxide reference microparticles which were not available so far were produced in Juelich and characterised together with collaborative partners.

Production of reference particles

The production of a microparticulate reference material (RM) is a multiple step process in which a network of laboratories and experts from several Member States Support Programmes are involved. The production of the HEU microparticle reference materials (FZJ-3050P; nominal 50% ^{235}U enrichment and FZJ-3090P; nominal 90% ^{235}U enrichment) is here exemplarily discussed for the FZJ-3090P campaign.

The microparticle reference materials are produced at FZJ using a modified VOAG (Vibrating Orifice Aerosol Generator, TSI 3450) set-up which is described in detail by Middendorp et al. [3], Neumeier et al. [4] and Kegler *et al.* [10] but will be addressed here briefly. The set-up (Fig. 1a)) consists of a syringe pump (a), the aerosol generator with a drying column (b), an aerosol heater (c) with a subsequent cooling area and the impactor (white square), which contains the 1-inch substrate, e.g. quartz or glass-like carbon discs (GCD) to collect the particles. The elemental and isotopic composition of the particles is defined by the composition of a certified uranyl-nitrate mother solution. The highly diluted ethanolic-aqueous (50 vol% : 50 vol%) uranyl nitrate production solution (a) is injected with a specific mass flow into the aerosol generator to form the monodisperse aerosol droplets (Fig. 1b), white arrows) by vibrating the silicon orifice with a high frequency (app. 70 kHz) (b). These droplets are drying and form uranyl-nitrate particles in the drying column. Subsequently, the particles are passing an aerosol heater (c) in which the uranyl-nitrate decomposes at a temperature of 500°C to form the final U-oxide particles. After cooling, the particles are collected on a substrate that is mounted in an inert impactor. To homogenise the number of particles as well as their distribution on the planchets an additional suspension step was applied [11]. The collected particles on quartz discs were firstly transferred into ethanol suspension supported by ultrasonication. Finally, the particles were homogeneously distributed on GCDs which is the final RM. The process parameters, e.g. the uranium concentration of the feed solution and the frequency for the aerosol jet generation were defined to adjust the particle diameter *d* according to the IAEA's requirements (FZJ-3090P/1, $d = \sim 0.9$ µm and FZJ-3090P/2, $d = \sim 1.4$ µm).

The certified mother solution was prepared and characterised by the Joint Research Centre in Geel, Belgium (JRC-Geel). For the FZJ-3090P campaign the certified IRMM-3090 reference solution from the IRMM-3000 series of the JRC-Geel was selected and shipped to FZJ to produce the particles. The procedure of preparation and analyses of the mother solution, IRMM-3000 series, can be taken from the certification report [12].

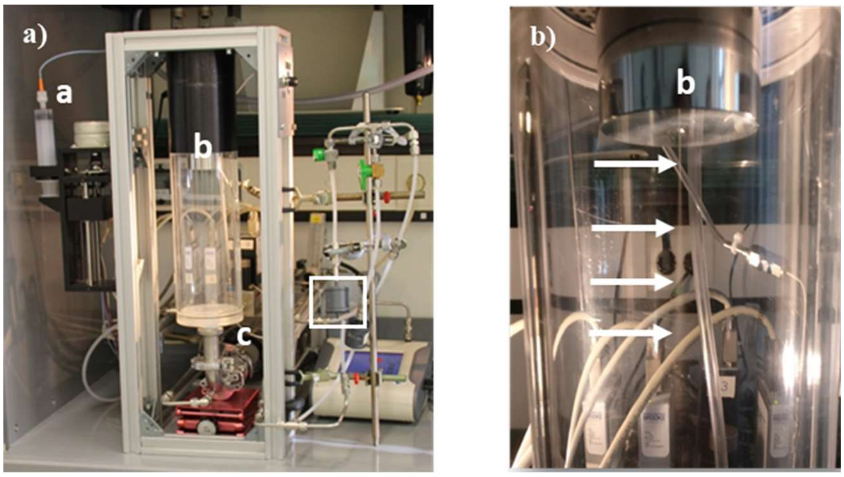

Figure 1: Photographs of specifically modified TSI VOAG set-up (a)) used at FZJ for the production of microparticulate reference materials and a magnification of the aerosol jet (b), white arrows).

