LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-PROC-433314

Micro-Raman Spectroscopy of Uranium Oxyfluoride Particulate Material for Nuclear Safeguards

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

May 25, 2010

Institute for Nuclear Materials Management Annual Meeting
Baltimore, MD, United States
July 11, 2010 through July 15, 2010

Disclaimer and auspices

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 was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and under the auspices of the European Commission, DG Joint Research Centre under Action Sheet 36. The analyzed samples were generated by the IRMM expressly for the purpose of this experiment and we have no evidence that fugitive emissions from a uranium enrichment facility would, or would not, appear similar to the analyzed samples.

LLNL-PROC-433314

Micro-Raman spectroscopy of Uranium Oxyfluoride Particulate Material for Nuclear Safeguards

R. Kips[1], J. Crowhurst[1], M. J. Kristo[1], E. Stefaniak[2], I. D. Hutcheon[1]

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

[2]European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Retieseweg 111, 2440 Geel, Belgium

ABSTRACT

Environmental samples collected by safeguards organizations such as the International Atomic Energy Agency often contain particles of uranium oxyfluoride (UO_2F_2). UO_2F_2 is a compound formed from the hydrolysis of uranium hexafluoride (UF_6). It is very hygroscopic and is known to lose fluorine over time and from exposure to certain environmental conditions. In order to investigate these changes, uranium oxyfluoride particulate material prepared in a laboratory setting was measured by micro-Raman spectroscopy. The uranyl symmetric stretching frequency of $(UO_2)^{2+}$ at around 865 cm^{-1} was detected in the majority of the spectra. Depending on the conditions under which the uranium oxyfluoride particles were prepared and stored, additional peaks and features appeared in the spectrum. These features were attributed to changes in hydration of the uranium oxyfluoride and the co-existence of multiple uranium phases in particle aggregates. Experiments were carried out using different incident laser wavelengths at the lowest possible power setting, as the particles appeared to be very heat-sensitive.

INTRODUCTION

An important tool in the detection of undeclared nuclear activities is the analysis of environmental samples. Since the early 1990s, safeguards organizations such as the International Atomic Energy Agency (IAEA) and Euratom have been collecting environmental samples at nuclear facilities across the world [1]. The strength of environmental sampling lies in the observation that processes involving the treatment of nuclear material release small amounts of process material to the environment. This process material, together with an excess amount of dust, is collected by swiping surfaces with pieces of cotton cloth. The uranium-bearing particles collected in these swipes are measured for their uranium isotopic composition at the analytical labs of the IAEA and Euratom.

In the case of uranium enrichment facilities, the environmental samples often contain very small particles or particle agglomerates of uranium oxyfluoride (UO_2F_2). UO_2F_2 is a compound formed from the hydrolysis of uranium hexafluoride (UF_6), a gas used in large quantities for the enrichment of uranium. UF_6 is very reactive, and even a small release of this material in the presence of water gives rise to UO_2F_2 particulate material and HF. Somewhat surprisingly, environmental samples from enrichment facilities were also found to contain uranium-bearing particles without a measurable amount of fluorine [2]. This seems to indicate UO_2F_2 loses its fluorine over time, or from exposure to certain environmental conditions. As both nuclear forensics and environmental sample analysis depend upon laboratory analysis of nuclear material that has often been exposed to the environment after it was produced, it is important to understand how those environmental conditions might have changed the chemical composition of the material over time, particularly for these chemically sensitive compounds.

Previous studies have already demonstrated that exposure to high temperature (350 °C), high relative humidity (> 70%) and ultraviolet light effectively accelerates the loss of fluorine in UO_2F_2. However, the exact conditions under which this happens and the molecular changes that accompany this degradation are not well understood. Here we use micro-Raman spectroscopy to investigate the behavior of UO_2F_2 particles exposed to a range of conditions including high temperature and different levels of relative humidity.

Experimental

Uranium oxyfluoride particulate material

The aerosol deposition chamber at the IRMM was used to produce UO_2F_2 particles from the controlled hydrolysis of UF_6 [3, 4]. The uranium oxyfluoride particulate material used for this study was prepared expressly for the purpose of these experiments, and it should be noted that we have no evidence that fugitive emissions from a uranium enrichment facility would, or would not, appear similar to the analyzed samples. Depleted UF_6 was used with a ^{235}U abundance of 0.28 %. Upon release in the deposition chamber, the UF_6 gas reacted with the atmospheric moisture forming uranium oxyfluoride particles and hydrogen fluoride [5, 6]:

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

The uranium oxyfluoride particles that were formed from this reaction were collected through gravitational settling at the base of the chamber on 9.5 mm graphite planchets. No further sample preparation was necessary for the measurement by micro-Raman spectroscopy.

