



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-410890

Study of Chemical Changes in Uranium Oxyfluoride Particles Progress Report June 2008 - February 2009

R. S. Kips, M. J. Kristo, I. D. Hutcheon

February 27, 2009

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Study of Chemical Changes in Uranium Oxyfluoride Particles

Progress report June 2008 - February 2009

Ruth S. Kips, Michael J. Kristo, Ian D. Hutcheon
Lawrence Livermore National Laboratory, Chemical Sciences Division
7000 East Avenue, Livermore, CA 94550

Executive summary

The present study aims to demonstrate how knowledge of time-dependent changes in uranium oxyfluoride particles can benefit particle analyses for environmental sampling. Environmental sampling depends upon laboratory analysis of nuclear material that has often been exposed to the environment after it was produced. It is therefore important to understand how those environmental conditions might have changed the chemical composition of the material over time. To investigate this, we prepared a set of uranium oxyfluoride particles at the Institute for Reference Materials and Measurements (IRMM - DG Joint Research Centre of the European Commission, Belgium). These UO_2F_2 particles were prepared from the release and subsequent hydrolysis of UF_6 gas, and were stored at LLNL in environmental chambers, set to different humidity, temperature and lighting conditions. An experimental plan was drafted to assess the number of analyses required to track the changes in particle composition, morphology, and structure.

Due to its high spatial resolution and excellent transmission, the NanoSIMS secondary ion mass spectrometer at LLNL was found to be the optimal tool to measure individual oxyfluoride particles. This was confirmed by our participation in the inter-laboratory measurement campaign for particle analysis (NUSIMEP-6), organized by the IRMM in June last year. The reported uranium isotope ratios demonstrated the precision and accuracy of the NanoSIMS and ims 3f SIMS measurements at LLNL, and provided a high degree of confidence that the new measurements on the UO_2F_2 samples will be of comparable high quality.

As fluorine is known to be a chemically-sensitive compound, we measured the intensity of the fluorine secondary ions relative to the ions generated by the matrix to evaluate the rate of particle degradation under different environmental conditions. A relative sensitivity factor was empirically determined to convert these measurements to absolute fluorine concentrations. Additional measurements in selected uranium compounds were carried out to account for variations in matrix composition. Because of the complexity of both the SIMS instruments, as well as the nature of the samples, we spent a substantial amount of time on instrument training and instrument set up. The latest NanoSIMS measurements on the freshly-prepared UO_2F_2 particles however, showed that we are on the right track when it comes to determining the chemical changes in individual uranium particles.

At PNNL, several optical techniques including cryogenic laser-induced time-resolved U(VI) fluorescence micro-spectroscopy, Raman spectroscopy, and Fourier transform infrared spectroscopy will be applied to investigate molecular transformations of the particles. As a control, dynamic SIMS measurements will also be performed on a subset of the samples sent to PNNL.

Sequence of events

This work has been performed under the auspices of the U.S. Department of Energy through a joint program between Lawrence Livermore National Laboratory (under contract DE-AC52-07NA27344) and the Pacific Northwest National Laboratory (under contract DE-AC05-76RL01830).

As an aid to the reader we provide a brief timeline of major events in this project:

- June 2006, IAEA issues SP-1 #06/PSA-03/*Study of Chemical Changes in Uranium Oxyfluoride Particles*.
- November 2006, LLNL receives SP-1 request from BNL.
- March 2007, LLNL submits an initial SP-1 proposal, “Study of Chemical Changes in Uranium Oxyfluoride Particles.”
- August 2007, LLNL and PNNL submit a combined SP-1 proposal, “Study of Chemical Changes in Uranium Oxyfluoride Particles.”
- December 2007, LLNL and PNNL make minor modifications to the SP-1 proposal to address USG concerns.
- March 2008, LLNL and PNNL notified that IAEA had awarded the SP-1 to Qinetiq and that NA-241 would fund the project.
- March 2008, Agreement reached with the interagency on tasking.
- April 2008 Funding received at LLNL/PNNL.
- June 2008, Ruth Kips arrives at LLNL.
- June 2008, Initial meeting between LLNL and PNNL to discuss project scope.
- July-October 2008, Laboratory set up and training.
- November 2008, IRMM indicates they will be unable to provide UOF particles on the time scale indicated in the SP-1.
- September – December 2008, initial analyses of standard uranium materials & development of analytical methods.
- January 2009, Ruth Kips visit to IRMM to produce particles required for this study.

Project Definition

Environmental swipe sampling was developed in the early 1990s as part of an effort to develop analytical techniques that are sufficiently sensitive and selective to detect traces of nuclear materials in the environment of a known or suspected facility [1]. Environmental sampling is performed by swiping surfaces in or outside the facility with pieces of cotton cloth. In the specific case of uranium enrichment facilities, uranium oxyfluoride particles are collected among millions of other dust particles. These uranium oxyfluoride particles stem from small releases of uranium hexafluoride (UF_6) gas, which hydrolyzes upon contact with moisture from the air.

The uranium isotopic composition of individual particles is used by safeguards organizations to verify whether a facility is compliant with its declarations. The present study aims to demonstrate how knowledge of time-dependent changes in chemical composition, particle morphology, and molecular structure can contribute to an even more reliable interpretation of the analytical results collected by environmental sampling. As uranium particles are known to be unstable with respect to loss of fluorine [2,3], the measurement of the residual amount of fluorine has the potential of placing boundaries on particle age and exposure history, complementing the information gleaned from uranium isotopics.

On June 30, 2008, Khris Olsen (PNNL) visited LLNL for the project kick-off meeting. The project outline was discussed and the following tasks were identified:

- *Sample preparation*

The Institute for Reference Materials and Measurements (IRMM - European Commission, DG Joint Research Centre, Geel, Belgium) was found to be the best source of uranium oxyfluoride particles. This research institute of the European Commission has the capability and equipment to produce uranium oxyfluoride particles from the release of uranium hexafluoride (UF_6) gas under controlled conditions. The apparatus is called the aerosol deposition chamber (Figure 1) and was specifically designed to produce uranium oxyfluoride particles that are similar in morphology and isotopic composition to the particles found in swipes from environmental sampling at uranium enrichment facilities [4].

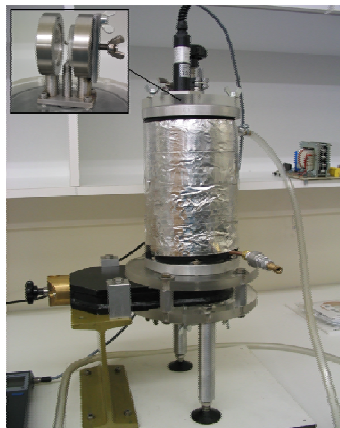


Fig. 1. The aerosol deposition chamber at the IRMM for the production of uranium oxyfluoride particles

During her Ph.D. project at the IRMM, Ruth Kips was involved with the design and optimization of the aerosol deposition process, as well as with the characterization of the particles produced by the chamber in different temperature and humidity conditions [5]. She has a thorough knowledge of the production process and of the analytical techniques and protocols best suited for characterization of uranium oxyfluoride particles. Ruth's contacts at IRMM will assist setting up a collaboration as the project moves ahead.

- *Sample storage*

It was decided at the kick-off meeting in June that all particle samples would be stored and aged at LLNL. The uranium particles produced at the IRMM should be shipped to LLNL as soon as possible after preparation to maintain control over the environmental conditions to which they are exposed. Preservation of the samples during shipment and international shipping requirements need to be addressed as well.

Upon arrival at LLNL, the particles should be stored in environmental chambers for which temperature, humidity and lighting can be set to fixed values. There were no environmental chambers readily available at the start of this project, and lab space also needed to be allocated. Previous experiments carried out by R. Kips and reports from D. Hembree and J. Carter [2,6] indicated that fluorine loss in uranium oxyfluoride particles typically occurs on the time scale of several months to years, depending on the environmental conditions. It was therefore decided to store the uranium oxyfluoride particles for up to 1 year.