Characterisation of FZJ-3090P microparticle reference material

The first characterisation step is a very precise analyses of the mother solution, IRMM-3090. The major isotopic ratios $n(^{235}U)/n(^{238}U)$ and the minor isotopic ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ were established gravimetrically and by several mass spectrometry methods (TIMS/MTE, TIMS/DS and Multi Collector-ICP-MS), respectively, performed at JRC-Geel. Verification measurements were conducted by the IAEA-SGAS (Office of Safeguards Analytical Services, Seibersdorf/Vienna, Austria) and the ORNL (Oak Ridge National Laboratory, Oak Ridge, TN, USA). For the FZJ-3090P campaign the isotopic composition of FZJ-3090P materials will be taken from the IRMM-3090 certificate [12].

In the particle production process several characterisation measures are integrated to control and monitor the processing of the particle production (process control) and to verify the quality of the final product (verification). They consist of determining (i) the particle size distribution by SEM, (ii) the isotopic composition of microparticles by MC-ICP-MS (in preparation at FZJ and ORNL) and (iii) the isotopic composition of single microparticles by LG-SIMS performed at Heidelberg University.

Figure 2 depicts exemplarily SEM micrographs with a typical shape, size and size distribution of the particles produced. The particles' size is in the expected range for the FZJ-3050P/1 (Fig. 2 a)) and FZJ-3050P/2 (Fig. 2b)) batches. A mean diameter of 0.9 – 1.0 µm and 1.50 – 1.65 µm was measured, respectively. The particle size distribution is broader for the FZJ-3090P/2 batch compared to other productions. The modification of the process parameter to produce that large particles requires some alignments to optimise the monodispersity of the particle size distribution.

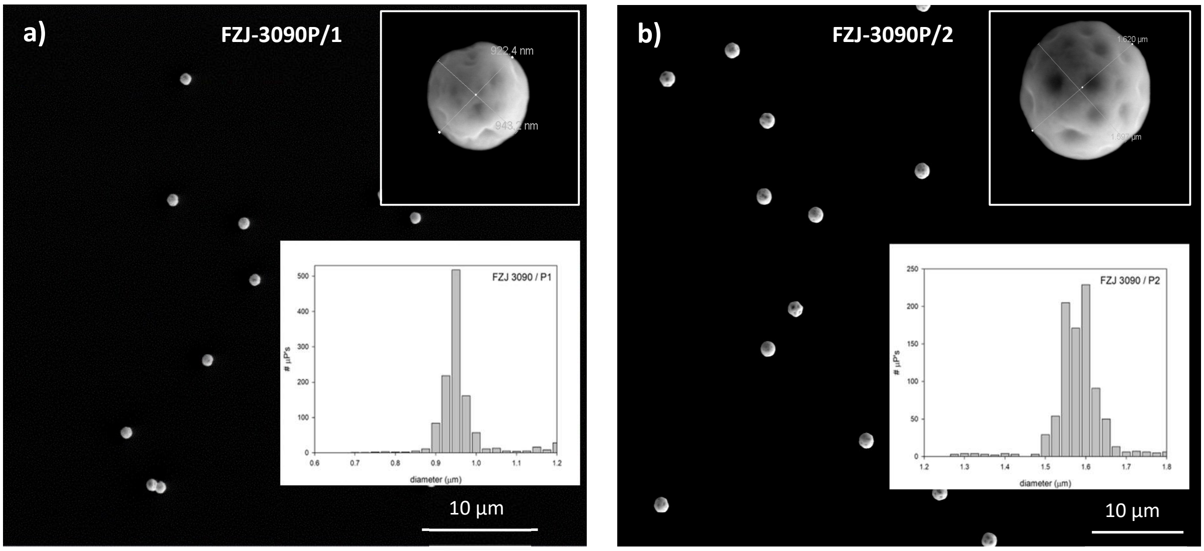

Figure 2: SEM micrographs from both batches of the particle production campaign. a) FZJ-3090P/1, particle diameter: 0.9 – 1.0 µm; b) FZJ-3090P/2, particle diameter: 1.50 – 1.65 µm.