Micro-Raman spectroscopy (MRS)

Raman measurements were mostly made using laser light of wavelength 632.8 nm (HeNe). Some measurements were made with the 514.5 nm line of an Ar-ion laser. Laser light was directed towards the sample using a laser band pass cube and was focused onto it with a 100X apochromatic objective lens (Mitutoyo), estimated to produce a focal spot of approximately 1 μm in diameter. Scattered light was collected with the same objective and was focused onto a pinhole (to improve spatial resolution) before being collimated and directed into the spectrometer. Holographic filters were used to reject elastically scattered laser light. The spectrometer was a Jobin Yvon HR460 equipped with 300 lines/mm and 1800 lines/mm gratings. The detector was an LN_2 cooled CCD. High resolution spectra acquired using the 1800 lines/mm grating were calibrated using a neon lamp acquired before each acquisition. Small instrumental nonlinearity across the corresponding spectral range was ignored. No normalizations to correct for variations in instrumental sensitivity to wavelength were carried out for any of the spectra shown below. Such variations were assumed to be unimportant for the present analysis. Peak fitting could not be performed in an non-arbitrary fashion due to the asymmetrical shape of the uranyl peaks. Therefore, the frequencies of the peaks in the high resolution spectra are estimated positions of the maximum Raman scatter intensity.

The small size of the particles and particle agglomerates required a small focused spot size (hence the use of the 100 X objective) to provide adequate spatial resolution for the Raman measurements. Incident power was minimized to avoid excessive intensity which was found to affect the samples. Also, comparison of the spectra taken at the two different wavelengths indicated that the use of the laser with the longest wavelength (632.8 nm red) and hence the least amount of energy per photon (~1.96 eV vs ~2.41 eV) produced the most reproducible spectra. Around 10 spectra were recorded for each sample, and an incident power of not more than 2.1 mW was used to obtain most of the spectra. At higher powers the uranium particles were often irreversibly transformed to U_3O_8 (according to the measured Raman spectra) presumably due to heating (see below). The acquisition time for the high resolution spectra varied between 1 and 10 minutes, and is specified for each of the figures.

RESULTS AND DISCUSSION

Baseline measurements on uranium oxyfluoride particles

The Raman and infrared (IR) spectra of the hydrolysis products of UF_6 have been described in detail by Armstrong et al. (Raman) [7], Sherrow et al. (IR) [8] and Armstrong et al. (IR) [9]. These studies indicated that excess water during UF_6 hydrolysis complexes with the UO_2F_2 particulate reaction product, resulting in $UO_2F_2.nH_2O$, where n varies between 1.5 and 4 [10, 11]. UO_2F_2 is a very hygroscopic compound and even after a week's exposure to less than 20 % relative humidity, the anhydrous UO_2F_2 has been reported to become at least partially hydrated [7]. The Raman spectrum of this hydrated UO_2F_2 fallout material is characterized by a distinct band from the uranyl stretch around 865 cm^{-1}, in addition to a much weaker and broader feature around 174 cm^{-1}, attributed to the U-O bending fundamental.

For the uranium oxyfluoride particle samples produced at IRMM from the controlled hydrolysis of UF_6, the small particle size posed the biggest analytical challenge. The samples used in this study were intended to serve as reference samples for secondary ion mass spectrometry (SIMS) [12], and hence the sample preparation was aimed at limiting the number of particles to 1-2 particles per 25 μm^2. However, the gas-phase condensation that produces the UO_2F_2 particulate fallout material is a process that is difficult to control, so larger particles and particle agglomerates of up to several microns were also found on the planchets. As expected, the most intense Raman spectra were obtained from these larger particles and agglomerates.

