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Production and Analyses of Uranium Oxide Microparticulate Reference Standards: Current Status and Outlook

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Abstract

The International Atomic Energy Agency (IAEA) and its worldwide Network of qualified Analytical Laboratories (NWAL) conduct analytical measurements on swipe samples taken during inspections at nuclear facilities to verify the absence of undeclared nuclear materials and activities. These efforts, together with the increasing number of samples (more than 450 per year) to be analysed require constant quality control, further advancement of highly sensitive analytical methods incl. the development and provision of tailor-made reference materials as well as the permanent build-up of new NWAL capabilities.

In 2020 the safeguards laboratories at Forschungszentrum Jülich GmbH (FZJ) were qualified as the first member for the provision of microparticulate reference materials. These reference particles are applied to strengthen the IAEA's quality control system for particle analyses including analytical instrument calibration, method development and validation as well as their application in interlaboratory exercises.

This paper will provide an impression of the several steps required towards the provision of the microparticulate reference materials. Exemplarily, these steps will be discussed on our recent campaign to the IAEA on the production of the first highly enriched uranium-oxide reference microparticles. They include (1) the discussion and agreement on the specification of the individual particles, e.g. composition and particle size, but also the number and nature of samples, (2) the preparation of the laboratories considering the internal Standard Operation Procedures (SOPs) for the safeguards laboratories at FZJ, (3) the certification of starting solutions at Joint Research Centre in Geel, such as the IRMM-3050 isotopic reference material and (4) the production of the particles at FZJ. A specific discussion will focus on (5) the required analyses, that includes the process control measurements as well as the verification measurements via advanced mass spectrometric methods (MC-ICP-MS and LG-SIMS) conducted at FZJ, Oak Ridge National Laboratory (ORNL) and Heidelberg University, respectively.

Introduction

Since 2020 the safeguards laboratories at Forschungszentrum in Juelich (FZJ) are officially qualified members of the worldwide Network of Analytical Laboratories for the provision of microparticulate uranium-oxide based reference materials. These particles are a fundamental part of the Quality Assurance and Control (QA/QC) system of analytical measurements on nuclear safeguards samples collected by inspectors of the IAEA during their in-field verification activities.

The reference microparticles are produced using a reliable aerosol-based process which was established and optimised in the safeguards laboratories at FZJ [1, 2] yielding in the provision of certified U_3O_8 microparticles reference materials [3-5] suitable to be used as reference material in an international comparison exercise NUSIMEP-9 [6, 7].

Currently, the activities in Juelich focus *inter alia* on the production of highly enriched uranium-oxide reference microparticles which are not available so far.

Production of Reference Particles

The production of a microparticulate reference material (RM) is a multi-step joint project in which different institutions from several Member States Support Programmes are involved.

Definition of a requested reference material by IAEA

The isotopic ratio of microparticles is the most important characteristic of the RM that is defined by the needs of the IAEA. Besides the isotopic composition the size of the microparticles and their particle size distribution, the number and nature of samples, e.g. microparticles deposited on planchets or in suspension, the number of particles per planchet as well as the analytical acceptance criteria need to be defined and agreed upon prior to the particle production campaign in the laboratories. To this effort, the IAEA's Office for Safeguards Analytical Services (IAEA-SGAS) is reaching out to the involved MSSPs for this specific support in form of a letter request.

Preparation of particle production campaign

The production of microparticle RM's requires a thorough preparation of laboratories and schedule of the involved laboratories, e.g. for particle analyses. At FZJ the production of the microparticle reference materials follow a strict quality management system (QMS) consisting Standard Operation Procedures (SOP).

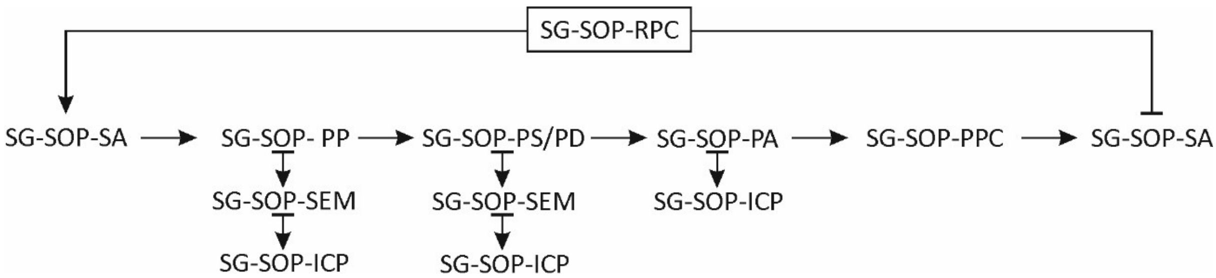

Fig. 1: Scheme of the SOP-based QMS for the production of microparticle reference materials at FZJ.

