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URANIUM OXIDE BASED MICROPARTICULATE REFERENCE MATERIALS FOR ANALYTICAL MEASUREMENTS IN NUCLEAR SAFEGUARDS – STATUS & PERSPECTIVE

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ABSTRACT

The analysis of individual micrometre- and submicrometre-sized particles collected by IAEA safeguards inspectors on swipe samples during in-field verification activities requires the implementation of a sustainable quality control system. This system needs to be further optimised by developing advanced mass spectrometric analytical methods and suitable reference materials. For the design of these microparticulate reference materials well-defined tuning of elemental and isotopic composition is required. Additionally, a refined understanding on material science aspects, such as morphology, chemistry, and structure is essential. This paper is throwing a retrospective glance on the historical evolution of the microparticle production task and its safeguards implementation during the last 25 years addressing (i) the requirements and IAEA needs on microparticle reference materials; (ii) the developments and advancements of relevant particle production routes and of analytical tools for particle analysis in nuclear safeguards and nuclear forensics. Exemplarily, the way from the idea of developing and establishing a sustainable reference particle production route in the laboratories of Forschungszentrum Juelich (FZJ) to the officially certified reference material, over the application of these reference particles in an international interlaboratory exercise and finally to the qualification of FZJ as a member within the IAEA's Network of Analytical Laboratories (NWAL) for the provision of microparticulate reference materials will be highlighted. The main focus will be spent on the production of monodisperse pure and lanthanide (*Ln*) doped uranium-oxide based microparticles utilising an aerosol-based particle production process as well as on the importance of material science aspects for an explicit description of the particles' properties. Electron microscopy and X-ray absorption spectroscopy confirm the monodispersity of the produced microspheres as well as the presence of *Ln* (lanthanides) in the compound particles. Complementarily conducted structural investigations reveal a refined insight into the mechanism on the formation of U_3O_8 microparticles for both compounds as well as on shelf-life and storage conditions of these reference materials. These results demonstrate that the process established in Juelich allows for a very flexible and reliable preparation of reference materials for particle analysis methods applied in nuclear safeguards and nuclear forensics.

INTRODUCTION

Quality Assurance and Control (QC) of analytical measurements on nuclear safeguards samples are of utmost importance to maintain the International Atomic Energy Agency's (IAEA's) credibility with its Member States. To implement a robust QC system for measurements of individual micrometre-sized particles collected by inspectors on swipe samples during inspections, reference materials in microparticulate form are needed.

For this purpose, a reliable aerosol-based process was developed and established in the safeguards laboratories at FZJ [1, 2], capable of producing uranium oxide microparticles with well-defined properties, such as narrow particle size distribution and consistent isotopic composition. The process was optimised yielding in the production, characterisation, and certification of U_3O_8 microparticles that are used as QC materials for particle analysis methods in nuclear safeguards [3; 4]. One batch of these certified U_3O_8 microparticles was successfully applied in an international interlaboratory exercise in the framework of Nuclear Signatures Interlaboratory Measurement Evaluation Program (NUSIMEP) organised by the European Commission's Joint Research Centre, Geel, Belgium (JRC-Geel) [5]. In 2020, the FZJ's safeguards laboratories were qualified as the first member for the provision of microparticle reference materials to the IAEA's Network of Analytical Laboratories (NWAL).

The isotopic ratio is the most important characteristic of microparticles to be applied as reference materials for particle analysis measurements in nuclear safeguards. The importance of materials science aspects such as chemistry, particularly the oxidation state, crystal structure and chemical stability are of minor significance and are therefore often underestimated. In very recent electron microscopy and X-ray absorption spectroscopy investigations on pure and Nd-doped U_3O_8 microparticles, the importance of material science aspects is demonstrated in terms of the formation of doped U_3O_8 microparticles and their storage stability [6].

PARTICLE PRODUCTION AND APPLICATION

Particle production and collection

For the production and collection of well-defined microparticles with a narrow size distribution, an aerosol-based process using a vibrating orifice aerosol generator (VOAG) as set-up was implemented at FZJ. The procedure to produce and collect microparticles via VOAG at FZJ is briefly described here. Detailed information was published by Middendorp *et al.* [1] and Neumeier *et al*. [2].