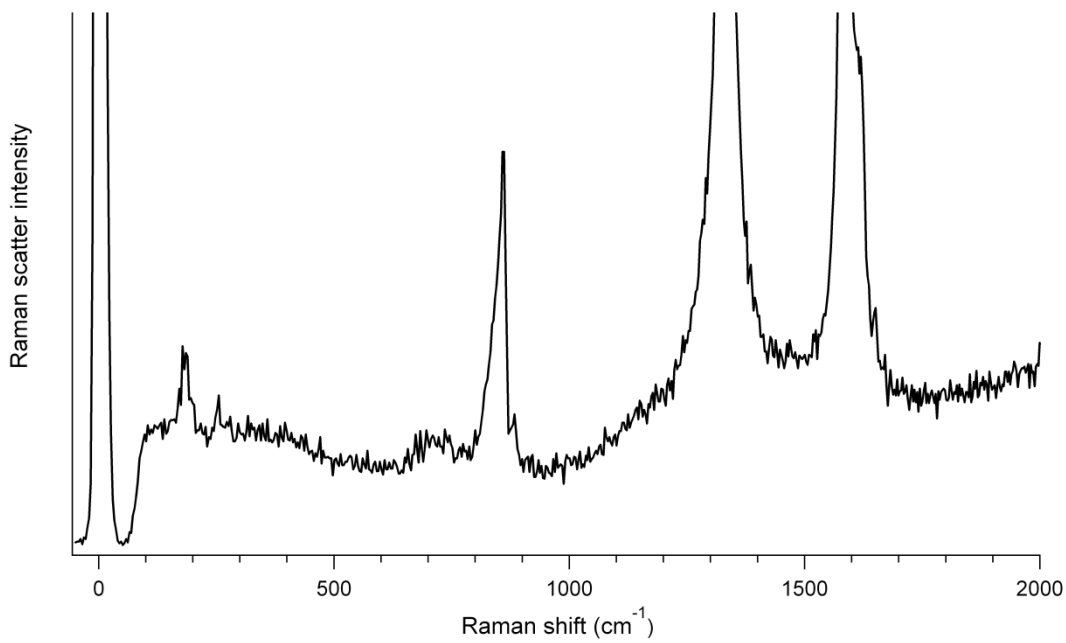

Fig. 1: Wide frequency range (low resolution, 30s acquisition time) Raman spectrum of a uranium oxyfluoride particle stored in argon since its preparation in the aerosol deposition chamber acquired with 632.8 nm incident radiation. The intense band around 865 cm^{-1} was attributed to the uranyl symmetric 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 spectrum acquired from a sample stored in an argon atmosphere since its preparation at IRMM was used as a baseline for comparison with samples exposed to specific environmental conditions (Figure 1). Storage in an inert atmosphere is assumed to preserve the particles' chemical and molecular structure, even though some exposure to air could not be avoided during the actual Raman analysis. The Raman spectrum of this 'non-exposed' baseline sample was in general agreement with the UO_2F_2

spectrum described by Armstrong et al [7]: the $(UO_2)^{2+}$ symmetric stretching frequency around 863 cm^{-1} was the most prominent peak in the spectrum, with a shoulder towards the lower frequency side. The low resolution spectrum in Figure 1 shows a broad and weak feature in the 500-600 cm^{-1} range. The peak around 180 cm^{-1} was attributed to the U-O bend. Other broad and fairly weak features in the 100-300 cm^{-1} range appeared in the spectrum. A high resolution spectrum was acquired from another particle from this sample, showing an asymmetrical uranyl peak around 863 cm^{-1} (Figure 2).