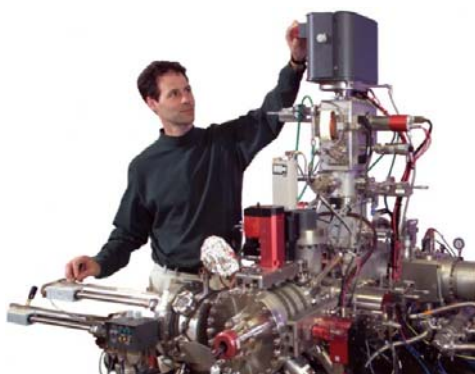


Fig. 2. Peter Weber and the NanoSIMS at LLNL

- *Particle characterization*

The task of characterizing the uranium oxyfluoride particles and determining the relative amount of fluorine after storage in the environmental chamber was divided between LLNL and PNNL. At PNNL, several optical techniques including cryogenic laser-induced time-resolved U(VI) fluorescence micro-spectroscopy, Raman spectrometry, and Fourier transform infrared spectroscopy would be used to investigate molecular transformations of the particles. As a control, dynamic SIMS measurements would be performed on a subset of the samples sent to PNNL.

The NanoSIMS at LLNL (Figure 2) offers the unique capability to measure the uranium-to-fluorine ratio in individual particles. The exceptional spatial resolution of this instrument allows for mapping of isotopic and elemental variations with a 50-100 nm resolution. The NanoSIMS is therefore capable of visualizing the fluorine distribution in particles of 1 micron or larger. In addition, it was agreed that conventional secondary ion mass spectrometry (SIMS) measurements of the relative amounts of fluorine in selected uranium compounds would be useful in providing benchmarks for comparison and quantitative evaluation of fluorine loss.

Although graphite planchets have been the substrate of preference for these uranium particle deposits, the wide range of analytical techniques used for particle characterization required the use of alternative substrate materials as well. Zinc selenide and sapphire were considered to be suitable substrates for the optical techniques carried out at PNNL. The determination of particle morphology and distribution on the (graphite) substrates through scanning electron microscopy (SEM) was assigned to LLNL.

Stage I - Experimental set up and instrument training (June - August 2008)

Before any of the uranium oxyfluoride particle (UO_2F_2) samples could be received by LLNL, suitable laboratory space to store and process the samples needed to be located. Instead of purchasing a new environmental chamber, we identified 4 environmental chambers on-site, that were not being used at that time (Figure 3). Not only was this approach more cost-efficient, but also allows us to carry out 4 experiments in parallel, with the 4 chambers at different humidity and temperature conditions.

The environmental chambers were installed in a dedicated and recently renovated laboratory in the basement of B151 and then tested at different relative humidity and temperature combinations. The aim was to set the chambers to those conditions that are realistic for certain climate conditions around the world. A warm and very dry environment is simulated with the ETS-type chambers, by setting the temperature to 40 degrees Celsius at a relative humidity of approximately 10%. The other ETS-type chamber is kept at the same low humidity, but a temperature of $25^\circ\text{C} \pm 0.5^\circ\text{C}$ is used.

The ThermoForma chambers (ThF1, ThF2), on the other hand, are used to attain very high humidity conditions of around $75\% \pm 1.5\%$. To be able to compare response of UO_2F_2 particles to differences in relative humidity, the same temperatures are used as for the ETS-type chambers, i.e., $25 \pm 0.5^\circ\text{C}$ and $40 \pm 0.6^\circ\text{C}$. Another environmental parameter that is likely to affect the rate of fluorine loss is exposure to light, ultraviolet light in particular. To accommodate this in our experimental set up, we replaced the fluorescent lamp in one of the ETS-type chamber with a natural daylight-simulating lamp that has UV-light in its spectrum. To evaluate the effect of lighting conditions, a perforated box was placed in two of the chambers to store a subset of the particle samples in the dark.



Fig. 3. The four environmental chambers at LLNL used for particle storage and conditioning

An Integrated Work Sheet (see Annex 1) summarizing the work to be carried out in the laboratory, including a description of the controls that will be implemented for those activities that have potential environmental, safety or health concerns was prepared. Next, an experimental plan was drafted to assess the number of analyses required to track the changes in particle composition, morphology, and structure (Table 1). This estimate allowed us to determine the number of particle samples required for this project. The IRMM was informed about our sample needs and agreed to provide the samples as part of a formalized collaboration (Action Sheet) between the Joint Research Centre of the European Commission and the U.S. Department of Energy (see Annex 2). However, the IRMM had a number of high priority orders for UF₆ certified reference materials and, having gone through a series of staff changes, the production of our uranium oxyfluoride samples was delayed from September-October 2008 to early 2009.

		ETS 1		ETS 2		ThF 1	ThF 2
		exp 1	exp 2	exp 1	exp 1	exp 1	exp 2
RH %	lighting	10	10	10	10	80	80
		UV	diffuse	diffuse	dark	diffuse	diffuse
		20	40	20	20	20	40
exp 1	1 day	x		x	x	x	x
	1 week	x		x	x	x	x
	2 weeks	x		x	x	x	
	3 weeks	x		x	x	x	
	1 month	x		x	x	x	x
	3 months	x		x	x	x	x
	1 year			x		x	x
exp 2	1 day		x				
	1 week		x				
	1 month		x				
	3 months		x				
	1 year		x				

Table 1. Experimental plan for the exposure conditions of the particle samples in the 4 environmental chambers (ETS1, ETS2, ThF1, ThF2)

While waiting for the UO₂F₂ samples to arrive, Ruth devoted a substantial effort to instrument training. The conventional secondary ion mass spectrometer (Cameca IMS 3f SIMS) and the NanoSIMS are complex instruments that require a lot of hands-on training. The training started off with sample loading/unloading, instrument start up and shutdown, primary and secondary beam alignment and mass calibration. Mass scans were performed on a set of uranium samples to become familiar with the interferences in the mass range around uranium. The analysis of a bulk UF₄ sample allowed for the identification of the uranium-fluoride secondary ions. Because of the large mass difference between fluorine ($m/z=19$) and the uranium oxyfluoride compounds ($m/z=235-276$), the NanoSIMS cannot detect both F and U-O-F secondary ions at the same time, i.e., using just one value for the magnetic field. (This issue does not arise for the ims 3f SIMS because this instrument operates only in single-collector mode and secondary ions are always measured by magnetic peak switching.) Therefore a detector set up was worked out that minimizes the number of jumps between magnetic field values, while covering all necessary masses.

The measurement of particle samples, as opposed to bulk materials, adds another degree of complexity to the analysis process: not only is a high spatial resolution required for these types of samples, the sputtering process and subsequent secondary ion yields are likely to depend on particle size and morphology. We therefore looked at uranium oxide particles, prepared from a bulk U-oxide sample, containing traces of fluorine. These particles proved particularly useful for setting up the mass calibration of the uranium oxyfluoride compounds.

Proficiency testing - NanoSIMS and SIMS particle analysis

As part of its quality assurance and control program, LLNL participates in round-robin exercises and inter-laboratory comparison campaigns. For the last Nuclear Signatures Inter-laboratory Measurement Evaluation Program (NUSIMEP), organized by the IRMM, participants received a sample of uranium particles with undisclosed isotope ratios on a graphite planchet. These isotope ratios were to be measured using the routine analytical procedures. The particle samples were prepared by the aerosol deposition chamber from the controlled hydrolysis of isotopically-certified uranium hexafluoride, and were therefore considered to be very similar to the particle samples that were going to be prepared for LLNL in the frame of this project. However, to insure stability of particle morphology and composition, the samples for the NUSIMEP exercise were heat-treated for several hours at 350 °C. This heat-treatment inherently removed most of the fluorine.

We determined the $^{235}\text{U}/^{238}\text{U}$ ratio in individual particles using the ims 3f and NanoSIMS spectrometers. The reported measurement results are presented in Figure 4 (ims 3f code 1767; NanoSIMS code 2110). Both techniques were capable of determining the isotopic composition with high accuracy and precision. However, the detection of individual particles on the ims 3f was hampered by the presence of a thin uranium film, covering the sample's surface. We therefore selected areas with increased uranium ion intensities for these analyses. The particle samples were analyzed by scanning electron microscopy afterwards.

