LLNL-PROC-488375

Characterization of Uranium Oxyfluoride Particles for Nuclear Safeguards

R. Kips, M. Kristo, J. Crowhurst, I. Hutcheon

June 16, 2011

Annual Meeting Institute for Nuclear Materials Management
Desert Springs, CA, United States
July 17, 2011 through July 21, 2011

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.

CHARACTERIZATION OF URANIUM OXYFLUORIDE PARTICLES FOR NUCLEAR SAFEGUARDS

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

Lawrence Livermore National Laboratory, P.O. Box 808, L-231, Livermore, CA 94551, USA

ABSTRACT

Nuclear safeguards at enrichment facilities largely relies on environmental sampling, where uranium particulate material is collected in swipe samples for mass spectrometric analysis. The fluorine-bearing uranium particles (UO_2F_2) found in these swipe samples are the reaction product of small releases of UF_6 to the atmosphere. Even though mass spectrometric analysis remains the primary analytical method used in environmental sampling, additional morphological, elemental and spectral characterization of the collected particulate material would provide a more complete picture of the activities at the inspected facility. In this study, scanning electron microscopy combined with energy-dispersive X-ray analysis (SEM-EDX), nano-scale secondary ion mass spectrometry (NanoSIMS) and micro-Raman spectroscopy were applied in a multi-technique approach to the characterization of lab-synthesized UO_2F_2 particles. An important part of this work was devoted to the development of a relocation method that enabled the characterization of the same set of particles by SEM and NanoSIMS. Selected UO_2F_2 particles of specific morphology were identified and characterized by SEM before and after NanoSIMS analysis to determine whether a correlation exists between the particle morphology, the level of sputtering and the relative amount of fluorine.

INTRODUCTION

Environmental sampling is one of the most powerful tools IAEA safeguards inspectors have at their disposal. It relies on the collection and analysis of traces of nuclear material that carry the same elemental and isotopic information as the processed, bulk material [1]. These so-called nuclear fingerprints are in fact very small uranium particles, collected among a majority of natural uranium and other dust particles. Despite their small number and size, the information that can be derived from these particles is substantial [2].

A typical analysis of an environmental sample is a two-fold process: the mass spectrometric measurement of the sample as a whole, i.e., bulk analysis, provides high sensitivity (pg – ng range) and selectivity, but suffers from the effects of averaging all the particles present in the sample [3]. The analysis of single particles is therefore a highly valuable complement, even though their size and number makes the analysis more complex and time-consuming.

Routine techniques applied for the analysis of single particles from environmental sampling include secondary ion mass spectrometry (SIMS) and fission-track thermal ionization mass spectrometry (FT-TIMS) [4,5]. Both techniques measure the uranium isotopic composition of individual particles, which is crucial to the identification of the nuclear process. However, isotopic composition is not the only piece of the information that can be derived from these particles.

Particle morphology, purity, structure, bonding and other characteristics may have high diagnostic value as well [6].

Case studies have already demonstrated the benefits of a multi-technique approach to the characterization of individual particles from the nuclear fuel cycle [2,6-9]. Techniques capable of analyzing particles in the micrometer size range, including SIMS and micro-Raman spectroscopy, have been applied in a purely fingerprinting manner to compare and categorize particle characteristics [6]. For this work, synthesized particles of uranium oxyfluoride (UO_2F_2) were analyzed by scanning electron microscopy combined with energy-dispersive X-ray analysis (SEM-EDX), nano-scale secondary ion mass spectrometry (NanoSIMS) and micro-Raman spectroscopy. An important part of this effort was devoted to the development of a procedure that enabled the relocation of the same set of particles between the different analytical instruments. Using this relocation technique, a number of UO_2F_2 particles with specific morphology were characterized by SEM before and after NanoSIMS analysis in order to correlate the ion depth profiles with the particle morphology and relative amount of fluorine.

EXPERIMENTAL

URANIUM OXYFLUORIDE PARTICLE SAMPLES

The UO_2F_2 particles analyzed in this work were obtained from the Institute for Reference Materials and Measurements (IRMM, European Commission, Belgium). Particles of UO_2F_2 were produced expressly for these experiments from the hydrolysis of gaseous UF_6 in a closed air volume. Upon release, the UF_6 quickly hydrolyzed to HF and particulate UO_2F_2 (Equation 1) [10]. Details on this method can be found in [11].