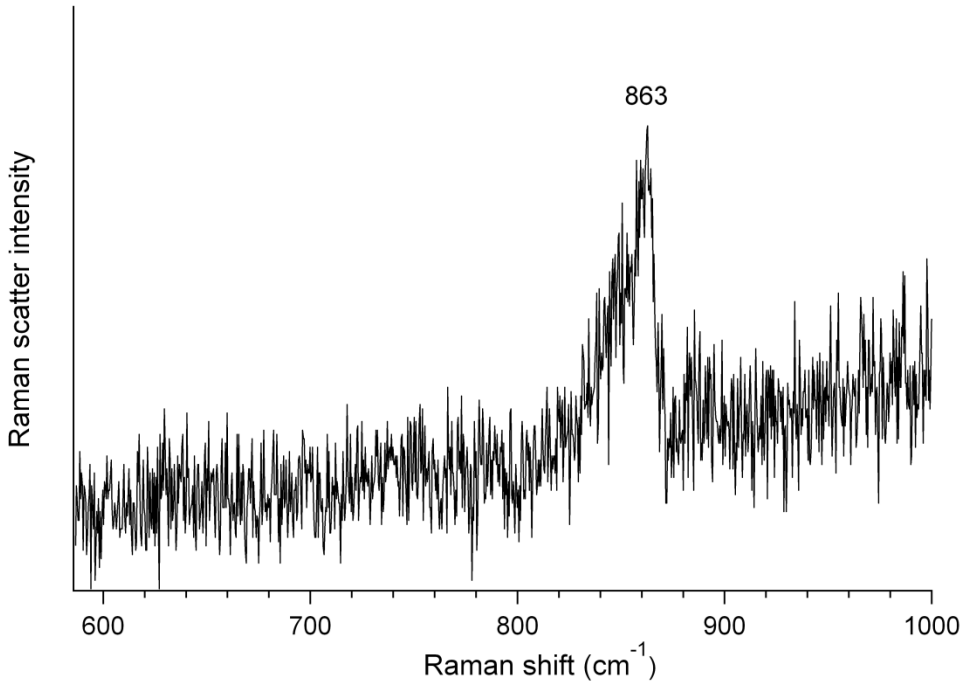

Fig. 2: High resolution Raman spectrum (632.8 nm incident radiation, 3 x 60s acq. time, power at sample not measured) of a uranium oxyfluoride particle from the same sample as in Figure 1. The uranyl peak at 863 cm^{-1} shows some asymmetry towards the lower frequency side.

Uranium oxyfluoride particles exposed to different degrees of humidity

Previous studies have indicated that humidity is the main factor accelerating the loss of fluorine in the hydrolysis product of UF_6 [4, 5]. Samples were therefore stored in either argon, or air with less than 15 % relative humidity. The spectrum of a UO_2F_2 particle sample kept in an argon atmosphere for several months followed by storage in dry air with a relative humidity of not more than 25 % was expected to look similar to the spectrum described above, yet an additional peak with a shoulder was detected around 845 cm^{-1} (Figure 3). This peak was generally stronger and broader than the peak at 863 cm^{-1}, still the small difference in Raman shift seemed to suggest that both peaks resulted from the uranyl symmetric stretch. UO_2F_2 has a layered structure, with the planes of uranium separated by 5.22 Å and the axis of the uranyl group normal to these planes. This structure allows the insertion of water molecules between the layers and therefore a series of uranium oxyfluoride hydrates are known [10, 11]. A change in hydration state may have led to the shift of the peak at 863 cm^{-1} towards lower frequencies. This distortion of the lattice structure typically results in peak broadening, which may explain the broadness of the peak at 847 cm^{-1}. Similar to the spectrum of the baseline sample (Figure 1), a broad and weak feature was detected around 750 cm^{-1}. It should be noted that this peak shifted to around 710 cm^{-1} when acquired with 514.5 nm excitation. Shifts in the position of the Raman features depending on excitation wavelength have been reported for other uranium compounds [13].