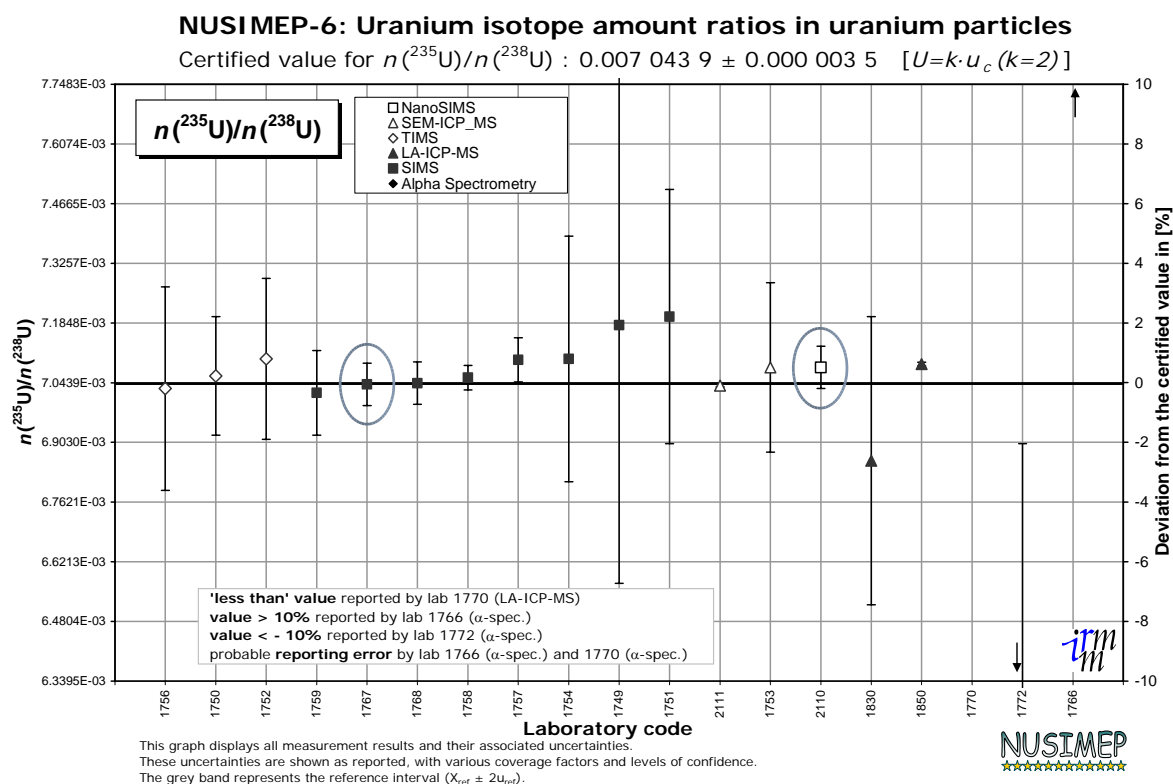


Fig. 4: $n(^{235}\text{U})/n(^{238}\text{U})$ for NUSIMEP-6 - Circled ratios were reported by LLNL through SIMS 3f and NanoSIMS

As this was the first NUSIMEP exercise on particle samples, feedback on the test samples was provided to the IRMM. The amount of particles on the substrate was on the high side for conventional SIMS analyses. The uranium background combined with the low spatial resolution (compared to NanoSIMS) made the detection of individual particles very difficult. The IRMM took this comment into account and will reduce the number of particles on the planchets for the next inter-laboratory measurement exercises. In parallel, we obtained a number of vacuum impactor heads from the Safeguards Analytical Laboratory of the International Atomic Energy Agency that will allow us to transfer some the particles from the graphite planchet onto a new planchet whenever the particle density is too high. This way, we will also eliminate the uranium background.

The data summarized in Fig. 4 demonstrate the precision and accuracy of the SIMS and NanoSIMS measurements carried out at LLNL and provide a high degree of confidence that the new measurements to be performed on the UO_2F_2 samples will be of comparably high quality.

Stage 2 -

Determination of the relative sensitivity factor (RSF) for F in U matrices (September - November 2008)

Secondary ionization mass spectrometry (SIMS) is a mature and highly successful analytical technique used to characterize the surface and near surface region of solids and some liquids [7]. The SIMS instruments at LLNL employ a beam of high energy primary ions (Cs^+ , O_2^+ , O^-) to sputter the sample surface, producing secondary ions that are detected by a double-focusing mass spectrometer. A primary beam of O_2^+ ions is typically used to produce electropositive species, whereas Cs^+ is preferred for electronegative secondary ions. The NanoSIMS uses O^- instead of O_2^+ primary ions for the production of electropositive species. The sputtering process is not limited to the surface layer, but consists of implantation of the primary ions into the sample and the removal of surface atoms through a so-called collision cascade. Typically, 3-6 mono-layers in depth are sampled.

SIMS data generally fall into three different categories: **mass spectra**, **depth profiles** and **ion images**. All three types of data were collected on the uranium samples.

Mass spectra show the secondary ion intensities as a function of mass and are generated by changing the magnetic field during sample sputtering. These spectra were collected on a set of uranium bulk and particle samples and were particularly useful in identifying those secondary ions that could be used to study the progressive changes in uranium oxyfluoride particles. As an example, the mass spectrum between m/z of 220 and 230 of a UO_2F_2 particle is presented in Figure 5. This spectrum was collected by the Cameca ims 3f at LLNL using an 12.5 keV O_2^+ primary beam. Although these measurement conditions typically result in a high degree of molecular fragmentation, major fluorine-containing molecular ions (UF^+ , UOF^+ , UF_2^+ , UF_3^+) were detected, in addition to the uranium peaks at mass 235 and 238. This survey spectrum therefore demonstrated that uranium-fluorine ions can be readily observed as positive molecular ions, even though fluorine and fluorine compounds are known to have high yields as negative secondary ions. The high intensity uranium oxide and dioxide molecular ions, at m/z of 254 and 270, respectively, were primarily formed by the UO_2F_2 particle, although a small fraction of these ions was produced by the combination of uranium with oxygen from the primary beam. Sputtering the sample with Cs^+ primary ions resulted in very high yields for F^- and F_2^- . These ions would make excellent indicators for the rate of fluorine loss, however, the secondary ion yields for the uranium and uranium oxide matrix compounds were considerably lower than with oxygen primary ion bombardment.