The main components of the VOAG are the aerosol generator, a drying column, an aerosol heater, and an impactor including a 1-inch substrate, e.g., quartz discs or glass-like carbon discs, which are mounted in the impactor and serve to collect the generated microparticles. To produce pure and mixed uranium oxide microparticles, a well-designed ethanolic-aqueous (50 vol% to 50 vol%) uranyl nitrate solution with the desired isotopic composition was injected into the aerosol generator with a defined volume flow. The monodisperse aerosol droplets were generated by perturbing of the input feed solution jet by means of a vibrating silicon orifice. Supported by a permanent airflow, the uranyl nitrate droplets begin to dry and pass through the drying column to enter the aerosol heater. In the aerosol heater, the droplets are completely dried at a temperature of 500 °C and uranyl nitrate microparticles are formed. Due to the temperature, the uranium precursor thermally decomposes and solid pure or mixed uranium oxide microparticles are generated with an adjustable diameter between 0.9 µm and 1.4 µm. The produced particles are collected on solid substrates, which are built into the inert impactors. To control the number of particles on the planchets as well as their homogeneous distribution an additional suspension step was developed at FZJ [7]. The collected particles on quartz discs were firstly transferred into ethanol suspension. In the second part of the suspension step the particles were homogeneously distributed on glass-like carbon discs.

Fig. 1. represents a typical distribution of U_3O_8 microparticles with an average diameter of 1.2 µm on glass-like carbon discs after the suspension step. It turns out that the particles are randomly distributed and accidently deposited with a very close particle-to-particle distance.

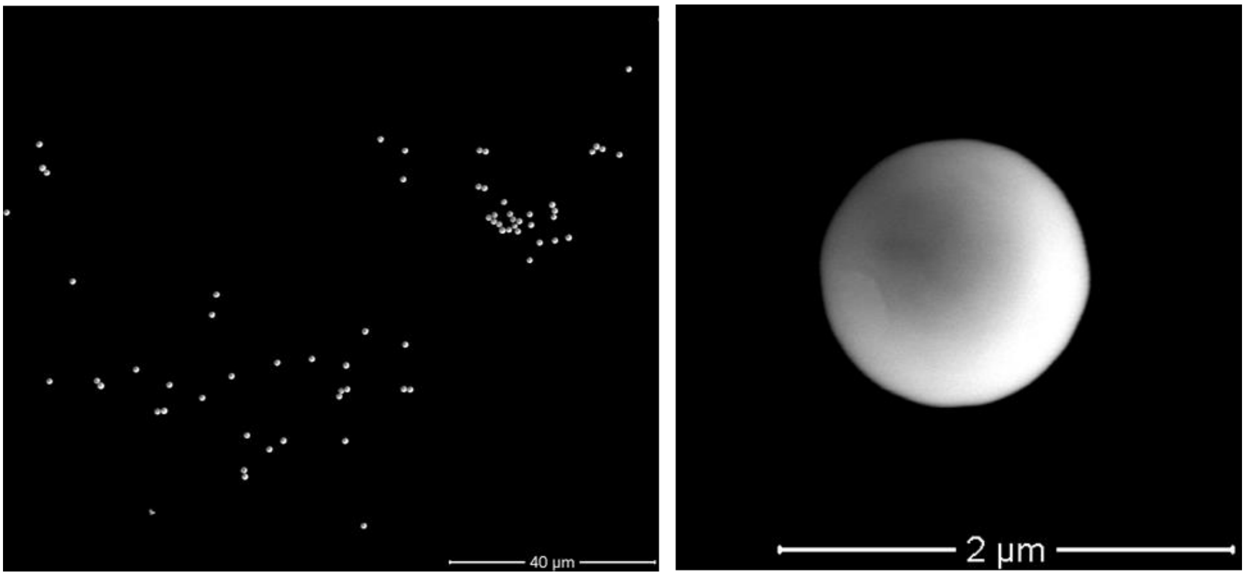

Fig. 1: SEM micrographs of U_3O_8 microparticles produced with the aerosol-based process after the suspension step (left) and a high-resolution image of a single particle (Ø = 1.2 µm).

Application

After successfully establishing the development of the aerosol-based particle production process in the safeguards laboratories in Juelich the production of two batches of LEU certified reference materials (IRMM-2329P [3] and IRMM-2331P [4]) was conducted in the framework of a joint trilateral project between International Atomic Energy Agency-Office if SafeGuards Analytical Services (IAEA-SGAS), the JRC-Geel and FZJ. The several steps and activities from the starting solution to the certification are highlighted in Fig. 2.

The first step of the production of a microparticulate certified reference material (CRM) is the preparation, analysis, and certification of the base uranyl nitrate solution with a specific isotopic composition. The isotopic composition of the base solution is defining the final isotopic composition of the reference particles. The selected isotopic composition for the microparticle production depends on the application of the certified reference particles and is therefore defined by the IAEA. In the next step the base solution was shipped to Juelich laboratories for the production and collection of particles using the aerosol-based process described above. After performing the suspension step, the number, morphology, and size distribution of the microparticles were analysed by Secondary Electron Microscopy (SEM) on randomly selected samples. Finally, the samples were shipped to IAEA and JRC-Geel for further analysis of the isotopic composition and the total uranium amount per particle by Multi Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) and Isotope Dilution Mass Spectrometry (IDMS) / Thermal Ionisation Mass Spectrometry (TIMS) measurements, respectively and finally for certification.