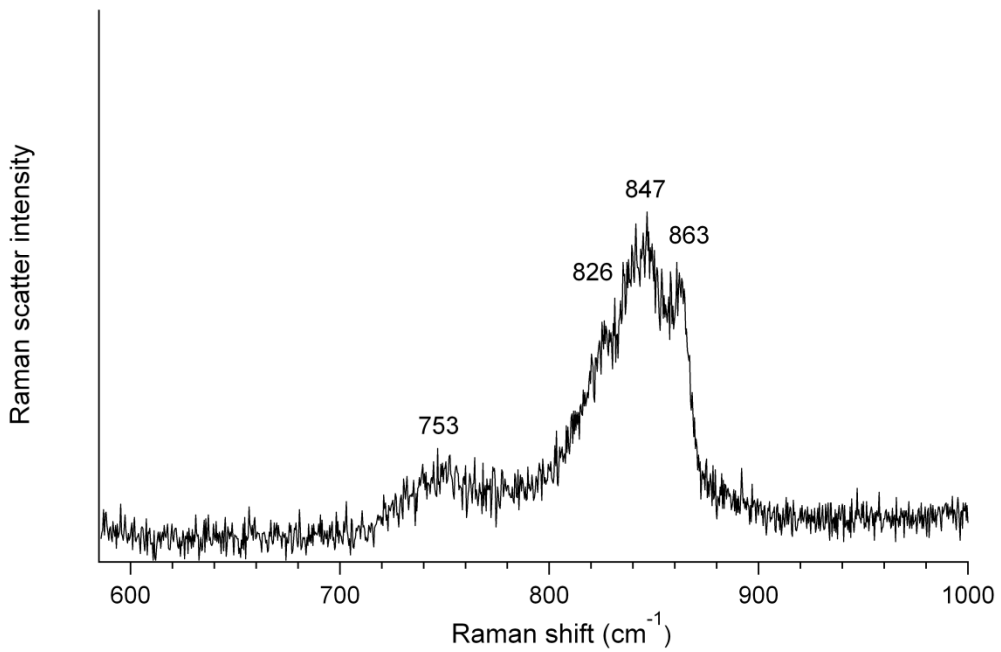

Fig. 3: High resolution Raman spectrum (632.8 nm incident radiation, 5 x 60s acq. time, 0.23 mW applied to the sample) of a uranium oxyfluoride particle kept in an argon atmosphere for several months, followed by storage in dry air. An additional peak at 847 cm^{-1} with a shoulder towards lower frequencies appeared in this spectrum.

The spectra of samples exposed for 3 months to air at room temperature and 30 % relative humidity were very similar to those of the sample kept in argon and then in dry air, although the peak at 843 cm^{-1} was somewhat less intense than the peak at 863 cm^{-1} (Figure 4). The Raman spectra of these samples is consistent with our hypothesis that exposure to humidity shifts the uranyl peak of the UO_2F_2 molecule to lower frequencies. Furthermore, the presence of two uranyl peaks (presumably) in this region suggests that multiple uranium phases coexist within a single particle or particle agglomerate.

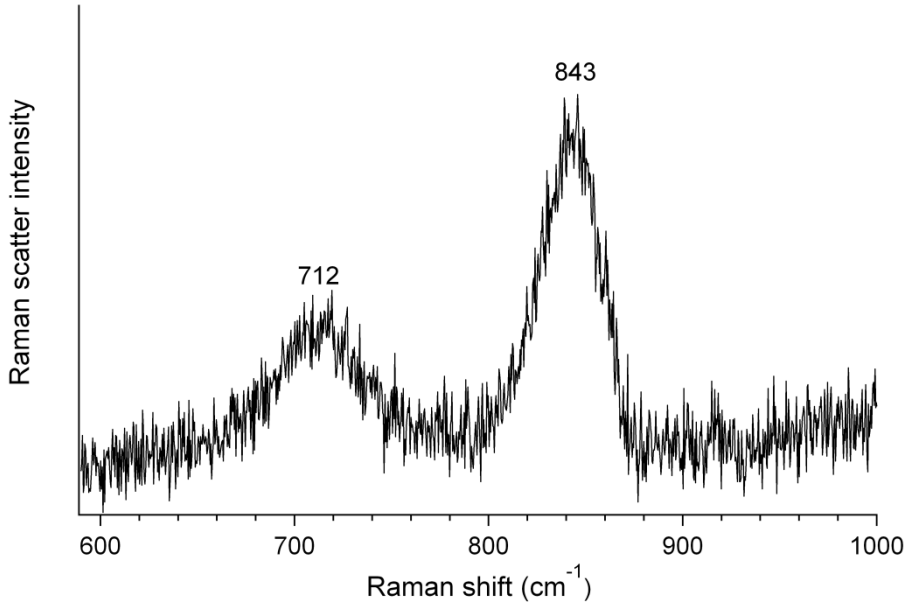

Fig. 4: High resolution Raman spectrum (632.8 nm, 60s acq. time, 0.8 mW at the sample) of a uranium oxyfluoride particle stored in 30 % relative humidity for 3 months.

Uranium oxyfluoride particles tend to become more spherical through the uptake of water, until they eventually turn into liquid solutions covering the planchet's surface, a process also referred to as deliquescence [4, 12]. One of the samples that was prepared at the IRMM was stored in air at 70 % relative humidity for a period of 5 days (117 hours) and then measured by Raman spectroscopy. The particles on this sample were generally larger than on the other samples and their spectrum showed a large, broad peak around 843 cm^{-1} (Figure 5). The peak at 863 cm^{-1} was not detected. These measurements therefore indicated that the uranyl peak which was initially detected around 865 cm^{-1}, broadened and shifted towards lower frequencies due to the absorption of water.