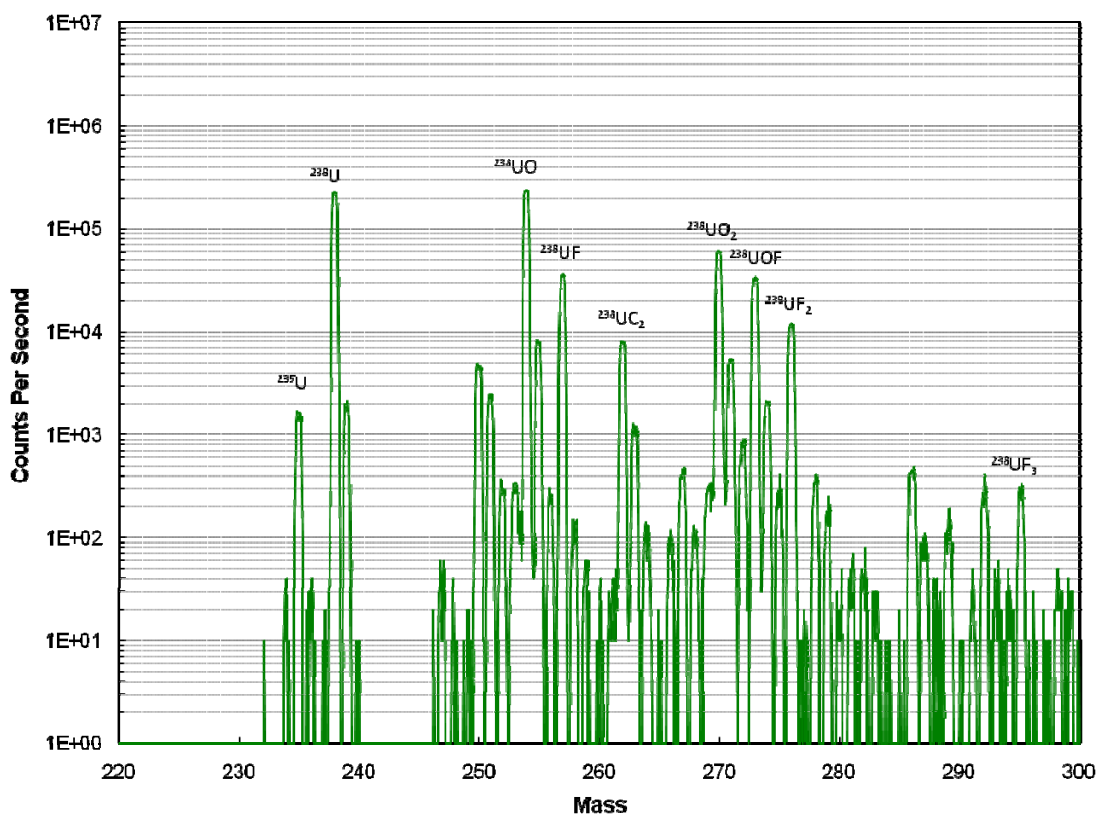


Fig 5. Mass spectrum between 220 and 300 amu of a UO_2F_2 particle as collected by the SIMS 3f at LLNL

When analyzing particles using NanoSIMS, data are typically collected as **ion images**. Ion images are generated by rastering a highly focused primary beam over a small area (2-20 μm on a side) on the sample surface. Each ion image or map shows the intensity of a certain secondary ion over the rastered area, usually containing 1 or more particles. The choice of secondary ions for these maps was determined by the mass survey spectra collected earlier. For the UO_2F_2 particle compounds analyzed with a Cs^+ primary beam, the following ion image species were selected: O^- , OF^- , F_2^- , O_2^- , $^{238}\text{U}^-$, UO^- , UF^- and UO_2^- . The primary beam was adjusted to increase the sensitivity for the uranium compounds. As a consequence, F could not be included in the analysis set up, as the count rate for the fluorine ions far exceeded the operation limits for the secondary electron multiplier (SEM) detector. The fluorine secondary ions were instead directed into a Faraday cup detector. From the ion images obtained with the NanoSIMS, we were able to determine the particle size and particle composition, as well as visualize elemental variations within individual, larger ($> 1 \mu\text{m}$) particles with a 50-100 nanometer spatial resolution. For data processing, custom software (L'Image, PXT PSearch) was used.

By repeating the collection of these ion images in a sequence made up of several measurement cycles, we gradually sputtered through the particle, generating a **depth profile**. In a depth profile, the secondary ion intensities are plotted as a function of the cycle number (analysis time). The collection of depth profiles allowed us to study the evolution of the relative intensities of the various single and molecular ions over time. In order to evaluate and compare the rate of fluorine loss between samples, however, we needed to establish a method to quantify the data. Quantification of secondary ion intensities remains difficult. As

demonstrated by the example described in the previous paragraph, secondary ion yields can vary over several orders of magnitude, and are often matrix dependent. These sensitivity variations cannot be accurately modeled based on theoretical calculations, and require the use of an empirically determined relative sensitivity factor (RSF) to convert the secondary ion count rates into concentration levels. For the trace analysis of fluorine in a uranium matrix, this RSF may be defined by:

$$C_F = RSF \cdot \frac{I_F}{I_{UO}}$$

In this equation, I_F and I_{UO} are the secondary ion intensities for fluorine and uranium oxide respectively, while C_F represents the fluorine concentration in atoms per unit of volume (atoms/cc). The RSF is therefore a function of both the element of interest and the matrix [7].

Experimental determination of the RSF for fluorine in a UO₂ matrix

The RSF for fluorine in a uranium oxide matrix was determined from Cameca ims 3f measurements on a uranium dioxide (UO₂) bulk sample that had been implanted with a known amount of fluorine ions. Depth profiles were recorded on a 225 x 225 μm raster over 240 cycles, with a Cs⁺ primary beam current of approximately 30 nA. The SIMS depth profile is depicted in Figure 6. The sample surface was contaminated with fluorine, resulting in an increase of the fluorine secondary ion intensity right after the start of the analysis. The implanted fluorine ions however, were only detected after several measurement cycles.

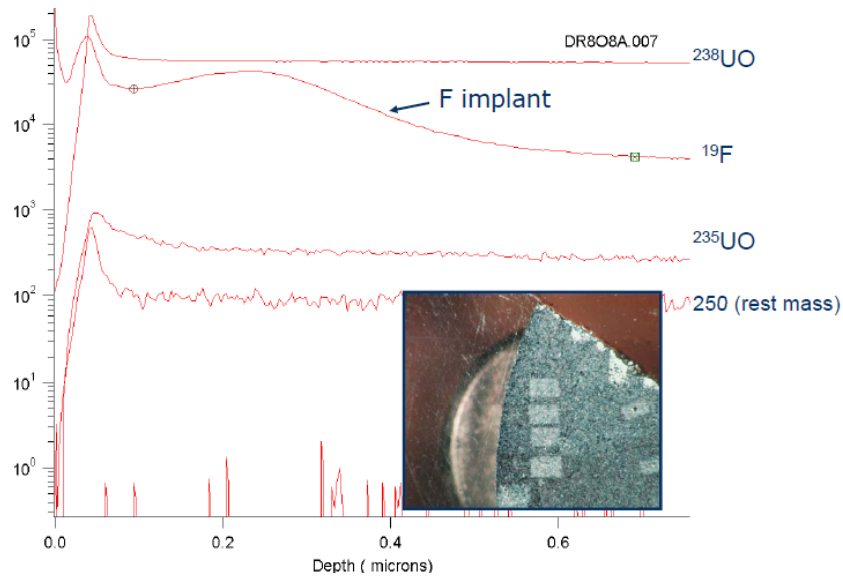


Fig 6. Depth profile of a fluorine-implanted UO₂ sample, collected by the SIMS 3f at LLNL
The picture shows a microscope image of the UO₂ sample, the SIMS rasters are clearly visible

While sputtering through the sample, and sequentially collecting the ions of $^{19}\text{F}^-$, $^{235}\text{UO}^-$, $^{238}\text{UO}^-$, a crater was formed in the UO_2 sample surface. We determined the dimensions of this crater at the end of the analysis through surface profilometry. Knowing the crater dimensions allowed us to calculate the volume of the UO_2 matrix material that was sputtered during the depth profile. By combining this information with other sample parameters such as sputtered area, atom density, etc. we were able to calculate the sensitivity factor for fluorine relative to uranium oxide. The average value of the RSF was found to be $7.54 \cdot 10^{18}$ atoms/cc, or 3076 (dimensionless) when multiplied with the atomic density of uranium oxide. No values were found in literature that could serve as a benchmark. We therefore repeated the measurements on a fluorine-implanted silicon metal and calculated the RSF for this sample. The RSF for fluorine in silicon has been determined by other research groups and our value was found to lie within the range reported in literature [7].

Determination of the fluorine concentration in uranium oxyfluoride particles

As a next step, the calculated RSF for fluorine in a uranium oxide matrix was applied to a set of nuclear forensics samples consisting of uranium oxyfluoride particles dispersed on a graphite planchet. By applying the RSF, we were able to convert the measured ratio of fluorine-to-uranium oxide secondary ions to an approximate fluorine concentration. First, a depth profile was recorded for two of the samples. The accelerating voltage of the Cs^+ primary ion beam was set to the same value as for the UO_2 F-implanted sample that was used to calculate the RSF. The primary current however, was reduced from 30 nA to 3.9 nA, as we were analyzing very fine uranium particles instead of a bulk material. To reduce the contribution of secondary ions from the graphite substrate, the sample area from which ions were collected was limited by a field aperture. In total, 7 particles from 2 different samples were analyzed. From these depth profiles, the approximate amount of fluorine was calculated by multiplying the F^- to UO^- ratio with the RSF ($7.54 \cdot 10^{18}$ atoms/cc). This resulted in a fluorine concentration ranging from 18 to 116 ppmw (Figure 7).