In Figure 1 a schematic overview of the QMS based on a sequence of SOPs for the production of microparticle reference materials is presented. The most important SOP is related to the Room Cleanliness Plan (SG-SOP-RCP). It defines a permanent room cleanliness monitoring based on a frequently measured set of samples that allows to detect even traces of contamination within the safeguards laboratories. Thus, these measurements are permanently conducted independent of a requested particle production by the IAEA. The other SOPs govern the activities through the entire particle production campaign starting with the acceptance of starting solutions to the shipment of the samples to analytical laboratories or IAEA-SGAS (SG-SOP-SA).
The activities during the particle production itself are managed through the SOPs regarding the Particle Production process (SG-SOP-PP), the Particle Distribution using a Particle Suspension (SG-SOP-PS/PD) as well as the Particle Analyses (SG-SOP-PA). The SOPs SG-SOP-SEM and SG-SOP-ICP define procedures for sample preparation and parameters for analyses related to particle size and integrity using Scanning Electron Microscopy (SEM) and isotopic composition using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), respectively. Finally, the post-production cleaning process of the aerosol generator is a very important step and is described within SG-SOP-PPC. This SOP ensures the avoidance of cross contaminations such as memory effects from current to the next particle production campaign. All particle production campaigns are performed following strictly this series of SOPs to guarantee a reliable workflow to produce well-defined microparticle reference materials with highest quality standards for the particle analysis within IAEA's NWAL.

Production of FZJ-3050P microparticle reference material

As can be seen from the number of SOPs needed to manage the particle production procedure at FZJ the production of the microparticle RM's is a multiple step process and requires a network of laboratories and experts. Here, the complexity of the process is discussed exemplarily on our very recent particle production campaign (FZJ-3050P), the production of high enriched uranium-oxide (HEU) RMs with an enrichment of 50% ^{235}U. In Figure 2 a flowsheet is visualising the several steps and the laboratories involved in the production of the FZJ-3050 material including the required characterisation.

After finalising the definition of the requested reference particles, the experimental part of the campaign starts with the preparation and characterisation of the mother solution by the Joint Research Centre in Geel (JRC-Geel). For the FZJ-3050P campaign the certified RM IRMM-3050 from the IRMM-3000 series of the JRC-Geel was selected and shipped to FZJ to produce the particles. The preparation and analyses of the mother solution, IRMM-3050, can be taken from the certification report of the IRMM-3000 series [8].

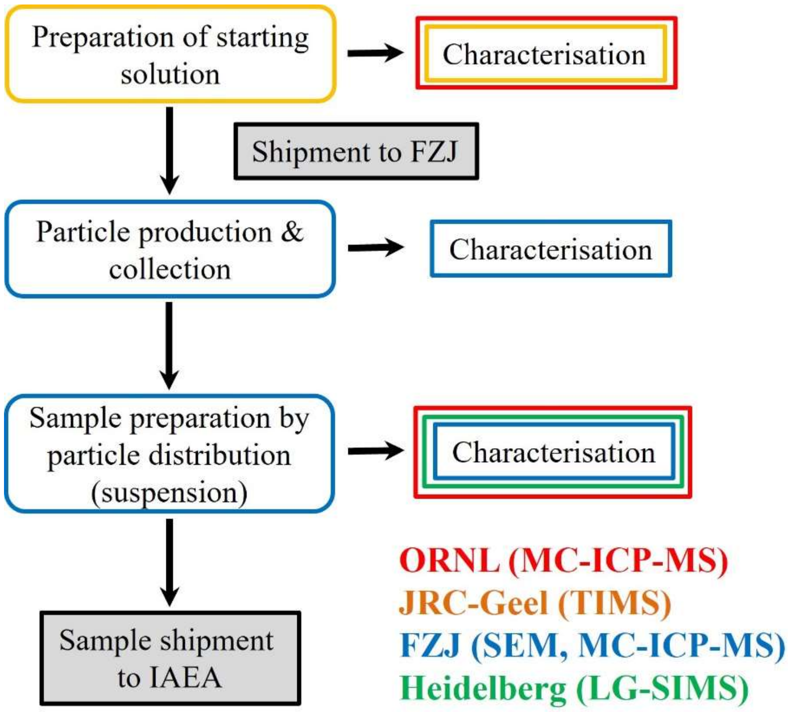

Figure 2: Flowsheet of the particle production campaign FZJ-3050P. The colour of the boxes represents the laboratory involved in the activities.