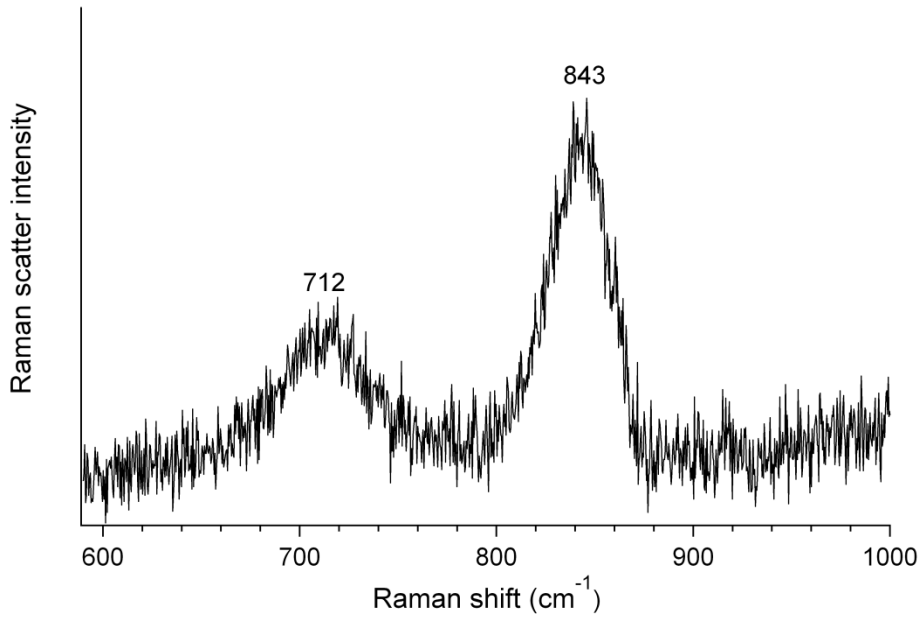

Fig. 5: High resolution Raman spectrum (632.8 nm, 2 x 300s acq. time, 0.16 mW at the sample) of a uranium oxyfluoride particle stored in 70 % relative humidity for 5 days. The peak at 843 cm^{-1} was the dominant peak in the spectrum, with an additional broad, unidentified band around 712 cm^{-1}.

The effect of annealing on uranium oxyfluoride particles

Although UO_2F_2 gradually loses its fluorine when exposed to humidity, it is fairly stable at moderate temperatures. Armstrong et al. [7] was able to produce anhydrous UO_2F_2 from hydrated UO_2F_2 by heating the material in a furnace at 120 °C to a constant weight and found that this process was reversible. The Raman spectrum of anhydrous UO_2F_2 has two characteristic bands: an intense band at 915 cm^{-1} from the symmetric U-O stretching fundamental and a weak band at 442 cm^{-1} produced by the U-F lattice vibration. For a hydrated UO_2F_2 sample that was heated in an open air furnace at 200 °C for 19 hours these bands were not detected, indicating that either the sample was not heated long enough to produce anhydrous UO_2F_2 or that the short exposure to ambient moisture between the time it was taken out of the oven until it was analyzed was sufficient to hydrolyze the material. The spectra of all seven areas that were measured on this sample were very similar to the spectrum from the baseline UO_2F_2 material. Figure 6 shows the $(UO_2)^{2+}$ symmetric stretching fundamental at 864 cm^{-1} with a shoulder on the lower frequency side. The bands around 180 cm^{-1} and 260 cm^{-1} were the most prominent in the lower frequency range (not shown). In contrast to the samples exposed to higher levels of humidity for a few days to several months, the spectrum of the annealed sample did not show a peak around 845 cm^{-1}.