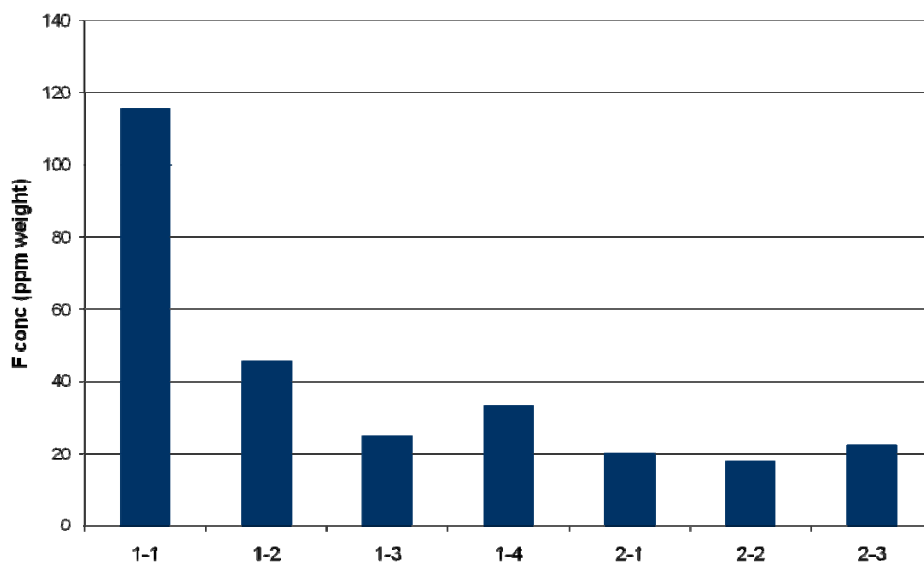


Fig 7. Fluorine quantification measurements on 2 nuclear forensic samples

A number of considerations need to be taken into account when applying a measured RSF to another type of uranium material. The sensitivity of a certain element, fluorine in this case, is often dependent on the matrix composition: a change of the chemical environment and chemical bonding may result in a change in ionization probability, and this has a direct effect on the secondary ion yield. In addition, the secondary ion yield for the element of interest may also vary depending on its concentration in the matrix.

We therefore investigated the relative secondary ion yield of fluorine in different uranium matrices with fluorine at varying concentration levels. The effect of the primary ion beam species (O^- , Cs^+ or O_2^+) was also included in this study. A UF_4 bulk sample and a fluorine-implanted UO_2 sample were analyzed, together with 2 particle samples. The first particle sample contained UO_2F_2 particles prepared from the hydrolysis of UF_6 in water, the other consisted of U_3O_8 particles with trace levels of fluorine. For all four samples, we collected energy dispersive X-ray spectra (EDX) by electron bombardment in the scanning electron microscope. The fluorine-to-uranium peak height was used to roughly compare the fluorine concentrations in the different sample types (Figure 8). The SEM-EDX spectra were also used to identify other elements in the samples, which may possibly interfere with the ions of interest during SIMS analysis.

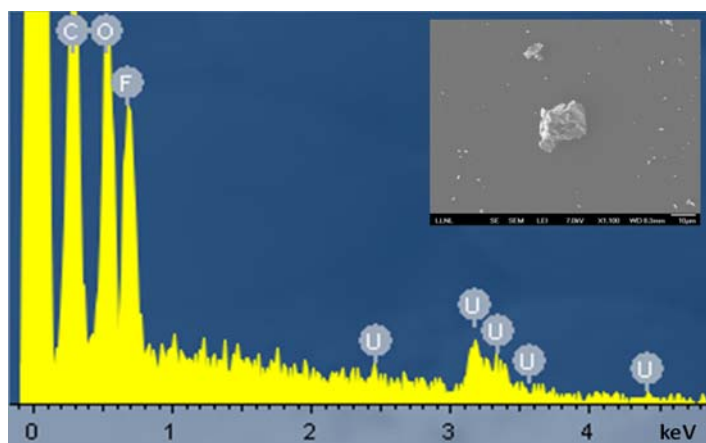


Fig 8. SEM image and EDX spectrum of a UO_2F_2 particle sample prepared from the hydrolysis of UF_6 in water
The fluorine-to-uranium peak height was used as an indicator for the relative amount of fluorine

In the second part of this investigation, we will determine the fluorine-to-uranium ion intensities by secondary ion mass spectrometry, which is several orders of magnitude more sensitive than SEM-EDX. The first NanoSIMS data were collected using a Cs^+ primary beam, while the ims 3f measurements were carried out in either Cs^+ or O_2^+ mode. The type of primary ion beam species that was used for the analysis depended on how the SIMS was set up at the time the instrument was available for our measurements. To quantify the rate of fluorine loss, the intensity of the fluorine ions is preferably compared to an ion species that does not include fluorine. For the initial UF_4 measurements on the NanoSIMS, however, the count rate on UO^+ was too low. We therefore used UF^+ as the reference ion, with an F^+ to UF^+ ratio of approximately 15 000. For bulk samples such as the UF_4 sample, the ion intensities stabilized after sputtering equilibrium was reached (plateau). The signal intensity for the particle samples on the other hand, was far less stable.

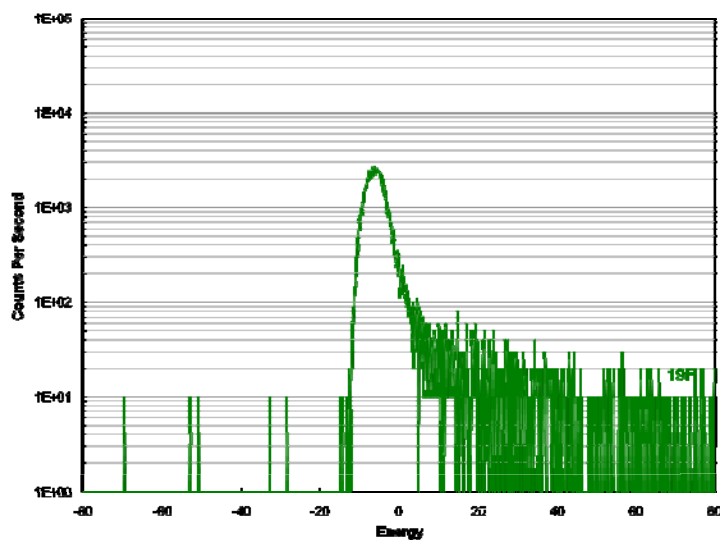


Fig 9. Measurement of the energy spectrum for fluorine with the energy slit set to a narrow energy band pass of ~5 eV at the peak's full width half maximum (FWHM)

For the SIMS 3f measurements, energy spectra were collected for the different ions of interest by gradually changing the voltage on the sample. Figure 9 and 10 show the importance of verifying the position of energy slit for all measurements. The ims 3f measurements were carried out with the energy slit fully open (Figure 10).

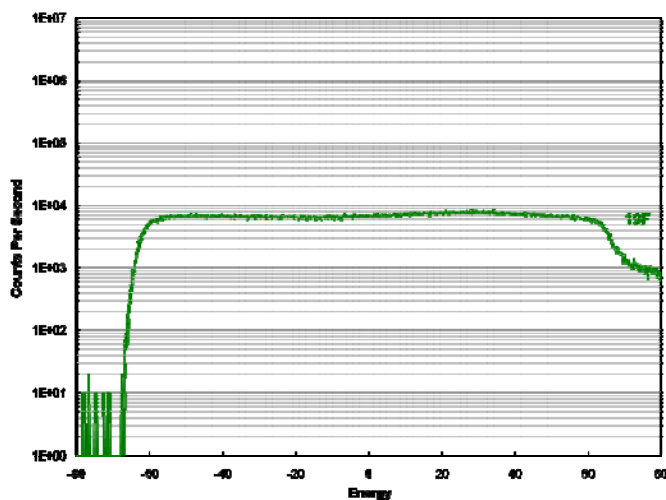


Fig 10. Measurement of the energy spectrum for fluorine with the energy slit fully open, i.e., energy band pass of > 130 eV

The ims 3f is less suitable for particle measurements due to its inferior spatial resolution, but generally produces higher count rates due to the use of substantially higher primary ion current. The first analyses on the UO_2F_2 particles using an O_2^+ primary beam, pointed towards an U^+ to F^+ ratio of 40. For the UF_4 bulk sample, a U^+ to F^+ ratio of 1.70 was achieved. With the instrument in Cs^+ mode, we obtained a F^- to UO^- ratio of around 250 for the F-implanted UO_2 sample.