For the production and collection of well-defined microparticles reference material, an aerosol-based process using a vibrating orifice aerosol generator (VOAG) as set-up was established 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.* [8] and Neumeier *et al*. [9] and Kegler *et al.* [10].

The VOAG mainly consists of the aerosol generator, a drying column, an aerosol heater, and an impactor including a 1-inch substrate, e.g. a quartz disc or a glass-like carbon disc (GCD), for the collection of the generated microparticles on the solid substrates. The HEU microparticles are produced by injecting a highly diluted ethanolic-aqueous (50 vol% to 50 vol%) uranyl nitrate production solution (based on the IRMM-3050 mother solution) into the aerosol generator with a defined volume flow. Monodisperse aerosol droplets were generated by perturbing the input feed solution through a vibrating silicon orifice. The droplets are drying while passing through the drying column to form uranyl nitrate particles. In the aerosol heater at a temperature of 500 °C the uranyl nitrate decomposes to form the final uranium oxide-based particles. The produced particles are collected on quartz discs placed in the inert impactors. To homogenise the number of particles as well as their distribution on the planchets an additional suspension step was applied [9]. The collected particles on quartz discs were firstly transferred into ethanol suspension supported by sonication. Finally, the particles were homogeneously distributed on glass-like carbon discs which is the final RM. Within this campaign the production of two batches of particles with identical isotopic composition but with different mean particle diameter (FZJ-3050P-1, d = ~ 0.9 µm and FZJ-3050P-2, d = ~1.4 µm) was requested. The size of the particles can be adjusted by modifying some parameters for the particle production, e.g. the uranium concentration of the feed solution and the frequency for the aerosol jet generation.

Characterisation of FZJ-3050P microparticle reference material

The particle production process contains several characterisation steps to control and monitor the processing of the particle production (process control) and to verify the quality of the final product (verification). For the FZJ-3050P campaign the isotopic composition of FZJ-3050P materials will be taken from the IRMM-3050 certificate, controlled and verified by „characterisation“ measurements at FZJ, Heidelberg University and ORNL.

The first characterisation step is a very precise analyses of the mother solution, IRMM-3050. The major isotopic ratios $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ and the minor isotopic ratios $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ were established gravimetrically and by several mass spectrometry methods (TIMS/MTE, TIMS/DS and Multi Collector-ICP-MS), respectively performed by JRC-Geel. Verification measurements were conducted by the IAEA-SGAS and the ORNL.

At FZJ the particle production and collection process as well as the suspension step is monitored by process control measurements applying mass spectrometry (i.e. MC-ICP-MS) and Secondary Electron Microscopy (SEM) measurements. MC-ICP-MS analyses were performed on the starting and diluted solution as well as on samples prepared by dissolving the microparticles with nitric acid from the quartz disc used for the collection of the microparticles. From these process control measurements, no unexpected deviation of the isotopic composition from the reference values of the certificate are evident. SEM measurements are conducted for process control on the very first quartz disc in the particle production and collection process to verify the overall size and shape as well as the number of collected particles.

The verification measurements of the final reference microparticles deposited on the GCDs produced during the suspension step 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 Large Geometry – Secondary Ion Mass Spectrometry (LG-SIMS) performed at Heidelberg University.

Figure 3 depicts exemplarily SEM micrographs with a typical shape, size and size distribution of the particles produced.