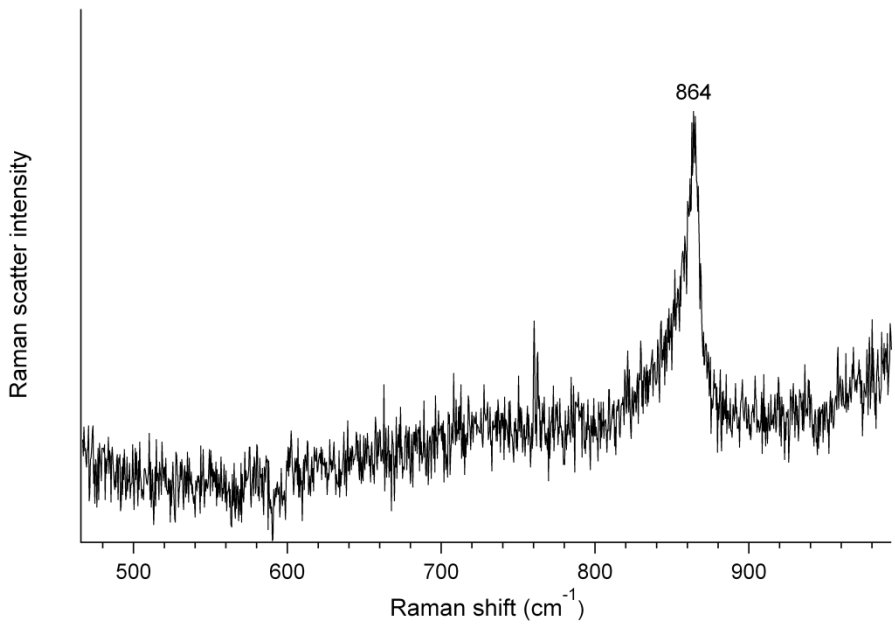

Fig. 6: High resolution Raman spectrum (632.8 nm, 5 x 60s acq. time, 2.1 mW at the sample) of a uranium oxyfluoride particle after heating in an open air furnace at 200 °C for 19 hours. The spectrum resembled that of the baseline spectrum in Figure 2.

When increasing the temperature above a certain threshold, either through heating in a furnace in air at 350 °C or applying a high enough laser power, the uranium (VI) in UO_2F_2 was irreversibly reduced to U_3O_8. Myers et al. [11] reported that UO_2F_2 is stable in air up to approximately 300 °C. Thermal decomposition occurs at temperatures higher than 300 °C, until it decomposes completely to U_3O_8 at about 800 °C. The change to U_3O_8 occurred very abruptly; an increase of the incident laser power merely changed the intensity of the uranyl peaks, until the power was stepped up from 2.1 mW to 5.4 mW, and the spectrum suddenly changed to that of Figure 7. This spectrum was found to compare well to the literature spectrum of U_3O_8 [14 Fig. 1].

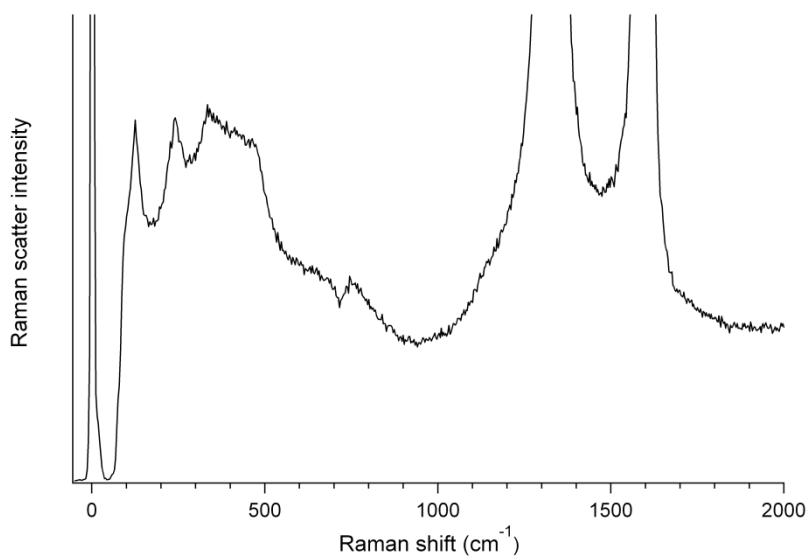

Fig. 7: Raman spectrum of a particle from the same sample as in Figure 3, this time acquired an incident power of 5.4 mW for 30s at 632.8 nm. This spectrum compares well with the spectrum of U_3O_8 reported in literature [14 Fig. 1].