The determination of isotopic composition on single particles were performed for both batches at the Heidelberg Ion Probe (HIP) facility with a CAMECA ims 1280-HR. First the entirety of particles was identified by screening the whole planchet surface with the Automated Particle Measurement (APM) software. A preliminary ^{235}U value for each identified particle was calculated. In Figure 3 the $^{235}U/^{238}U$ ratio of single particles is plotted versus the intensity in cps for FZJ-3090P/1 (Fig. 3a)) and FZJ-3090P/2 (Fig. 3b)). The plot is showing a typical distribution of the calculated particle composition around the mean value (green line). From these measurements the absence of particles with unexpected isotopic value of ^{235}U can be concluded. The mean value does not reflect the exact reference value of 6.57731 $^{235}U/^{238}U$ from the certificate of the mother solution (IRMM-3090) because the APM measurement is a screening technique to calculate preliminary ^{235}U values and absolute values are very sensitive to different instrument parameters. It is used to show that the relative isotopic deviation of the entirety of the microparticles is within an acceptable range and there are no isotopic outliers from any kind of contamination.

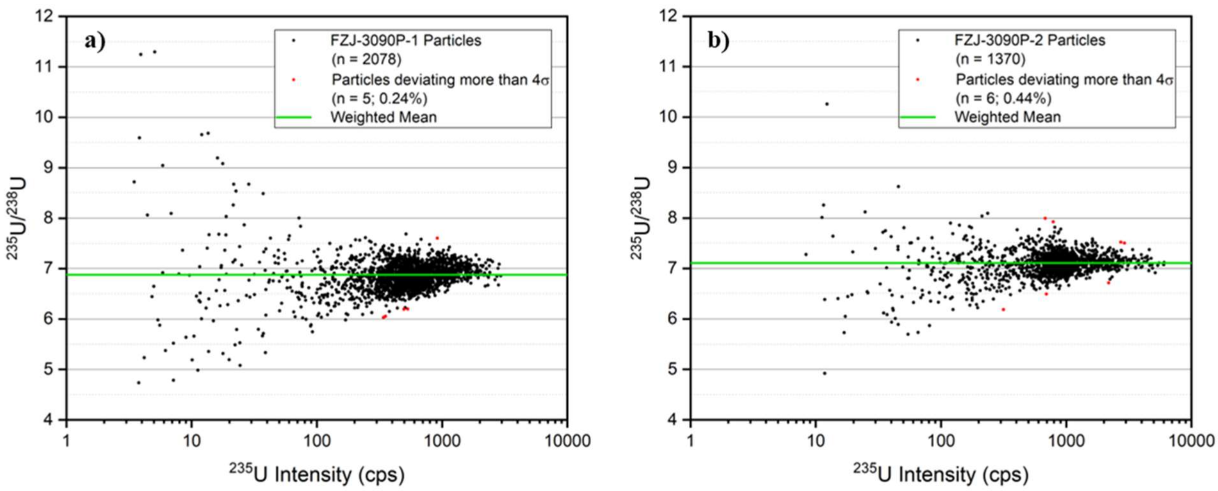

Figure 3: APM measurements (^{235}U screening) on sample planchets containing reference microparticles with a diameter of 0.9 – 1.0 µm (FZJ-3090P/1, a)) and of 1.5 – 1.65 µm (FZJ-3050P/2, b)) [13].