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF \quad \text{(Eq. 1)}$$

The UO_2F_2 particles were collected on graphite substrates (Ernest F. Fullam, New York) by gravitational settling and were placed in containers filled with argon for shipment to Lawrence Livermore National Laboratory (LLNL, US Department of Energy, Livermore, California, USA). The graphite planchets could be directly inserted into the different analytical instruments, yet for particle relocation purposes, the particles were transferred from their original substrates to a 1” diameter vitreous carbon planchet (Ted Pella, USA). The vitreous carbon planchets have a mirror-finish surface and were divided into quadrants for relocation on the SEM and NanoSIMS. The device that was used for the particle transfer is a so-called vacuum impactor, and is also used by the IAEA. It uses a stream of air at a flow rate of approximately 4.5 l/min to remove particles from their original substrate and deposit them onto a vitreous carbon planchet in the center of the impactor head. The efficiency of our set up is low due to bounce-off and size separation effects. However, given the very high number of particles on the original graphite substrates, the number of particles on the vitreous carbon planchet was found to be optimal for relocation and analysis purposes.

SCANNING ELECTRON MICROSCOPY – ENERGY-DISPERSIVE X-RAY ANALYSIS (SEM-EDX)

An FEI Inspect F scanning electron microscope was applied to characterize the morphology of the UO_2F_2 particles. Imaging was performed in both secondary and backscattered electron mode. Typical operating conditions of the instrument were 15 keV at 10 mm working distance.

MICRO-RAMAN SPECTROSCOPY

The Raman measurements were collected with 632.8 nm (red) incident radiation produced by a HeNe laser. This was the longest wavelength available, and carried the least amount of energy per photon. The laser power was limited to 2.1 mW using neutral density filters. The laser light was directed towards the sample using a band pass cube focused to about 1 μm spot size with a 100× apochromatic objective lens (Mitutoyo, Japan). Scattered light was collected with the same objective and was focused onto a pinhole before being directed into the spectrometer (Horiba Jobin Yvon HR460, Japan). Holographic filters were used to reject elastically scattered laser light. The position of the spectral lines produced by a neon lamp were recorded for calibration purposes. Then again, the width of the Raman peaks produced by the samples was generally much larger than the spectral resolution, therefore small instrumental non-linearities were ignored. Also, no correction was made over the relatively small spectral range for variations in instrumental sensitivity. The indicated frequencies of the Raman bands represent the estimated positions of the maximum Raman scatter intensity (without peak fitting).

NANOSCALE SECONDARY ION MASS SPECTROMETRY (NANOSIMS)

The NanoSIMS 50 (Cameca, France) is a secondary ion mass spectrometer that produces ion images of exceptionally high spatial resolution. The combination of a short working distance, normal ion beam incidence and high brightness ion source results in a lateral resolution in the order of a few hundred nanometers (compared to several microns for conventional SIMS instruments). The UO_2F_2 particles were measured by a 16 keV beam of O^- ions produced by a duoplasmatron directed onto the sample in a raster of 8 x 8 μm. The primary ion beam current at the sample was approximately 50 pA with a spot size of about 300-400 nm. The positively-charged secondary ions that were produced by the sputtering process were separated and detected by a double-focusing mass analyzer and secondary electron multipliers. The intensity of the F^+ and U^+, UO^+ and UF^+ secondary ions was measured by cycling the magnetic field setting (peak jumping). Specific image processing software (L'Image, Larry Nittler) was used for data reduction.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of UO_2F_2 particles on the original graphite substrate and after transfer to a vitreous carbon planchet by the vacuum impactor device. Given the low transfer efficiency of our set up, the particles on the vitreous carbon planchet were in fact collected from three different graphite substrates prepared at the IRMM. The SEM images of the planchet with the transferred particles showed that the particles were mostly agglomerated with sizes ranging from less than a micron to 2-3 μm and separated by at least several μm. This was found to be ideal for relocation on the NanoSIMS (see below).