CONCLUSIONS

Micro-Raman spectroscopy has shown that the particulate reaction product formed from UF_6 hydrolysis in excess water is predominantly hydrated UO_2F_2. For all the particle samples stored in an inert atmosphere prior to analysis, the uranyl symmetric stretching frequency around 865 cm^{-1} was detected, together with the U-O bend around 180 cm^{-1} and a series of weaker features in the lower frequency region. An unidentified weak and broad feature was detected between 700 - 760 cm^{-1}, although its exact frequency and relative intensity varied between samples and may have been dependent on incident laser wavelength. The particles were found to be very heat sensitive and changed irreversibly to U_3O_8 when exposed to air in an oven at 350 °C, or when excessive laser power was applied to the sample. A HeNe laser with a wavelength of 632.8 nm (red) and a power of not more than 2.1 mW was found to be the least intrusive and produced reproducible spectra without noticeably altering the particle composition.
Storage of the samples in an argon atmosphere preserved the chemical and molecular composition of the uranium oxyfluoride hydrate over longer periods of time. When exposed to intermediate levels of humidity, an additional peak around 845 cm^{-1} appeared in the spectrum, indicating that several hydrates of UO_2F_2 co-exist within the particles. This peak was no longer detected after annealing the particles in an oven at 200 °C, although the peak around 865 cm^{-1} had a shoulder on the lower frequency side. For particles exposed to a very humid atmosphere of 70 % relative humidity for 5 days, the peak at 845 cm^{-1} was very broad and intense, while the 865 cm^{-1} peak disappeared from the spectrum.
These measurements demonstrated that even though the decomposition of uranium oxyfluoride happens very slowly, micro-Raman spectroscopy can distinguish subtle differences in uranium oxyfluoride particles depending on the humidity and temperature conditions to which they were exposed. This so-called ‘molecular fingerprinting’ of single particles and small particle agglomerates is considered to be a valuable complement to the information obtained from more quantitative techniques such as secondary ion mass spectrometry.

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 and under the auspices of the DG Joint Research Centre of the European Commission. The authors would like to thank J. M. Zaug, C. D. Grant (Lawrence Livermore National Laboratory), F. Pointurier, O. Marie (Commissariat à l’Energie Atomique, France) and A. Kirmiz (University of California in Davis, USA) for their valuable input and advice.
The authors would also like to thank 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] J. W. A. Tushingham, UK Safeguards Support Programme - Report on Activities and Progress during the period 1 April 2007 to 31 March 2008, UK Safeguards Support for the IAEA 13 SRDP-PR28 (2008) pp. 13.

[3] 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.

[4] R. S. Kips, 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, Spectrochim. Acta B 64 (2009) pp. 199-207.

[5] J.A. Carter, 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, Oak Ridge Gaseous Diffusion Plant, 1998.

[6] 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, Oak Ridge Gaseous Diffusion Plant, 1982.

[7] D.P. Armstrong, R.J. Jarabek, W.H. Fletcher, Micro-Raman spectroscopy of selected solid UxOyFz compounds, Appl. Spectrosc. 43 (1989) pp. 461-468.

[8] S. A. Sherrow, R. D. Hunt, FTIR Spectra of the Hydrolysis of Uranium Hexafluoride, J. Phys. Chem. 96 (1992) pp. 1095-1099.

[9] D. P. Armstrong, W. D. Bostick, W. H. Fletcher, An FT-IR Study of the Atmospheric Hydrolysis of Uranium Hexafluoride, Appl. Spectrosc. 45 (1991) pp. 1008-1015.

[10] L. H. Brooks, E. V. Garner, E. Whitehead, Chemical and X-Ray Chrystallographic Studies on Uranyl Fluoride, IGR-TN/CA-277, United Kingdom Atomic Energy Authority, Lancashire, 1958.

[11] W. L. Myers, A Literature Review on the Chemical and Physical Properties of Uranyl Fluoride (UO_2F_2), LA--11896-MS, Los Alamos National Laboratory, 1990.

[12] R. Kips, Development of Uranium Reference Particles for Nuclear Safeguards and Non-Proliferation Control, Doctoral Thesis, University of Antwerp, Belgium, 2007.

[13] 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.

[14] I.S. Butler, G. C. Allen, N. A. Tuan, Micro-Raman Spectrum of Triuranium Octoxide, U_3O_8, Appl. Spec. 42 (1988) pp. 901-902.