Stage 3 -

Preparation of UO_2F_2 particle samples from the hydrolysis of UF_6

(December 2008 - February 2009)

Selection of the most suitable graphite substrate

The particles used for this project were prepared in the aerosol deposition chamber developed at the IRMM (Figure 1). This instrument produces uranium oxyfluoride particles from the release of UF_6 gas in an atmosphere with controlled temperature and humidity. Upon release in the aerosol deposition chamber, the UF_6 gas reacts with the atmospheric moisture forming uranium oxyfluoride particles and hydrogen fluoride. The particles formed this way are collected at the base of the chamber on graphite planchets. The aerosol deposition chamber is equipped with a platform that holds six 1" planchets. Because of the high amount of samples needed for this project, we preferred the use of smaller 3/8" planchets to increase the number of samples for every release of UF_6 . A set of 3/8" polished graphite planchets (Fullam, New York, no. 17620 grade A carbon) was sent to the IRMM for testing.

At LLNL, NanoSIMS measurements were performed on a suite of blank graphite planchets to check both the surface roughness and the fluorine background, as well as the presence of other contaminants. The following ion species were collected in a depth profile of 60 cycles using Cs^+ primary ion bombardment: $^{12}\text{C}^-$, $^{16}\text{O}^-$, $^{19}\text{F}^-$, $^{28}\text{Si}^-$ and $^{35}\text{Cl}^-$. The raster size was initially set to $50 \times 50 \mu\text{m}$. For the 3/8" polished planchets, the count rate for fluorine varied around 2000 cps and this was acceptable. The ion images however, did show fluorine 'hot spots' as opposed to a uniform and diffuse background of fluorine (Figure 11).

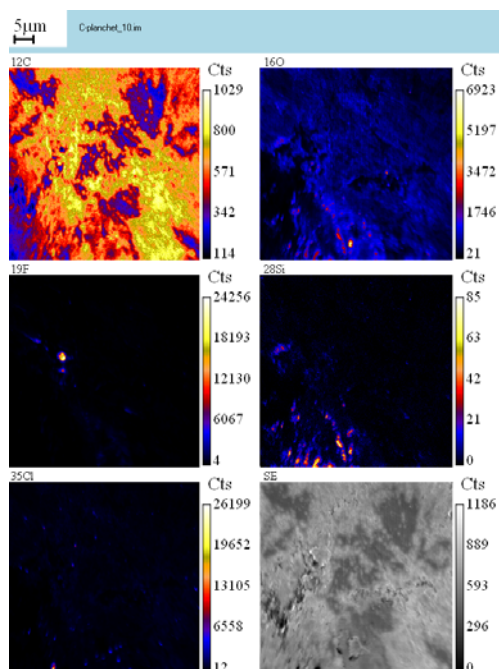


Fig 11. 5 ion images and 1 secondary electron image (bottom right) obtained via NanoSIMS by sputtering a $50 \times 50 \mu\text{m}$ raster. The ion images represent the individual maps of the secondary ion intensity for ^{12}C , ^{16}O , ^{19}F , ^{28}Si and ^{35}Cl . The fluorine ion image shows that there are high intensity 'hot spots' on the graphite planchet surface.

These fluorine hot spots were still detected after a depth profile measurement of 10 cycles, using a 5 x 5 μm raster. The ion images also showed a very low and diffuse background for silicon. The other substrates materials that were analyzed (Ted Pella vitreous carbon, Fullam pyrolytic graphite) were much smoother on the surface, but showed similar ion images for fluorine and silicon. It was therefore concluded that when particles with increased fluorine levels are detected on the samples, their uranium ion intensity should be checked to ensure the high levels of fluorine do not result from the graphite planchets.

Particle preparation and shipment

The 3/8" graphite planchets were sent to the IRMM, together with special sample containers for shipping the samples back to LLNL. Pacific Northwest National Laboratory (PNNL) sent their own substrates. These included zinc selenide and sapphire discs for the optical spectroscopy measurements (CLIFS, Raman, IR) and two different sizes of (pyrolytic) graphite planchets for ims 3f analysis.

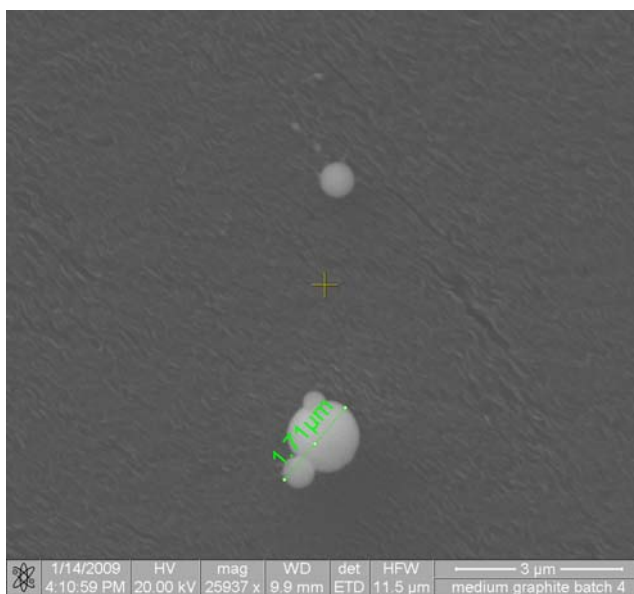


Fig 12. Scanning electron microscope (SEM) image of uranium oxyfluoride particles prepared from the hydrolysis of UF_6 gas in the aerosol deposition chamber

By the end of 2008, it was still unclear when the uranium particle samples for LLNL would be produced. The person responsible for the uranium particle production, Elzbieta Stefaniak, had only recently started at the IRMM and was not fully trained on the aerosol deposition chamber. LLNL and the IRMM therefore agreed to send Ruth to the IRMM in Belgium to train Elzbieta on the particle production, while at the same time producing the particle samples that were needed for this project.

Sample preparation at the IRMM started on January 5, 2009 and was completed on January 22, 2009. Ruth prepared a total of 11 batches of uranium oxyfluoride particle samples. Slightly depleted uranium hexafluoride gas ($^{235}\text{U} = 0.704\%$) was used for all of the samples. This UF_6 gas was distilled from an ampoule into a small glass vial. By cooling down the ampoule, we were able to control the amount of UF_6 transferred to the vial. The ampoule temperature was varied between 0 and -4°C to optimize the number of particles on the substrates. The glass vial containing milligram amounts of UF_6 was then placed into

the aerosol deposition chamber, which has a pin to break the vial once the desired humidity and temperature are reached. Studies have shown that the humidity of the air in which the UF_6 is released greatly determines the particle morphology. Most of the particle samples were prepared in high relative humidity conditions ($\sim 60\%$), resulting in spherical particles with little agglomeration. One experiment however, was carried out in air with a humidity of only 14.6%. In dry air, the uranium oxyfluoride particles are typically smaller and highly agglomerated [5,8], but this was not observed for that particular experiment. Elzbieta Stefaniak from the IRMM will therefore repeat the experiment and send us the particle samples that are characteristic for hydrolysis in low humidity air. The temperature of the air inside the chamber was around 22°C . Particles were collected in the aerosol deposition chamber for up to 20 hours after the UF_6 was released, and were then stored in a glove box with an inert atmosphere to minimize sample degradation. In total, we prepared 174 particle samples (graphite, zinc selenide and sapphire). From every batch, we selected 2 graphite samples for SEM imaging. These SEM images were necessary to record the particle morphology right after the particles were formed, and it also allowed us to estimate the number of particles on the substrate (Figure 12). The samples that had not been used for the SEM were numbered and shipped to LLNL in small containers filled with argon gas.

