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Disclaimer and auspices

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Development of uranium reference particles to support nuclear safeguards

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Abstract

Controlled hydrolysis of certified uranium hexafluoride, carried out in a specifically constructed aerosol chamber, leads to the production of uranyl fluoride particulates which – deposited on a graphite planchet support - may be used as a quality control reference material. The particle size and surface distribution depends on several parameters, such as the relative humidity inside the aerosol chamber and the concentration of gaseous uranium hexafluoride, determined by the distillation conditions. The best quality samples were obtained at RH ranging from 55 to 70% and low gas amount. These improvements for a single deposition were used to prepare a reference sample with two different uranium enrichments. Preliminary SIMS measurements proved good results with respect to both types of particles. It was also revealed that – in some cases – the micrometer size uranium particles are accompanied by a large uranium background

Introduction

So-called “environmental sampling” is a powerful tool for the implementation of the Additional Protocol for the application of nuclear safeguards [1] to verify completeness and correctness of a state’s nuclear activities. The swipe samples collected by safeguards inspectors contain U-bearing particles, which are analyzed by the International Atomic Energy Agency (IAEA) network of analytical laboratories (NWAL). In order to strengthen this technique and help them in their analytical performance, there is a need for the development of uranium reference particles that resemble real-life particles and can be used as quality control samples.

Production of reference uranium particles has been carried out so far either by the controlled hydrolysis of uranium hexafluoride (UF_6) [2, 3, 4] or via nebulization of uranium nitrate solution [5, 6]. In the latter case, the particles are formed from dried droplets of a nebulized aqueous solution. They are monodisperse and their size depends on the aerosol quality. In case of UF_6 hydrolysis, the process is performed in an aerosol chamber [2, 4], where some of the gaseous UF_6 reacts with air moisture, forming UO_2F_2. A similar process also occurs in uranium enrichment plants when small amounts of UF_6 are released inadvertently into the atmosphere.

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

The solid phase formed in this reaction is hydrated uranyl fluoride which settles down as sub-micron size particles and HF remaining in the gas phase [7]. Te diameter of uranyl fluoride particles varies with values ranging from 0.5 to 2.2 μm and with a majority of particles having a diameter of around 0.7 μm [3]. A major factor influencing the particle size is the relative humidity in the aerosol chamber - particles formed at a relative humidity of less than 15% are found to be shaped as branched chains of tiny spheres, while those at 70% RH appear as individual, isolated, regular spheres. A relative humidity of more than 70% leads to progressive dissolution of their surface layers.

One of the ongoing research projects at EC JRC IRMM to support nuclear safeguards in the field of environmental sampling is the production of new certified test samples for NUSIMEP (Nuclear Signatures Interlaboratory Measurement Evaluation Programme) inter-laboratory comparisons, such as uranium reference particles. The particles are prepared from a well-characterized IRMM uranium hexafluoride reference material, certified for major and minor uranium isotope ratios. The first IRMM inter-laboratory comparison devoted to particle analysis, NUSIMEP-6 [8] was very successful with a positive feedback from the participants. This paper focuses on the development of the uranium reference particle production using the preliminary results of the recently optimized procedure for single and double deposition.

Materials and methods

Production of uranium reference particles via UF_6 hydrolysis has already been described elsewhere [2,3,4]. Briefly, a small amount of gaseous UF_6 trapped in a glass bulb is released, by breaking the bulb, into a specially-made aerosol chamber, where the RH is controlled by a humidity standard LiCl solution (Rotronic, Switzerland). The amount of UF_6 is dependent on the distillation time and temperature; the ampoule with UF_6 is kept at $-3^{o}C$ and the time of distillation varies from 20 to 40 s. Once the glass vial is broken inside the chamber, the particle supports, normally polished carbon disks, are inserted into the chamber to collect the freshly formed particles. The time elapsed between the gas release and particle collection, as well as the time of particle deposition varies from 20 to 40 min and from 3 to 4 hours, respectively. Imaging of the single and double deposition samples was carried out using a tungsten-filament FEI Quanta 200 3D scanning electron microscope (SEM). Secondary ion mass spectrometry (SIMS) measurements were performed applying a NanoSIMS CAMECA SAS, with which we obtained 10 μm x 10 μm ion images of particles deposited on the planchet with a spatial resolution of 300-400 nm using an O^- primary ion beam of about 50 pA.