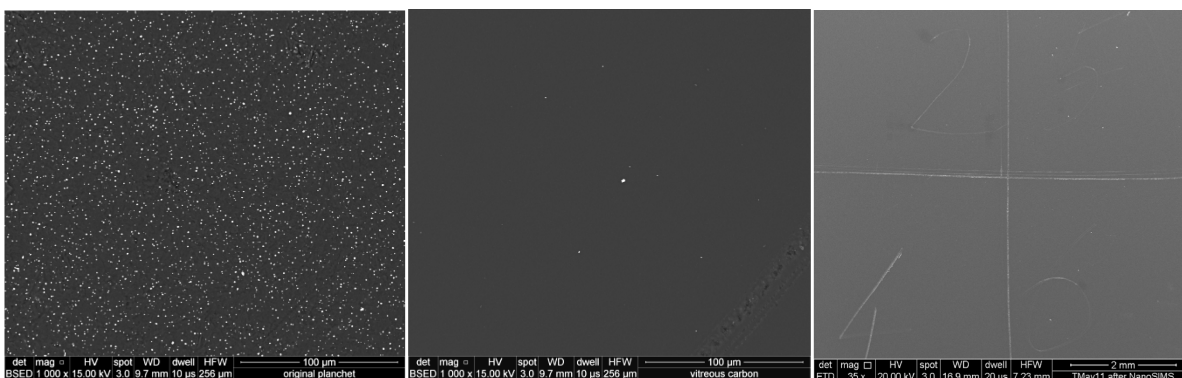

Fig. 1: Backscattered electron image (1000×) of the particle density on the original graphite substrate (left) and after transfer to a vitreous carbon planchet by a vacuum impactor device (middle). The right image is the secondary electron image (35×) of the vitreous carbon planchet with reference marks.

For Raman spectroscopy however, the very small particle size was the main challenge for the measurements. For these experiments, we used the original graphite substrates with high particle density. After optimization of the laser settings (power, focusing, position), reproducible spectra with adequate signal-to-noise ratios were obtained. Figure 2 shows the wide frequency Raman spectrum of a UO_2F_2 particle stored in an inert atmosphere since preparation from UF_6 hydrolysis. The spectra were in general agreement with the spectrum of hydrated UO_2F_2 described by Armstrong et al.: the $(UO_2)^{2+}$ symmetric stretching frequency around 865 cm^{-1} was the most prominent peak in the 200 – 1000 cm^{-1} range, with a shoulder towards the lower frequency side. The feature around 180 cm^{-1} was attributed to the U-O bend. Other broad, much weaker bands were detected in the 100-300 cm^{-1} range and around 750 cm^{-1}, but could not be identified. The two strong bands in the 1000-2000 cm^{-1} region were produced by the graphite planchet.

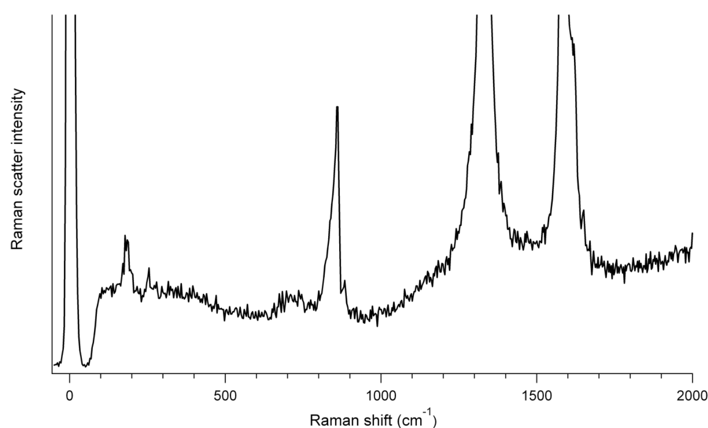

Fig. 2: Wide frequency range Raman spectrum of a UO_2F_2 particle. The intense band around 865 cm^{-1} was attributed to the $(UO_2)^{2+}$ symmetric stretching frequency, while the weaker peak around 180 cm^{-1} was identified as the U-O bend. The two strong bands in the 1000-2000 cm^{-1} region were produced by the graphite planchet.

The Raman spectroscopy measurements confirmed the particles to be hydrated UO_2F_2. In order to determine 1) if fluorine is homogeneously distributed throughout the particles and 2) whether a

correlation exists between the particle morphology (size and shape) and the relative amount of fluorine, 8 particles or particle agglomerates were selected on the vitreous carbon planchet for measurement on the NanoSIMS (Fig. 3). The particles were selected close to the reference marks on the vitreous carbon surface so that they could be relocated on the white light microscope image and on the total ion image of the NanoSIMS.