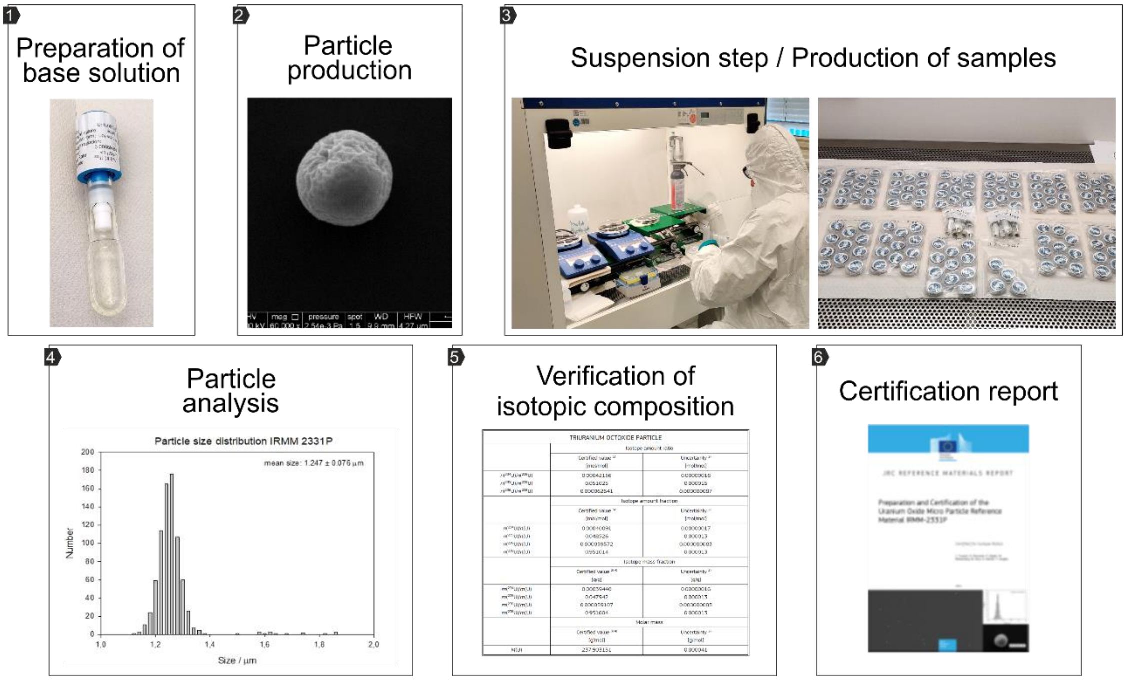

Fig. 2: Schematic representation of the production steps of a microparticulate reference material.

Within this collaboration two batches of LEU microparticles reference materials (IRMM-2329P and IRMM-2331P) were produced following a strict protocol based on a set of Standard Operation Procedures (SOPs) as part of the Quality Management System (QMS) in Juelich for the provision of microparticle reference materials to the IAEA. These batches were successfully certified according to ISO 17034 by JRC-Geel for a defined isotopic composition and the U content per particle (only IRMM-2329P) [8]. The CRMs are available at the catalogue of reference materials of the JRC-Geel (https://crm.jrc.ec.europa.eu/e/4/How-to-order). Additionally, IRMM-2329P samples are used in an international interlaboratory comparison exercise as an external quality control program with the objective of providing material measurements of trace amounts of nuclear materials in environmental matrices (e.g. NUSIMEP-9 [5]).

Finally, the establishment of the aerosol-based set-up, the reproducible production of microparticles with defined properties (e.g. particle size and isotopic composition), the establishment of a QMS for a reliable production of these particles in the safeguards laboratories in Juelich result in the qualification of the safeguards laboratories at FZJ as the first member for the provision of microparticle reference materials to the IAEA and its NWAL partners.

MATERIAL SCIENCE ASPECTS OF U-OXIDE MICROPARTICLES

For the investigation of the formation of *Ln*-doped microparticles and the stability in the suspension media, pure and Nd-doped (15 mol%) uranium oxide microparticles were produced using the VOAG. The Nd-doped microparticles are similar in size compared to the pure particles and the Nd content was confirmed by Energy Dispersive X-ray (EDX) spectroscopy [2]. The stability of both batches of microparticles in suspension medium ethanol was thoroughly investigated over a period of 4 and 2.5 years, respectively by SEM (Fig. 3).

It turns out that both the pure (Fig. 3; left) as well as the Nd-doped (Fig. 3; right) uranium oxide particles are chemically stable in ethanol over a period of 2.5 years with minor effects of deformation in size and morphology while storing these particles in ethanol. The elemental composition and the homogeneous distribution of Nd over the doped particles was confirmed by the EDX measurements. These results indicate that doping with neodymium does not significantly affect the chemical stability of the uranium oxide particles because a preferential dissolution of Nd from the particles was not detected.