Results and discussion

NUSIMEP-6 participants' feedback spurred the efforts made at IRMM to modify and improve the quality of the certified test samples used for inter-laboratory comparisons on uranium reference particles. Major concerns were the surface density of particles, the particle size and the uranium background detected on the disk surface around the particles. The reaction of UF_6 hydrolysis appeared to be influenced by a number of factors, of which relative humidity, rate of formation and amount of uranyl hexafluoride are considered the most important.

Single deposition

In order to decrease surface loading, we have changed the conditions of UF_6 distillation to reduce the amount of hydrolyzed gas. As the particle size depends also on the relative humidity, it was necessary to keep the RH inside the aerosol chamber between 55% and 70%. Keeping the RH within an even smaller range is difficult to achieve since the hydrolysis is carried out in ambient air with a given level of humidity. During the experiments, the RH could be kept at about 60% for most of the time, which resulted in good quality samples.

Another factor influencing the U-reference sample quality is the rate of UO_2F_2 formation, related to how the UF_6 is released into the air in the aerosol chamber. Fig 1 presents two SEM pictures of uranium oxyfluoride particles produced in two depositions. During the first one (Fig.1, left) UF_6 slowly diffused out of the vial, while during the second one (Fig.1, right) it was released immediately. Although the amount of UF_6 was doubled in the first case, the particle density was smaller than for the second deposition.

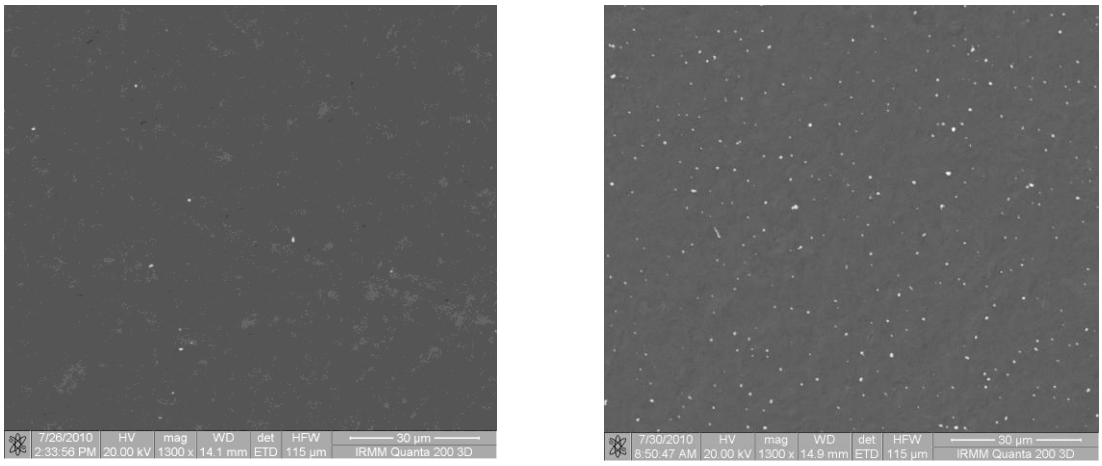

Fig.1. Two single depositions of uranyl fluoride particles

The presence of uranium background is also related to the rate of UF_6 release and hydration. According to the feedback of participants in NUSIMEP-6 the surface of some of the graphite disks was coated not only by particles but a uranium smear or film was also observed, creating a strong background signal (Fig.2).