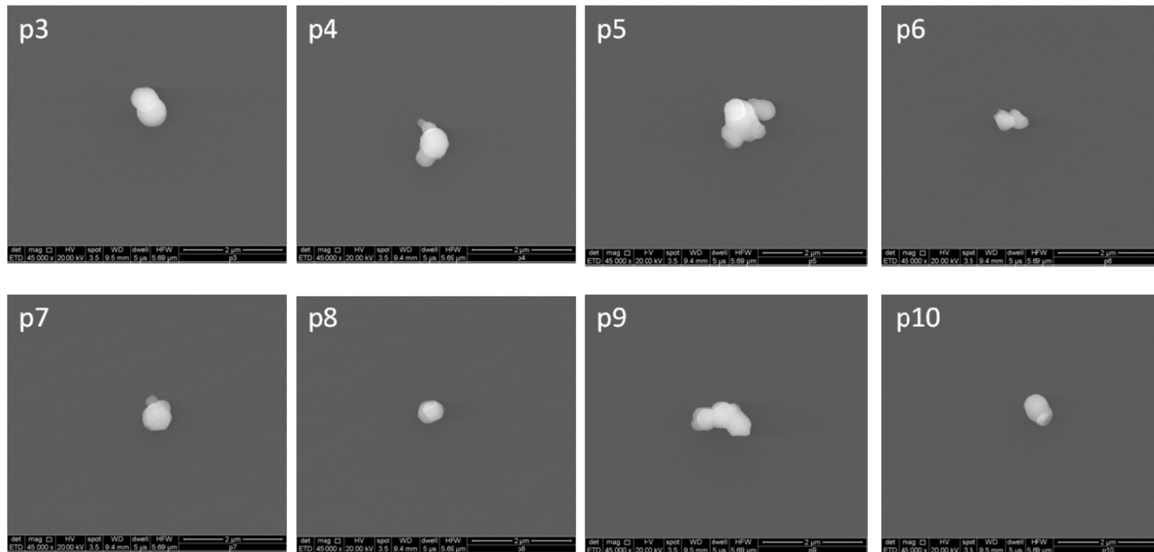

Fig. 3: Secondary ion images (45000×) of 8 particles or particle agglomerates selected on a vitreous carbon planchet after transfer by a vacuum impactor device.

Secondary ions of F^+, U^+, UO^+ and UF^+ were generated through sputtering with a 50 pA O^- primary ion beam while cycling the magnetic field of the analyzer (peak jumping). A depth profile was obtained by plotting the secondary ion intensity for the different ion species as a function of cycle number (which is directly proportional to time). The sputtering process was stopped after 12, 25, 50, 100 or 210 cycles to determine the rate of sputtering and the level of particle erosion. For each of these cycles, the secondary ion images were recorded for all 4 ion species. These (2-dimensional) ion images indicated that fluorine is located in the center of the particle (Figure 4).

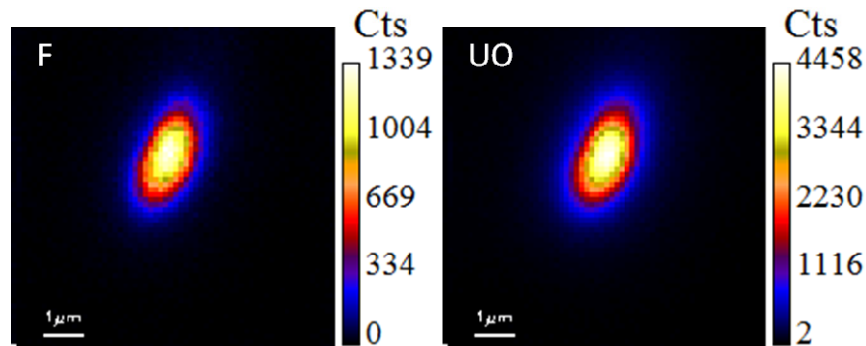

Fig. 4: Secondary ion images (8 µm x 8 µm) of F^+ and UO^+ suggesting fluorine is located in the center of the particle.

The depth profiles however, showed a clear difference in the variation of the fluorine and uranium-bearing ion species with time. As an example, the depth profiles and corresponding SEM images of a particle sputtered for 12 cycles (p4), and one sputtered for 210 cycles (p6) are compared in Figure 5. For particle p4 (sputtered for 12 cycles, i.e. order of minutes), the F^+ intensity had just reached its maximum when the analysis was stopped, while the uranium-bearing species were still rising. SEM imaging of this agglomerate after NanoSIMS analysis did not show any noticeable signs of ion beam sputtering. When the analysis was extended to 210 cycles (on a different particle), the same initial behavior was observed: the F^+ and UF^+ ions reached a maximum quickly after the start of the analysis, while the U^+ and UO^+ continued to increase until the particle became more and more eroded. After the first 10-15 cycles however, the F^+ and UF^+ ions steadily decreased to about 200 cps at the end of the analysis, whereas the U^+ and UO^+ ions were still an order of magnitude higher. This secondary ion behavior was consistent for all particles analyzed, where the depth profile showed a peak in the F^+ ion intensity at start of the analysis. Also, no direct correlation was found between the relative intensity of the ions and the particle morphology, although the ion intensity was generally higher for the larger particles.