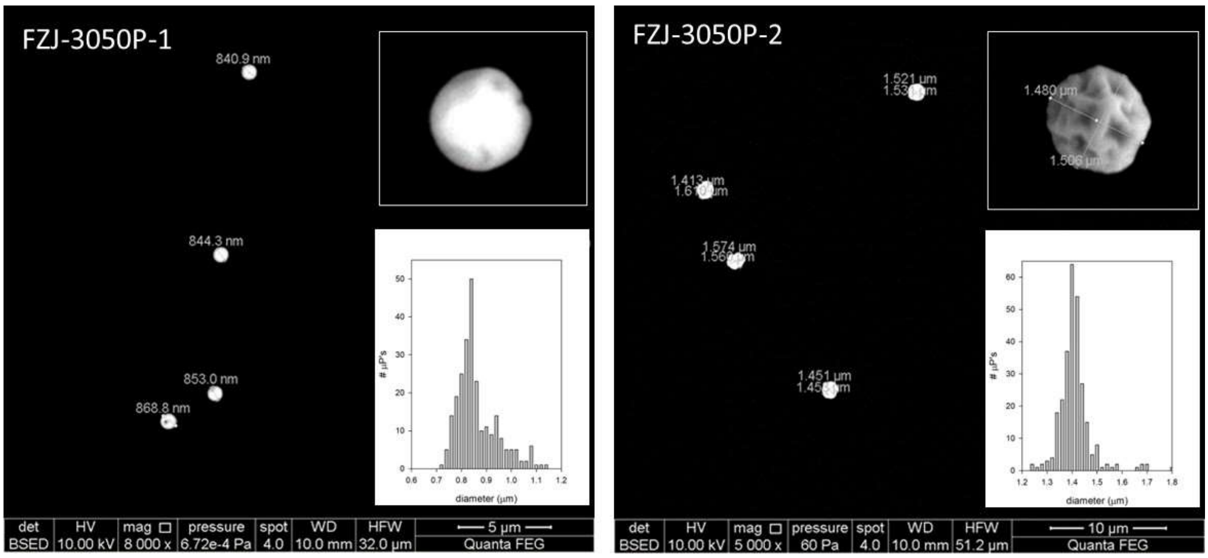

Figure 3: SEM micrographs from both batches of the particle production campaign. Left: FZJ-3050P-1, mean particle diameter of 0.84 µm; Right: FZJ-3050P-2, mean particle diameter of 1.40 µm.

The particles' size is in the expected range for the FZJ-3050P-1 and FZJ-3050P-2 batches. A mean size of 0.84 µm and 1.40 µm was measured, respectively. The particle size distribution is rather broad for the FZJ-3050P-1 batch in comparison to the particles of the FZJ-3050P-2 batch. The small particles were produced using a higher frequency (80 kHz) than the large particles (70 kHz) yielding in a larger number of droplets produced in the aerosol. Therefore, the probability of unification of two or even more droplets is much higher. Additionally, the modification of the frequency needs some process parameter alignment to optimise the monodispersity of the particle size distribution.

The determination of isotopic composition on single particles were performed for both batches at the Heidelberg Ion Probe 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 4 the particles with an intensity of more than 100 cps ^{235}U are plotted versus content of ^{235}U (atom%). The plot is showing a typical distribution of the calculated particle composition around the mean average value. From these measurements the absence of particles with unexpected isotopic value of ^{235}U is established and therefore, the effectivity of the post-production cleaning process demonstrated. The mean value does not reflect the exact reference value of 50.58 % ^{235}U from the certificate 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.

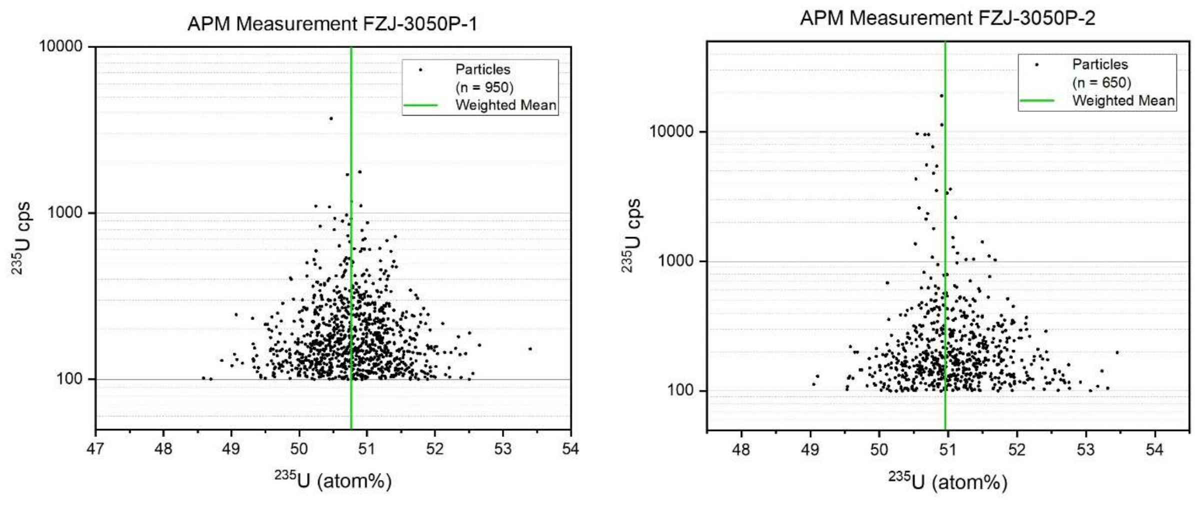

Figure 4: APM measurements on sample planchets containing reference microparticles with a mean diameter of 0.9 µm (FZJ-3050P-1) and of 1.4 µm (FZJ-3050P-2).