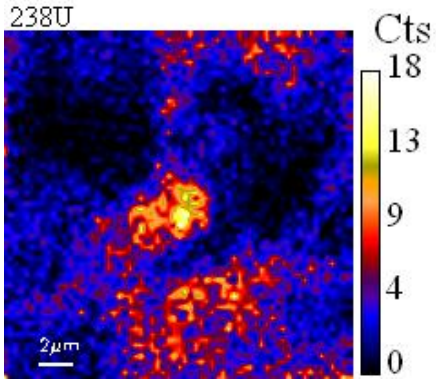

Fig.2. SIMS image of an individual uranium particle, with a large background of uranium.

This “U-smear” was considered as the most limiting factor for proper particle analysis by the NUSIMEP-6 participants. Therefore major emphasis was placed in reducing this U-film. From the preliminary results of further experiments we tend to believe that this uranium smear is composed of very small nm-sized particles that settle down on the surface together with the larger ones. This occurs particularly when uranium hexafluoride is slowly released into the air, instead of rapidly. However, this assumption needs to be investigated further.

Double deposition

We applied the procedure described above, optimized for a single deposition, to prepare a sample with particles of two different enrichments. The sample was composed of low-enriched uranium with a $n(^{235}U)/n(^{238}U)$ratio of ca 2% (LEU) and high enriched uranium with a $n(^{235}U)/n(^{238}U)$ ratio of 20% (HEU). The preliminary results, obtained from NanoSIMS measurements, showed that it is possible to distinguish particles with different uranium isotopic ratios on the same planchet (Fig.3.)

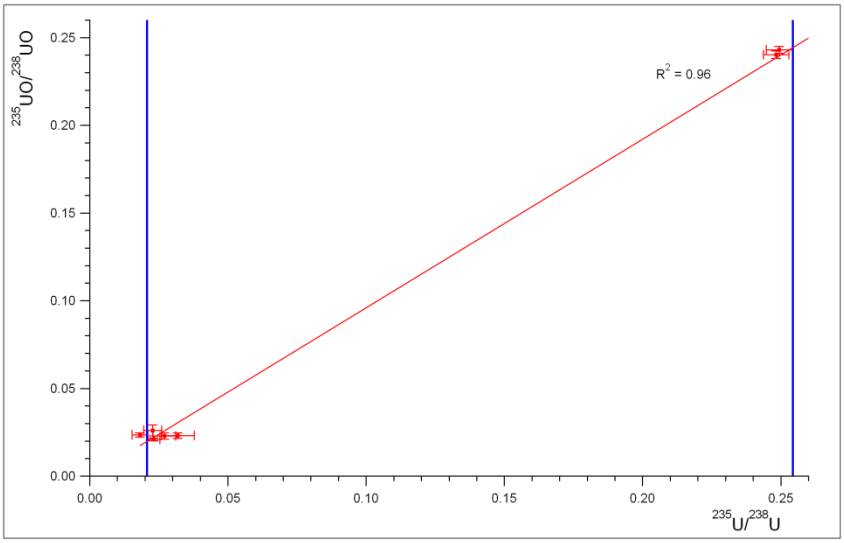

Fig.3 SIMS results of all the particles of $n(^{235}U)/n(^{238}U)$ratio of ca 2% (LEU) and $n(^{235}U)/n(^{238}U)$ ratio of 20% (HEU). Blue lines indicate $n(^{235}U)/n(^{238}U)$ ratio of the reference materials used for particle production.

Conclusions

By controlling the particle size and distribution of uranium reference particles on graphite supports, obtained by hydrolysis of UF_6, the quality of test samples has been improved. Tighter control of relative humidity during the reaction and reduction of the UF_6 concentration was an essential but not exclusive factor. The rate of gas release into the deposition chamber appears to be the determining factor for uranium background formation. However, this needs to be further investigated. Preliminary results on test samples with two uranium enrichments, i.e. 2% and 20% of U-235 proved that it is feasible to distinguish and analyse the particles with different isotopic compositions on the same graphite disk. This

optimised procedure will be applied for the preparation of the certified test samples in the next NUSIMEP inter-laboratory comparison organised for the IAEA Network of Analytical Laboratories

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