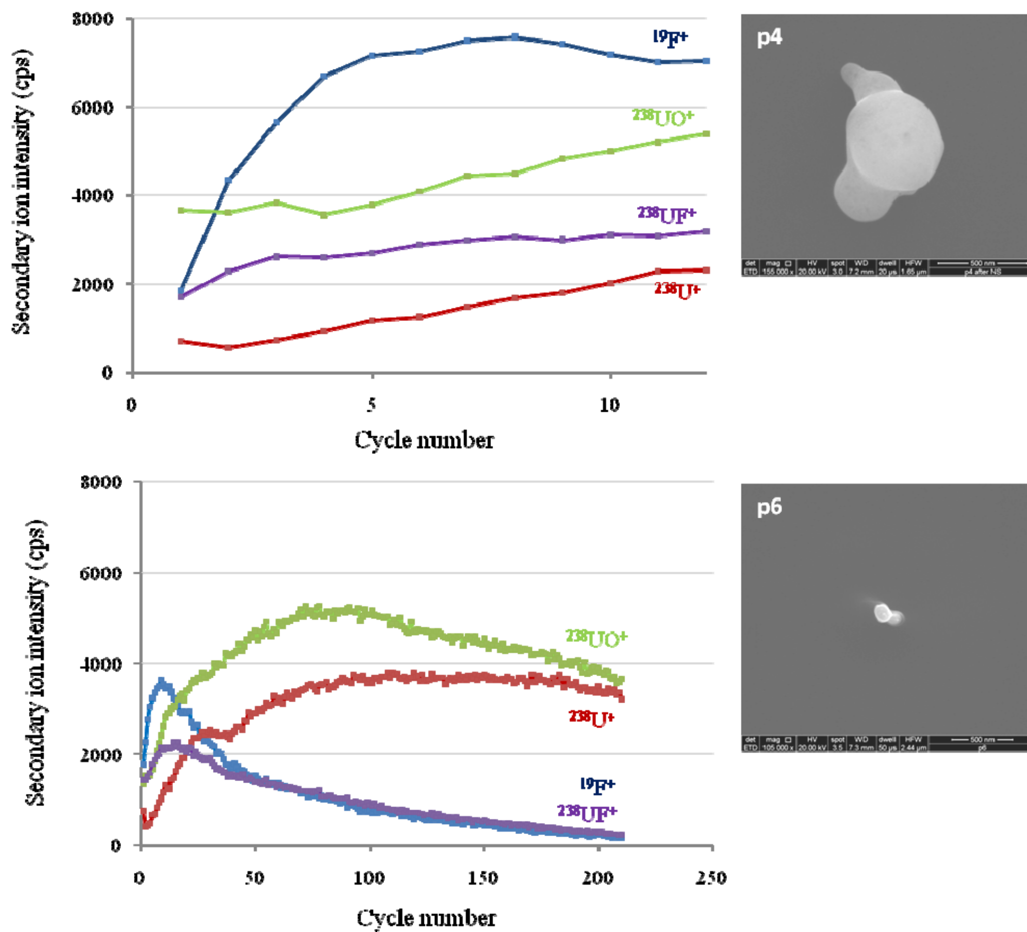

Fig. 5: Depth profiles of particles p4 and p6, sputtered for respectively 12 and 210 cycles, showing the secondary ion intensity of F^+, U^+, UO^+ and UF^+ as a function of cycle number. The SEM images on the right show the particle morphology after NanoSIMS analysis.

For the next series of NanoSIMS experiments, we will focus on determining whether the peak that is observed for the F^+ depth profile is sample-related or a measurement artifact. Relocation of the particles after NanoSIMS analysis showed that the F^+ peak occurred in the very early stages of sputtering, when the particle was still more or less intact. This could imply that the particle is covered by a layer of high fluorine content that is quickly sputtered away. Then again, restarting the measurement on a particle that had already been analyzed earlier showed a similar spike in the F^+ ion intensity. These findings therefore seem to indicate that the increased F^+ count rate at the start of the analysis is a surface enhancement effect. A comparable set of NanoSIMS analyses using a cesium primary ion beam, which has a significantly higher sensitivity for both fluorine and oxygen (at the cost of uranium sensitivity), will allow us to confirm this hypothesis.