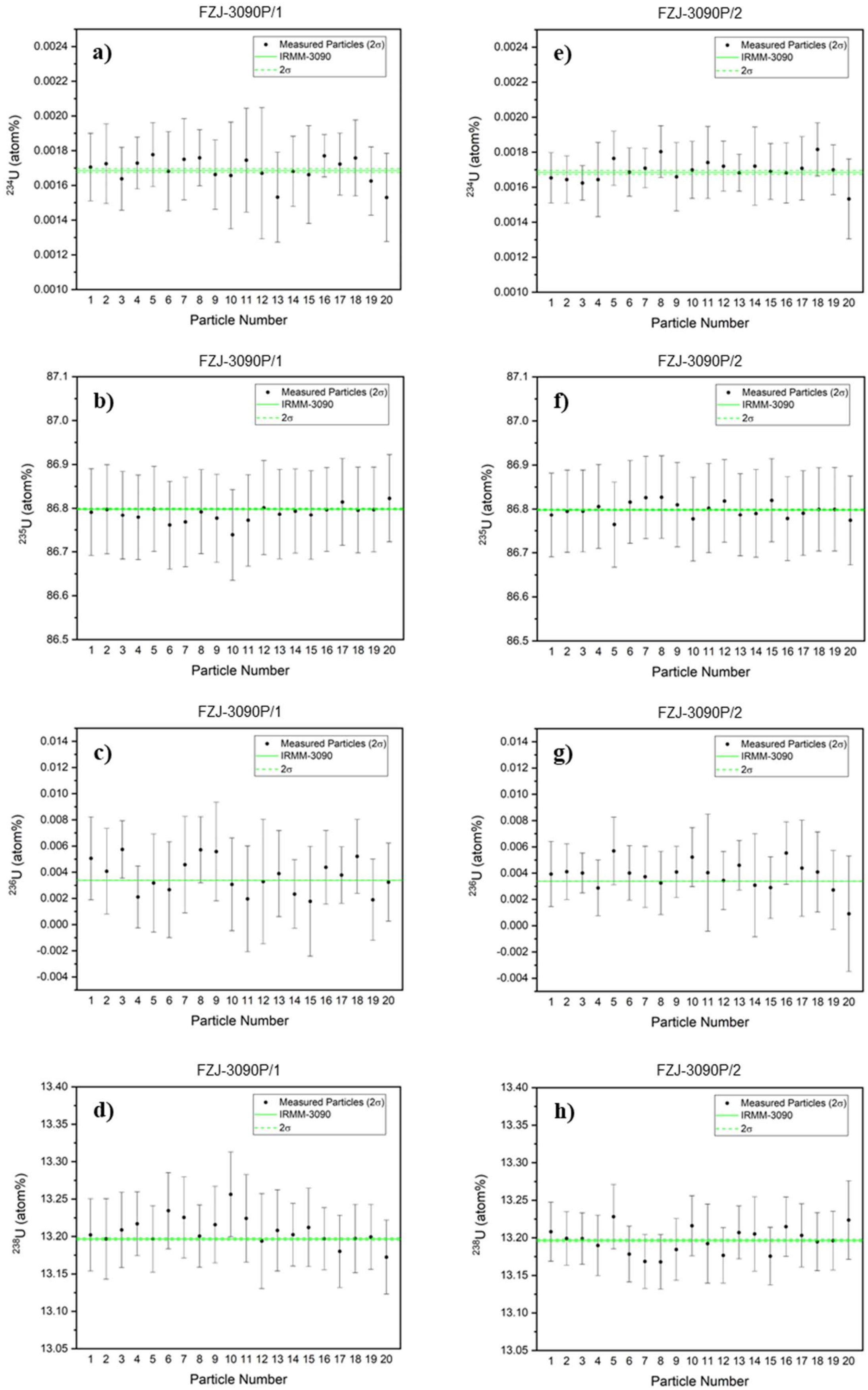

Figure 4: High resolution LG-SIMS microparticle measurements of isotopic composition performed on single particles of both batches (FZJ-3090P/1, a)-d); FZJ-3090P/2, e)-h)). Green line: Certificate value of IRMM-3090 mother solution; dashed green line: 2σ.

High resolution single particles measurements of isotopic composition were conducted on 20 randomly selected particles. In Figure 4 the content of ^{234}U, ^{235}U, ^{236}U and ^{238}U for 20 single particles is plotted for both batches of particles and compared to the reference value for the different isotopes from the certificate of IRMM-3090 mother solution (green line). The isotopic compositions from measured particles are within the uncertainty of 2 σ in very good agreement to the reference values. These results have been discussed already with experts from IAEA-SGAS and have been accepted.

In Figure 5 ^{235}U enrichment ($^{235}U/U$) values from verification measurements performed on the IRMM-3090 solution are compiled. These measurements were conducted during the certification process of the entire IRMM-3000 series (blue squares). The mean value of the ^{235}U enrichment derived from LG-SIMS measurements on single FZJ-3090P/2 particles (open circle) matches very well the values from IRMM-3090 solution verification. The next particle production campaigns requested by the IAEA are already planned and will focus on another set of HEU particles (Nominal enrichment: 20%, 35% and 75% ^{235}U). The certified mother solutions were already produced, characterised and shipped to FZJ by the JRC-Geel.

