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Action Sheet 36 Final Report

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Final Report on Action Sheet 36
Study of Chemical Changes in Uranium Oxyfluoride Particles

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Pursuant to the Arrangement between the European Commission DG Joint Research Centre (EC-JRC) and the Department of Energy (DOE) to continue cooperation on research, development, testing, and evaluation of technology, equipment, and procedures in order to improve nuclear material control, accountancy, verification, physical protection, and advanced containment and surveillance technologies for international safeguards, dated 1 September 2008, the IRMM and LLNL established cooperation in a program on the Study of Chemical Changes in Uranium Oxyfluoride Particles under IRMM-LLNL Action Sheet 36.

The work under this action sheet had 2 objectives:

- Achieve a better understanding of the loss of fluorine in UO_2F_2 particles after exposure to certain environmental conditions
- Provide feedback to the EC-JRC on sample reproducibility and characteristics

Accomplishments under Action Sheet 36:

Expressly for the purposes of this study, Ruth Kips from LLNL traveled to Belgium and prepared two sets of uranium oxyfluoride particles at the Institute for Reference Materials and Measurements (EU-JRC-IRMM). The first set was prepared in January 2009 and the second set in January 2010. Approximately 250 UO_2F_2 particle samples were produced during these 2 visits. The uranium oxyfluoride particles were prepared from the hydrolysis of UF_6 and deposited onto graphite planchettes. Samples were shipped to LLNL in sealed containers under an inert atmosphere. Once at LLNL, they were removed from the inert atmosphere and placed into a controlled environment at a specific temperature and humidity.

For the study of chemical changes in uranium oxyfluoride particles, which started in June 2008, lab-synthesized UO_2F_2 particle samples were stored in different environmental conditions for various amounts of time. Changes in particle morphology, chemical composition and molecular bonds were measured by scanning electron microscopy combined with energy-dispersive X-ray analysis (SEM-EDX), micro-Raman spectroscopy (MRS), cryogenic laser-induced fluorescence spectroscopy (CLIFS) and nano-secondary ion mass spectrometry (NanoSIMS). In general, the decomposition of UO_2F_2 was found to be a very slow process, with fluorine still detectable by NanoSIMS after several months of storage. The rate of the loss of fluorine however, was found to be dependent on the relative humidity to which the particles were exposed.

The exchange visits between LLNL and IRMM scientists on the preparation and analysis of uranium oxyfluoride particles are part of the Action Sheet 36. It is within this context that Dr. Elzbieta Stefaniak (IRMM) visited LLNL for a period of 5 days in April 2010. During Dr.

Stefaniak's visit to the lab we demonstrated the analysis of uranium oxyfluoride particles produced at the IRMM using both the NanoSIMS and the SIMS 3f, hereby focusing on two specific programmatic responsibilities stated in the Action Sheet:

- LLNL will analyze the uranium oxyfluoride particles at defined time intervals to study the effects of time, humidity, temperature and lighting on the rate of fluorine loss
- LLNL will investigate the particle morphology, the density of particles on the graphite planchette and the presence or absence of a uranium film covering the planchette surface

The latter was verified by means of a Resistive Anode Encoder (RAE) on the SIMS 3f, which allows for the imaging of a 150 µm diameter area on the planchette's surface. Images of the uranium secondary ions recorded with the RAE detector after 5 and 900 seconds of sputtering are shown in *Figure 1*. The number of particles was very high for this area, which made it difficult to resolve individual particles. The particles appeared somewhat more clearly after 900 seconds of sputtering, but it remained inconclusive whether there was a film of uranium covering the surface.

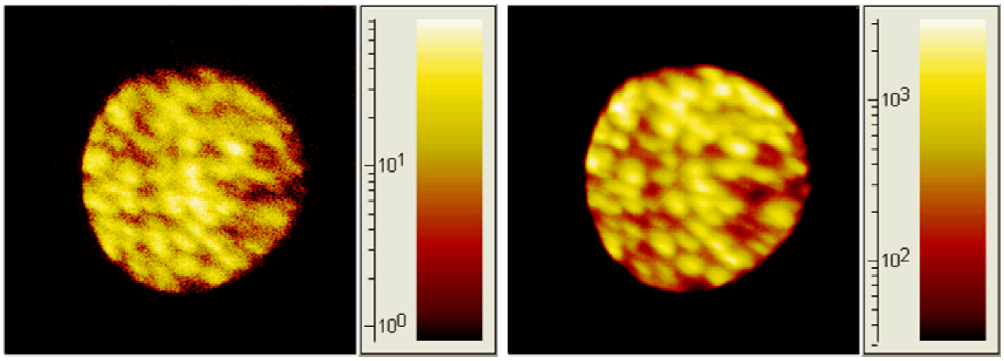

Fig 1: 150 µm RAE images of $^{238}U^+$ secondary ions collected after 5 seconds (left) and 900 seconds (right) of sputtering. The brighter the color in the images, the more secondary ions were collected at that position.These images show that the number of particles per surface area was very high for this sample, and that most of the uranium particles were still present after 900 seconds of sputtering.