CONCLUSIONS

The experiments described in this paper demonstrated that a combination of complementary techniques is the best approach to characterize UO_2F_2 particles produced from UF_6 hydrolysis. The small particle size required the use of highly sensitive and selective analytical tools. NanoSIMS, SEM and micro-Raman spectroscopy were applied to determine the particle morphology, chemical composition and structure. Raman spectroscopy identified the particulate reaction product as hydrated UO_2F_2. For the NanoSIMS measurements, the particles were transferred to a vitreous carbon planchet with fiducial marks using a vacuum impactor device. On this vitreous carbon planchet, 8 particles were selected by electron microscopy. This allowed verification of the particle morphology before and after NanoSIMS analysis. The ion images taken by the NanoSIMS indicated fluorine was distributed homogeneously throughout the particle, even though the depth profiles showed a spike of fluorine at the start of the analysis. Relocation of the particles by SEM imaging confirmed that this spike occurred in the very early stages of sputtering, when the particle did not yet show clear signs of erosion. It was therefore concluded that this peak in fluorine intensity could be caused by a high fluorine surface layer, or may be attributed to a NanoSIMS surface enhanced artifact. Planned experiments using a cesium primary ion beam will confirm either hypothesis.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The authors would like to thank E. Stefaniak, J. Truyens and Y. Aregbe (IRMM) for the preparation of the UO_2F_2 particle samples and P. Weber and J. Matzel for their help with the NanoSIMS measurements. The authors are also grateful to the NNSA Office of Nonproliferation and International Security for its generous support of this project.

REFERENCES

[1] D.L. Donohue, 'Strengthening IAEA Safeguards through Environmental Sampling and Analysis,' J. Alloys Compd. 271-273 (1998) pp. 11-18

[2] D. Donohue, A. Ciurapinski, J. Cliff III, F. Ruedenauer, T. Kuno, J. Poths, 'Microscopic Studies of Spherical Particles for Nuclear Safeguards,' Appl. Surf. Sci. 255 (2008) pp. 2561-2568

[3] D. Donohue, J. Parus, A. Ciurapinski, 'Scanning Electron Microscope Studies of U and Pu-Containing Particles from Environmental Swipe Samples,' Proc. 21st ESARDA Conference, Seville, Spain, 1999

[4] G. Tamborini, M. Betti, V. Forcina, T. Hiernaut, B. Giovannone, L. Koch, 'Application of Secondary Ion Mass Spectrometry to the Identification of Single Particles of Uranium and their Isotopic Measurement,' Spectrochim. Acta B 53 (1998) pp. 1289-1302

[5] Y. Shen, Y. Zhao, S. Guo, J. Cui, Y. Liu, J. Li, J. Xu, H. Zhang, 'Study on Analysis of Isotopic Ratio of Uranium-bearing Particle in Swipe Samples by FT-TIMS,' J. Rad. Meas. 43 (2008) pp. S299-S302

[6] A.J. Pidduck, M.R. Houlton, G.m. Williams, D.L. Donohue, 'A Multi-Technique Approach to Environmental Particle Analysis for Nuclear Safeguards', IAEA-CN-148/115, Proc. IAEA Symp. Intl. Safeguards, Vienna, Austria, 2006

[7] F. Pointurier, O. Marie,'Identification of the chemical forms of Uranium Compounds in micrometer-size Particles by means of Micro-Raman Spectrometry and Scanning Electron Microscope', Spectrochim. Acta B 64 (2010) pp. 797-804

[8] E. A. Stefaniak, A. Alsecz, I. E. Sajo, A. Worobiec, Z. Mathé, S. Török, R. Van Grieken,' Recognition of Uranium Oxides in Soil Particulate Matter by means of μ-Raman spectrometry', J. Nucl. Mat. 381 (2008) pp. 278-283

[9] E. A. Stefaniak, A. Worobiec, S. Potgieter-Vermaak, A. Alsecz, S. Török, R. Van Grieken, 'Molecular and Elemental Characterization of Mineral Particles by Means of Parallel Micro-Raman Spectrometry and Scanning Electron Microscopy/Energy Dispersive X-ray Analysis,' Spectochim. Acta B 61 (2006) pp. 824-830

[10] P.W. Pickrell, 'Characterization of the Solid, Airborne Materials created by the Interaction of UF6 with Atmospheric Moisture in a Contained Volume,' K/PS-144-DE82 015436, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, 1982

[11] R. S. 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,' Microsc. Microanal. 13 (2007) pp. 156-164