First NanoSIMS analyses on uranium oxyfluoride particles from the IRMM

To evaluate the rate of fluorine loss in particles exposed to different temperature, humidity and lighting conditions, we needed a reference value for the initial amount of fluorine. This value was determined by NanoSIMS analyses on a subset of uranium oxyfluoride particles that were stored in an inert atmosphere for 2-3 weeks before they were shipped to LLNL. For the first series of measurements a Cs^+ primary ion beam was used to determine the F/UF^- ratio. The measurements were carried either manually, by setting the raster to $2\text{-}3\ \mu\text{m}$ and sputtering through the particle in less than 30 minutes, or in automated mode, where a larger raster was selected (typically $9\text{-}20\ \mu\text{m}$) to cover several particles in one depth profile (Figure 13). The latter required further image processing (defining regions of interest) to determine the F/UF^- ratio of the individual particles. In both cases, the fluorine intensity decreased rapidly, and was reduced to background level at the end of each depth profile. Similar to previous analyses carried out in Cs^+ mode, the UF^- ion intensity was considerably lower than the intensity for the fluorine ions, and the UO^- ions were not detected.

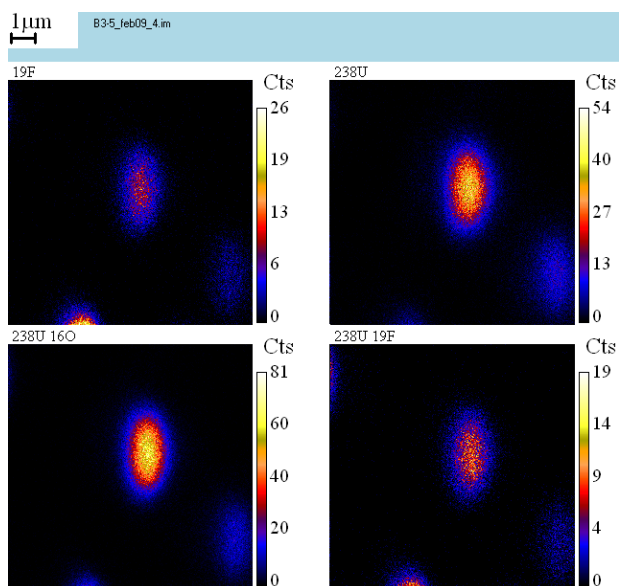


Fig 13. NanoSIMS ion images for $^{19}\text{F}^+$, $^{238}\text{U}^+$, UO^+ and UF^+ of a freshly-prepared uranium oxyfluoride particle

The data processing for these measurements is still ongoing. Measurements on the NanoSIMS using an O^- primary beam will increase the intensity of the uranium secondary ions and are planned for the end of February 2009. This increased sensitivity for uranium will also allow us to investigate the presence of a thin uranium film covering the planchet surface, as part of the Action Sheet collaboration between the U.S. Department of Energy and the European Commission's Joint Research Centre (see Annex 2). The presence of a thin uranium film was reported by several labs that analyzed the NUSIMEP-6 samples and was found to obstruct the analysis of individual uranium particles in these samples.

Conclusion & Outlook

In the first 8 months of this project we outfitted a dedicated laboratory and gathered all the necessary materials, equipment and instrumentation to adequately store and age uranium oxyfluoride particles. The European Commission's Institute for Reference Materials and Measurements (IRMM) was identified as the best source of uranium oxyfluoride particle samples and agreed to provide a number of samples as part of an Action Sheet collaboration. A proposal for this Action Sheet was drafted and submitted to NA-241. The particle production at the IRMM was delayed by several months, however, due to staff changes and unexpected high priority orders. It was therefore decided to send Ruth Kips to the IRMM to prepare the uranium oxyfluoride particle samples and move ahead with the project.

The task of characterizing the uranium oxyfluoride particles was divided between LLNL and PNNL. At LLNL, secondary ion mass spectrometry (SIMS) was used to determine the relative amount of fluorine in individual particles. Two instruments were applied: the Cameca IMS 3f ion probe and the high spatial resolution Cameca NanoSIMS 50. Although both instruments have been used for uranium analyses in the past, the analysis of fluorine and uranium in very small particles requires a well thought-out instrument set up in terms of detector position, primary ion beam, mass resolving power, etc. A substantial amount of time was therefore spent on instrument tuning and training.

To convert the measured fluorine-to-uranium ratios to an absolute fluorine concentration, we need to experimentally determine the relative sensitivity factor (RSF). We measured a suite of uranium samples and derived the RSF from a fluorine-implanted UO_2 sample. The RSF obtained from these measurements was applied to a set of uranium particle samples. The fluorine concentration that was calculated was in agreement with that obtained from previous measurements. However, the RSF is known to depend on fluorine concentration and matrix composition. We will therefore continue these measurements using both the ims 3f and NanoSIMS. The results from this study will not only be valuable for this project, but will benefit SIMS uranium-fluorine measurements in general.

Most of our research efforts in the second year of this project will be spent on the NanoSIMS analysis of the uranium oxyfluoride particles prepared at the IRMM in January, 2009 (addressing the original goal of the proposal submitted to NA-241 in May 2008). So far, 5 particle samples have been analyzed in both Cs^+ and O^- mode, to determine the fluorine-to-uranium ratio right after the particles were prepared ($t=0$ measurements). The other samples are being exposed to various temperature, lighting and humidity conditions in the environmental chambers at LLNL. They will be analyzed by NanoSIMS at specific time intervals, as laid out in Table 1. Due to the rather slow nature of particle weathering and the large number of samples to be analyzed, we expect these measurements to take up to one year. The particle morphology after exposure to the different environmental conditions and after NanoSIMS analysis will be verified by scanning electron microscopy (SEM).

In the frame of the Action Sheet collaboration with the IRMM, we will provide feedback on the uranium particle density (number of particles per rastered area) and whether a uniform uranium background was detected for these samples. In case the particle loading is too high for NanoSIMS or SIMS analysis, we will install the vacuum impactors, provided to us by the IAEA, to transfer a subset of the particles onto a new graphite planchet.

Finally, we will present the outcome of this work in peer-reviewed papers and at conferences.

References

- [1] D. L. Donohue, *Strengthening IAEA safeguards through environmental sampling and analysis*, Journal of Alloys and Compounds, **271-273** (1998) pp. 11-18.
- [2] J. A. Carter and D. M. Hembree, *Formation and characterization of UO_2F_2 particles as a result of UF_6 hydrolysis*, Task A.200.3, K/NSP-777, (1998) Oak Ridge Gaseous Diffusion Plant.
- [3] W. D. Bostick, W. H. McCulla, P. W. Pickrell and D. A. Branam, *Sampling and characterization of aerosols formed in the atmospheric hydrolysis of UF_6* , Oak Ridge Gaseous Diffusion Plant, (1983) Oak Ridge, USA.
- [4] R. Kips, A. Leenaers, G. Tamborini, M. Betti, S. Van den Berghe, R. Wellum and P. D. P. Taylor, *Characterization of uranium particles produced by hydrolysis of UF_6 using SEM and SIMS*, Microscopy and Microanalysis, **13** (2007) pp. 156-164.
- [5] R. Kips, *Development of uranium reference particles for nuclear safeguards and non-proliferation control*, University of Antwerp, (2008) PhD dissertation.
- [6] R. Kips, A. J. Pidduck, M. R. Houlton, A. Leenaers, J. D. Mace, O. Marie, F. Pointurier, E. A. Stefaniak, P. D. P. Taylor, S. Van den Berghe, P. Van Espen, R. Van Grieken and R. Wellum, *Determination of Fluorine in Uranium Oxyfluoride Particles as an Indicator of Particle Age*, Spectrochimica Acta Part B (in press).
- [7] R. G. Wilson, F. A. Stevie, C. W. Magee, *Secondary ion mass spectrometry - A practical handbook for depth profiling and bulk impurity analysis*, (1989) John Wiley & Sons.
- [8] P. W. Pickrell, *Characterization of the solid, airborne materials created by the interaction of UF_6 with atmospheric moisture in a contained volume*, K/PS-144-DE82 015436, Union Carbide Corporation, Nuclear Division, (1982) Oak Ridge Gaseous Diffusion Plant.