One of the ongoing nuclear safeguards projects at the IRMM with respect to environmental sampling is the production of new certified test samples for NUSIMEP inter-laboratory comparisons. The last NUSIMEP campaign, NUSIMEP-6, was concluded in 2008 and involved the isotopic analysis of uranium oxyfluoride particles using secondary ion mass spectrometry. The feedback provided by the participating labs (including LLNL) allowed the IRMM to further improve the sample preparation process. For the next NUSIMEP campaign, the IRMM plans to use uranium oxyfluoride particle samples with two different enrichment levels. In this context, a stainless steel sample containing uranium oxyfluoride particles with an enrichment of 2 % and 25 % ^{235}U respectively was sent to LLNL for initial testing. SEM imaging showed a fairly low particle density (# particles/area) for this sample

(*Fig. 2*). Nine particles were located and measured for their uranium isotopic composition using NanoSIMS.

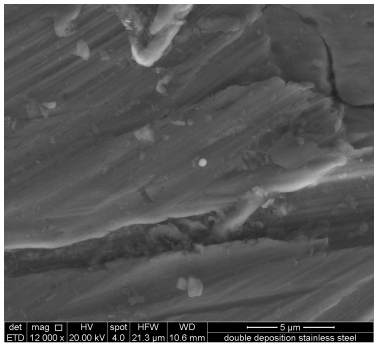

Fig 2: SEM image of a uranium oxyfluoride particle (white dot) on a stainless steel substrate.

The plot shown in *Figure 3* summarizing the $^{235}U/^{238}U$ ratio vs. $^{235}UO/^{238}UO$ ratio for the 9 particles analyzed indicated that no significant mixing occurred between the two different enrichment on this stainless steel substrate. Additional measurements on (graphite) planchettes with a higher particle load will have to confirm this conclusion.

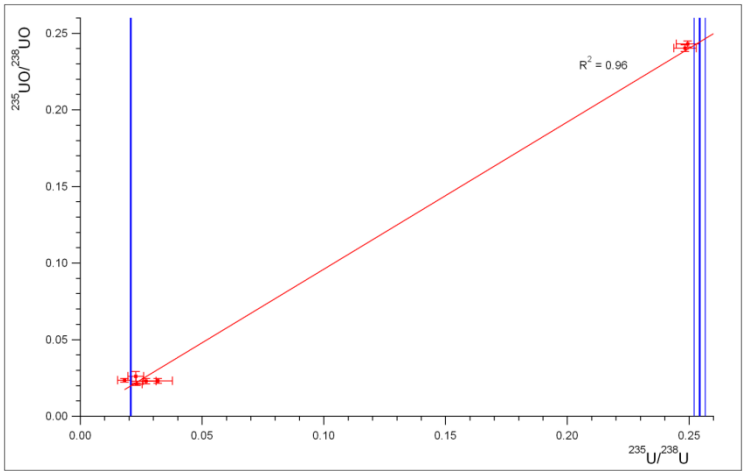

Fig 3: $^{235}U/^{238}U$ ratio plotted vs. $^{235}UO/^{238}UO$ ratio for 9 different particles showing 2 distinct uranium enrichment levels. Vertical lines indicate the certified isotopic composition of the two UF_6 materials used for this mixed deposition.

In addition to this experimental work, Dr. Stefaniak gave a presentation on the work performed at the IRMM and her project on 'The Development of Uranium Reference Particles' in particular. She also received a general lab tour.

<u>The work under this action sheet has had the following scientific and programmatic impact:</u>

- We developed protocols for analyzing individual micron-sized UO_2F_2 particles
- We found that the loss of fluorine from UO_2F_2 was a slow process in ambient air

- We identified relative humidity as the main factor in accelerating fluorine loss in UO_2F_2
- We found that the Raman signature was useful as a diagnostic tool for particles exposed to different relative humidities.
- We provided feedback on particle sample characteristics to IRMM, so that they could optimize their preparation process.
- We published several joint papers (Radiochim. Acta, J. Radioanal. Nucl. Chem), posters (IAEA Safeguards Symp.) and conference presentations and proceedings (MARC VIII, APSORC, INMM, IAEA SG Symposium, Pacifichem).