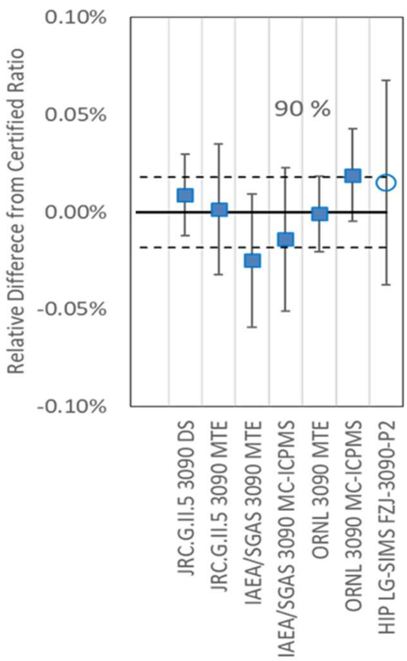

Figure 5: Overview of mean values from ^{235}U enrichment ($^{235}U/U$) verification measurements of the IRMM-3090 mother solution (blue squares) from certification process in comparison to the mean value of high-resolution LG-SIMS microparticle measurements of isotopic composition performed on single particles of the FZJ-3090P/2 batch (open circle).

Development of Th-doped microparticles for age-dating verification

One of the high priority topics expressed in the *Development and Implementation Support Programme for Nuclear Verification 2024–2025* [2] by the IAEA is the development and production of ^{230}Th-doped microparticles for age-dating verification measurements. For the development of a reliable and reproducible process to produce compound reference particles with homogeneous distribution of Th over the entire particle volume, structural investigations were performed at FZJ in order to derive a refined understanding if Th-ions can be incorporated into the uranium oxide structure forming a homogeneous Th/U solid solution or if a Th-dioxide phase will segregate during thermal treatment. A phase segregation would directly yield in the formation of an inhomogeneous mixed oxide compound that is disadvantageous for the design of reference particles for particle analysis applications.

However, the structural investigation of microparticles is very challenging for single particles since the quantities of material that are produced with the physical aerosol-based set-up in Juelich are very limited (app. 3.6 pg/particle [5, 7]) and not measurable with in-house analytical techniques. Therefore, a synthesis route was adapted to produce 1 mol% Th-doped ammonium diuranate (ADU, $(NH_4)_2U_2O_7$) powder as a sort of “internal reference materials” as a bulky model system for comparison. These ”internal reference materials” were calcined at defined temperatures derived from thermogravimetric investigations (TG-DSC) and characterised by X-ray diffraction (XRD). The results are summarised here very briefly. More detailed information can be obtained from Potts et al. [14 – 16].

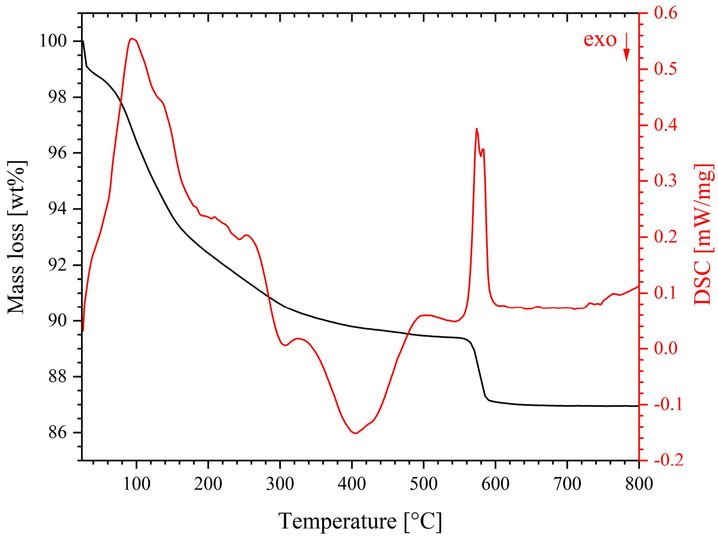

Figure 6: TG-DSC data obtained during heating of 1 mol% Th-doped $(NH_4)_2U_2O_7$ from room temperature to 800°C measured in synthetic air.