Annex I - Integration Work Sheet

IWS Summary:			
IWS #:	WAL:	Int Start Date:	Est Comp Date:
14671 r2	B	01-OCT-08	On-Going
Title:			
Study of Chemical Changes in Uranium Oxyfluoride Particles			
Description:			
<p>This study involves the characterization of uranium oxyfluoride particles stored in environmental chambers at different humidity and temperature levels for varying amounts of time. Polished graphite planchets (25 mm diameter) containing micrometer-sized uranium oxyfluoride particles will be exposed to air of varying relative humidity and temperature. The planchets will be distributed over 4 environmental chambers, each having a different relative humidity and temperature setting. Air temperature in the chamber will vary between 10-50 degrees Celsius. The relative humidity will be set to either less than 20% or more than 70%. Two types of environmental chambers will be used: 2 ETS-518 glove box type chambers and 2 ThermoForma 29 cu. ft. chambers. The chambers may be connected to a bottle with liquid CO2 for additional cooling. The work proposal also includes exposure to ultraviolet (UV) light. A UV lamp will be implemented in at least 2 of the chambers. To determine the long-term effects of these exposure conditions, the planchets will be stored in the chambers for up to 2 years. The uranium in these particles is primarily depleted uranium. The amount of uranium on each of these planchets is in the microgram range. The individual particle size ranges from approx. 10 nm to 2.5 micrometer. Up to 50 samples are estimated to be stored in the environmental chambers. The activity of each of these samples was calculated to be significantly less than 1 nCi. The planchets will be removed from the chamber at certain time intervals for a micro-analytical study of the particle morphology and composition. This analytical work will be carried out at different locations and is covered by other Integration Work Sheets.</p>			
Authorizing Organization:			Authorizing Individual:

Science and Technology Principal Directorate • Physical and Life Sciences • CHEM (Chemical Sciences Div)					GAYLORD, REGINALD F	
Responsible Individual:					Submitter:	
KRISTO, MICHAEL J					KIPS, RUTH S	
Concurrence Statuses:						
Loc • Fac/Wing • Room • Team	ES&H	FAC	Add Con Loc	RI	Add Con IWS	AI
LLNL-Facility • 151 • B-124 • ES&H Team 2	CONCUR 21-OCT-08 Borenstein	CONCUR 28-OCT-08 Marks	N/A	CONCUR 19-SEP-08 Kristo	N/A	AUTHORIZED 28-OCT-08 Gaylord
Attached Documents: <i>View documents attached to this IWS</i>						
Name:			Modified:			
Activity estimation - [Download]			09/30/2008 - 02:28pm			
Privacy and Legal Notice						

Annex II - Action Sheet Proposal between US DOE and EC-JRC

ACTION SHEET 13

between

The United States Department of Energy (DOE)

And

European Commission – Joint Research Centre (EC-JRC)

For

Study of Chemical Changes in Uranium Oxyfluoride Particles

1. Introduction

Pursuant to the Agreement between the U.S. Department of Energy (DOE), National Nuclear Security Administration (NNSA) and the European Atomic Energy Community, represented by the Commission of the European Communities (the European Commission) in the field of nuclear materials safeguards research and development, signed January 6, 1995, DOE/NNSA and the European Commission (the Parties) will continue cooperation on a program to collaborate on the Study of Chemical Changes in Uranium Oxyfluoride Particles.

2. Background

The IAEA incorporated environmental swipe sampling into their overall Safeguards program in the early 1990s as part of an effort to detect traces of nuclear materials in the environment of a known or suspected facility. In the specific case of uranium enrichment facilities, uranium oxyfluoride particles are collected among the millions of other dust particles. These uranium oxyfluoride particles stem from small releases of uranium hexafluoride (UF₆) gas, which hydrolyzes upon contact with moisture from the air. The IAEA uses the uranium isotopic composition of individual particles to verify whether a facility is compliant with its declarations. The present study, however, aims to demonstrate how knowledge of time-dependent changes in chemical composition, particle morphology, and molecular structure can complement the information gleaned from the uranium isotopics. Since environmental sampling depends upon laboratory analysis of nuclear material that has often been exposed the environment after material production it is important to understand how those environmental conditions might have changed the chemical composition of the material over time, particularly for chemically sensitive compounds.

3. Scope of Work

This Action Sheet provides for the collaboration between DOE and EC-JRC on the preparation and analysis of uranium oxyfluoride particles. This collaborative effort is a joint activity between DOE/NNSA and EC-JRC. Activities will be coordinated between these two collaborators.

The activity under this action sheet will include technical collaborations between DOE laboratories and EC-JRC. These technical collaborations will include activities such as the preparation of uranium oxyfluoride particles from the controlled hydrolysis of UF_6 gas, the analysis of these particles by a wide range of analytical techniques to identify the parameters that control the rate of fluorine loss in these particles, and the exchange of samples and information that are required to carry out this research.

4. Program Management

The work is to be performed by Lawrence Livermore National Laboratory (LLNL) and the EC-JRC. It is understood that LLNL will manage all interfaces between LLNL and the EC-JRC. The level of effort for each party is outlined in Appendix 1. Appendix 2 identifies key personnel to work on this project. Appendices 1 and 2 shall be reviewed annually and updated as appropriate.

Project reports will be prepared and distributed to DOE and EC-JRC as necessary, and a complete status report will be prepared prior to the end of each fiscal year

5. Fiscal Management

DOE shall be responsible for the budget planning and financial management of LLNL activities and shall make best efforts to complete the activities agreed upon in Appendix I satisfactorily.

EC-JRC shall be responsible for the budget planning and financial management of EC-JRC activities and shall make best efforts to complete the activities agreed upon in Appendix I satisfactorily.

6. Duration and Termination

This Action Sheet shall enter into force upon the later date of signature and shall continue in force until mutually agreed by the parties that all activities under this Action Sheet are completed.

For the EC-JRC

For the United States Department of Energy

Signature: _____

Signature: _____

Printed Name:

Printed Name:

Kurt Siemon

Title:

Title: Director, Office of Dismantlement and
Transparency

Date: _____

Date: _____

1. Project Outline

This project involves collaboration between LLNL and European Commission – DG Joint Research Centre - Institute for Reference Materials and Measurements (EC-JRC-IRMM) on the Study of Chemical Changes in Uranium Oxyfluoride Particles.

- A. Preparation of uranium oxyfluoride particles from the controlled hydrolysis of UF_6
- B. Acquisition of environmental chambers for the storage of the uranium oxyfluoride particles under controlled temperature, humidity and lighting conditions
- C. Scanning electron microscope measurements to investigate changes in particle morphology
- D. NanoSIMS analysis of uranium oxyfluoride particles to determine changes in chemical composition, especially the (relative) amount of fluorine in individual particle
- E. Exchange visits of LLNL and IRMM scientists on the preparation of uranium oxyfluoride particles and the analysis of nuclear material by isotope mass spectrometry
- F. Report preparation

2. Programmatic Responsibilities

- A. IRMM will prepare a set of uranium oxyfluoride particles from the controlled hydrolysis of UF_6 using the aerosol deposition chamber. The number of samples and the specific conditions in which these samples will be prepared will be agreed on by both parties.
- B. IRMM will take care of the packaging and shipment of these samples to LLNL. LLNL will provide the necessary sample containers to ship the samples.
- C. LLNL will carry out Secondary Ion Mass Spectrometry measurements with a spatial resolution in the 50-100 nm range (NanoSIMS) upon sample arrival to obtain a 't = 0 value' for the amount of fluorine in individual particles.
- D. LLNL will perform Scanning Electron Microscopy (SEM) to capture the particle morphology before storage in the environmental chamber.
- E. LLNL will provide storage space in an environmental chamber to keep the particle samples at certain humidity, UV-light and temperature levels during storage.
- F. LLNL will analyse the uranium oxyfluoride particles at defined time intervals to study the effects of time, humidity, temperature and lighting on the rate of fluorine loss.
As a complement to the measurements in (F), LLNL will investigate the particle morphology, the density of particles on the graphite planchet and the presence or absence of a uranium film covering the planchets surface.
The analysis techniques that will be applied for this include Scanning Electron
- G. Microscopy combined with Energy-Dispersive X-ray Analysis (SEM-EDX) and NanoSIMS.
- H. LLNL will report on the outcome of these experiments.
- I. Joint report/publication by LLNL and IRMM.