High resolution single particles measurements of isotopic composition were conducted on 20 particles randomly selected. In Figure 5 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-3050 mother solution. All isotopic compositions from measured particles are within the uncertainty of 2 σ in very good agreement to the reference values. These values have been discussed already with experts from IAEA-SGAS and have been accepted.

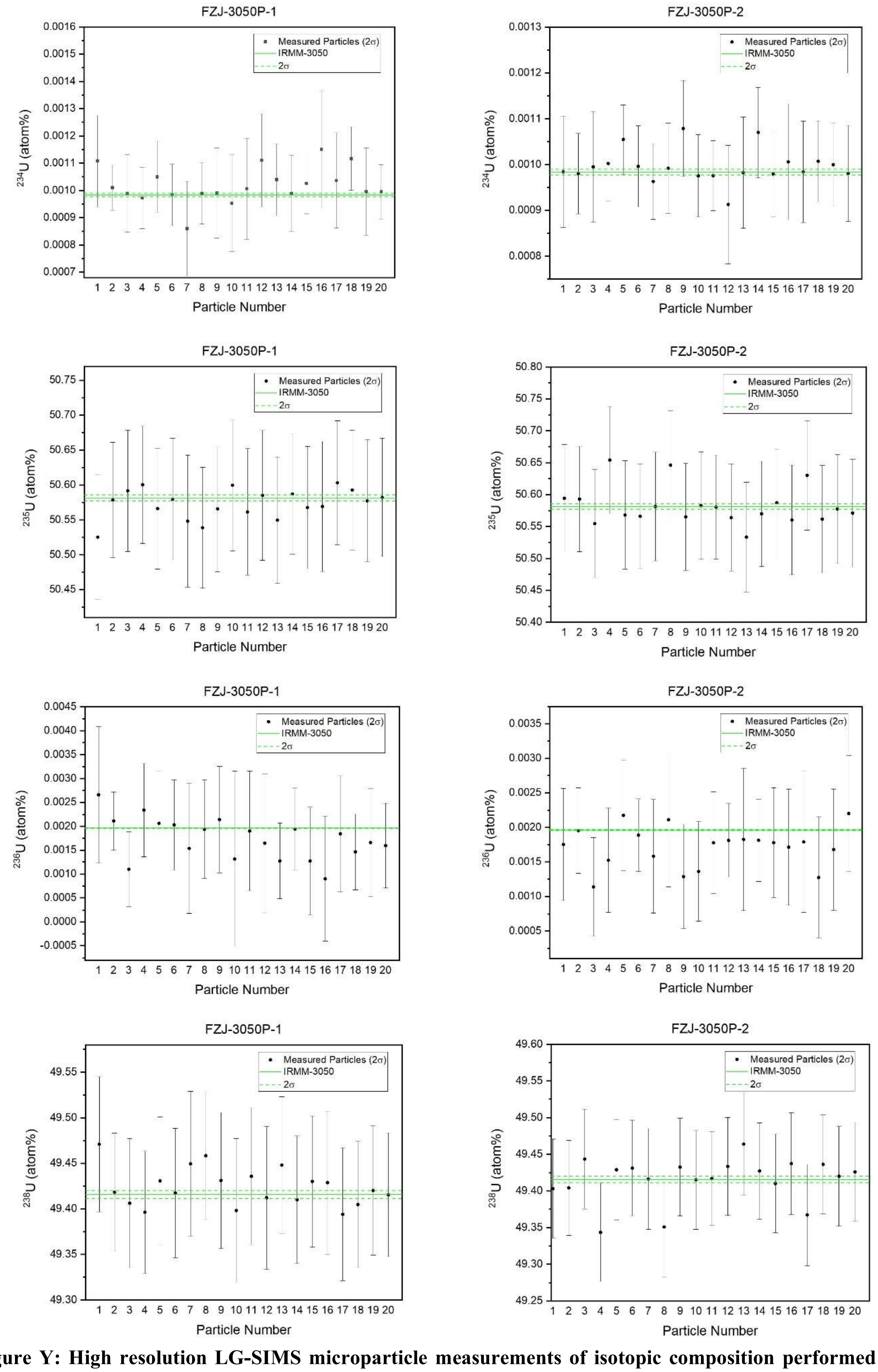

Figure Y: High resolution LG-SIMS microparticle measurements of isotopic composition performed on single particles of both batches.

Conclusions

For the first time high enriched uranium-oxide microparticle reference materials were successfully produced at the Forschungszentrum Jülich and characterised in cooperation with the 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 optimization as well as for method validation studies.

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