Results from TG-DSC measurements performed on a 1 mol% Th-doped sample indicate the decomposition of the Th-doped ADU and identify the temperature region of the occurring phase transitions (Fig. 6). The main mass loss (black curve) occurring at a temperature up to 405°C is combined with a strong endothermic DSC signal (red curve) and can be assigned to the removal of H_2O and NH_3 [17]. The subsequent exothermic region (400 – 430°C) indicates the formation of a β-UO_3 phase. Finally, an endothermic phase transition to a crystalline U_3O_8 phase occurs in the temperature range between 520°C and 635°C.

From the thermogram, 520°C and 700°C were defined as calcination temperature for structural investigations to monitor structural changes due to thermal treatment. Therefore, XRD measurements were performed on 1 mol% Th-doped samples after calcination at 520°C and 700°C (cf. Fig. 7).

The XRD measurement of the calcined Th-doped material at 520°C (Fig. 7a)) indicate the formation of a phase mixture of α-UO_3 with a significant high proportion of an amorphous phase in comparison to the undoped ADU [15]. Moreover, the broad reflexes of the 1 mol% Th-doped sample after calcination at 520°C point to a preferentially formed β-UO_3 phase while the undoped calcined ADU material consists of a mixture of α-UO_3 and β-UO_3 phases.

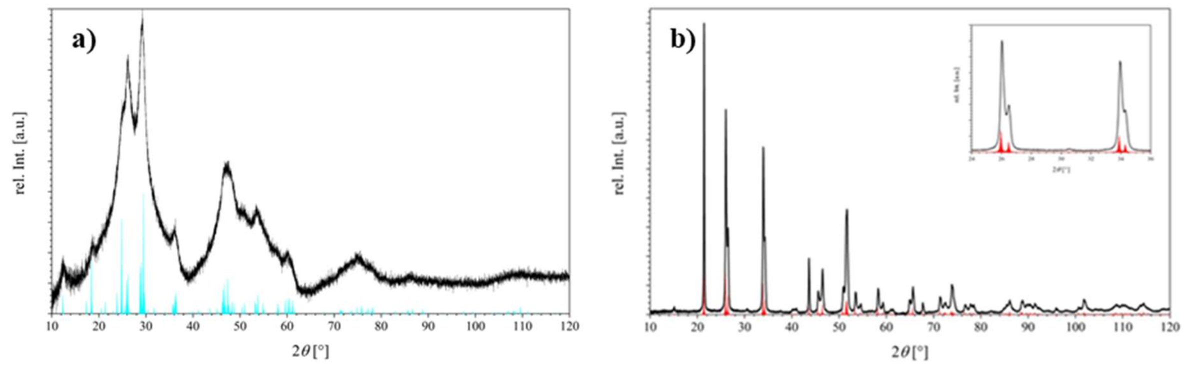

Figure 7: X-ray diffractograms of the 1 mol% Th-doped sample after calcination at 520°C (a); reference: α-UO_3 with the space group *$P2_1$* (cyan) [18]) and after calcination at 700°C (b); reference: α-U_3O_8 with the space group *C2mm* (red) [19]).

From the XRD pattern of the 1 mol% Th-doped sample (Fig. 4 b)) calcined at 700°C a phase transition to an orthorhombic U_3O_8 phase with the space group *C2mm* [19] comparable to the undoped ADU after calcination at 700°C [14] can be observed. The double reflexes at about 2θ values of 26° and 34° (Fig. 7 b), zoom in) in the XRD pattern of the doped sample is the response to changes in the lattice parameter and consequently the volume of the unit cell and a clear indication that 1 mol% Th is incorporated into the U_3O_8 structure.

Conclusions & Outlook

For the first time high enriched uranium-oxide microparticle reference materials with 90% enrichment were successfully produced at FZJ and characterised in cooperation with Heidelberg University. These HEU particle-based reference materials complement the collection of reference materials used by IAEA-SGAS for particle analysis activities, e.g. for instrument calibration and optimisation as well as for method validation studies. Currently the production of more batches of HEU reference particles with different ^{235}U enrichment (25%, 35% and 75% ^{235}U) is planned with the IAEA-SGAS.

From structural investigations on the 1 mol% Th-doped bulky internal reference materials the conclusion can be drawn that the preparation of homogeneous Th-doped suitable as reference materials for age-dating reference materials using the aerosol-based particle production process at FZJ is feasible. The production of these age-dating materials is planned at FZJ by the production of well-selected ^{230}Th spiked U-oxide standards.

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