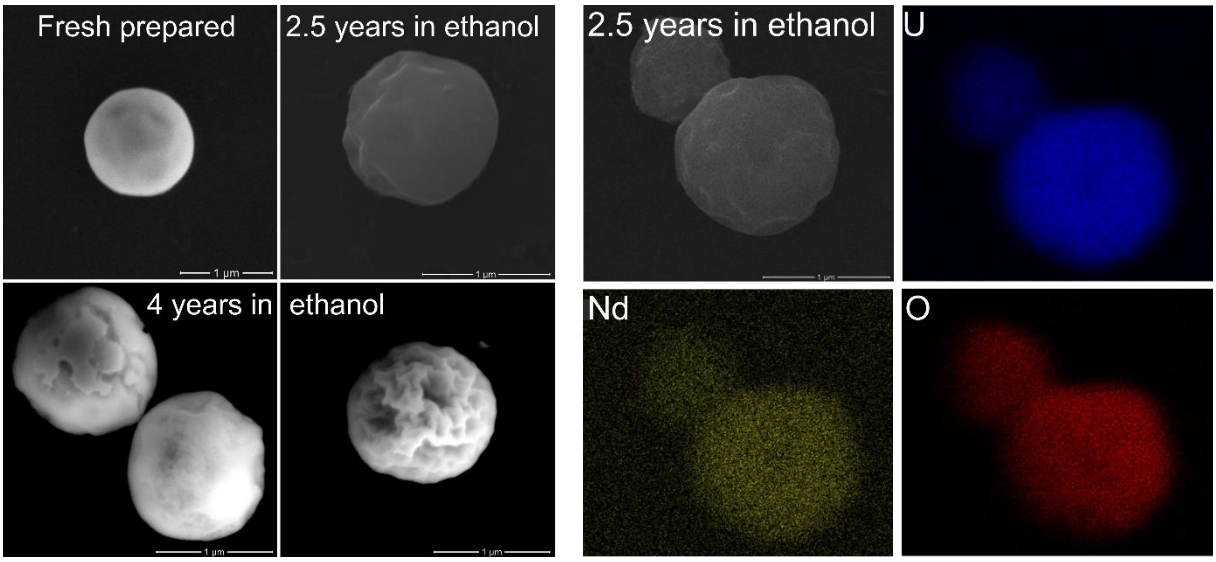

Fig. 2: High resolution SEM micrographs of pure U-oxide (left) and Nd-doped (right) U-oxide particles, incl. EDX mapping. The time dependent series of U-oxide particles demonstrate the stability and deformation of particles over a period of 4 years storage in suspension medium ethanol. The Nd-doped U-oxide particles were store over 2.5 years in ethanol. The coloured EDX mappings illustrate the elemental composition (U (blue); Nd (yellow); oxygen (red).

Very recently with the help of X-ray Absorption Near Edge Spectroscopy (XANES) and Raman measurements performed at Karlsruhe Institute of Technology (KIT INE-Beamline and ACT station @ KIT synchrotron radiation source, KARA, Karlsruhe, Germany) and CEA-DAM, Arpajon, respectively new insight into the chemistry and structure of the particles produced with the aerosol-based process was achieved. The results demonstrate that the oxidation state of the microparticles is increasing over time to a higher portion of oxidation state +VI. This is very important because simultaneously Schoepite (hydrated form of UO_3) is formed in presence of atmospheric water in the environment. From these results it can be concluded that the microparticles produced with the VOAG are preferentially stored under dry and inert conditions (argon or nitrogen). To derive a refined understanding of the storage conditions of these U-oxide particles stored on planchets and in different suspension media a systematic shelf-life study was initiated at Juelich.

CONCLUSIONS

In the safeguards laboratories at the Forschungszentrum in Jülich an aerosol-based microparticle production process is successfully established for the production of microparticulate uranium-oxide CRMs. The applicability has been demonstrated by the production and certification of two batches of LEU microparticle reference materials for the isotopic composition and for the amount of U per particle for one batch. These samples were additionally used as reference materials in an international interlaboratory comparison exercise (NUSIMEP-9). As a consequence, Juelich's safeguards laboratories were qualified as the first member of the IAEA's NWAL for the production and provision of uranium-oxide based CRM's for particle analysis in safeguards.

It has been demonstrated that material science aspects must be considered in the R&D concepts for the design and development of reference materials, particularly in view of the incorporation of foreign ions (e.g. lanthanides, Th or Pu) in the uranium oxide crystal structure and the shelf-life of the particles. A refined understanding on the properties of these materials allows for a precise prediction of storage and performance conditions of the reference materials in order to guarantee a long-term shelf-life and therefore, applicability of these CRMs.

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