

# Fluorine as a Safeguards Tool for Age Dating of Uranium Oxyfluoride Particles?

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## Abstract

*When uranium hexafluoride ( $UF_6$ ) is released into the environment, it reacts with the atmospheric moisture forming uranium oxyfluoride particles and hydrogen fluoride (HF). Fluorine-containing compounds such as HF are recognized as signatures for enrichment activities. In this study, the connection between the fluorine in the particles and the age of the particles has been investigated. Establishing this link is not evident, as uranium oxyfluoride particles are highly hygroscopic and little is known about their reaction mechanisms and stability. There are various environmental factors such as time, humidity and light or heat exposure that could affect the amount of fluorine. Even after the particles are collected, the fluorine could decrease further due to sample preparation or storage conditions.*

*The influence of ultraviolet light exposure combined with the time elapsed after preparation has been investigated on uranium oxyfluoride particles prepared at the Institute for Reference Materials and Measurements (EC-JRC-IRMM) using an aerosol deposition chamber. The presence of fluorine in particles was confirmed by energy-dispersive X-ray analysis (EDX). Semi-quantitative information was obtained by evaluating specific peak height ratios obtained by secondary ion mass spectrometry (SIMS). With these measurements, possible correlations existing between the amount of fluorine and the age of a particle could be investigated, taking into account the environmental conditions to which the uranium oxyfluoride particles were exposed.*

**Keywords:** safeguards; uranium hexafluoride; uranium oxyfluoride particles; SEM-EDX; SIMS

## 1. Introduction

Environmental sampling, as introduced in 1996 as part of routine INFCIRC-153 safeguards agreements and strengthened since the late 1990's by the Additional Protocol (INFCIRC-540) of the International Atomic Energy Agency (IAEA), has proven to be an important safeguards tool in the verification of the absence of undeclared nuclear activities [1, 2]. By wiping surfaces in or around nuclear facilities,

using small pieces of cotton cloth called swipes, uranium-bearing particles are collected among millions of other dust particles. The analysis of these uranium particles can reveal key information on a site's current and past activities. Although the emphasis is currently on the analysis of the uranium isotopes, a lot of information can be deduced from the particle's morphology, surface structure, crystallinity or elemental composition [3].

Uranium-bearing particles from swipe samples taken at uranium enrichment facilities often contain fluorine. Although these particles may result from deposits that are formed when adsorbed water and uranium hexafluoride ( $UF_6$ ) interact, many of them result from the gaseous release of small amounts  $UF_6$ . Initially, uranium oxyfluoride ( $UO_2F_2$ ) particles are formed when  $UF_6$  reacts with atmospheric moisture. However, there are several variables that affect the particle composition and the amount of fluorine present. These include exposure to humidity, heat and light, both during and after particle formation, in addition to the time elapsed since particle formation.

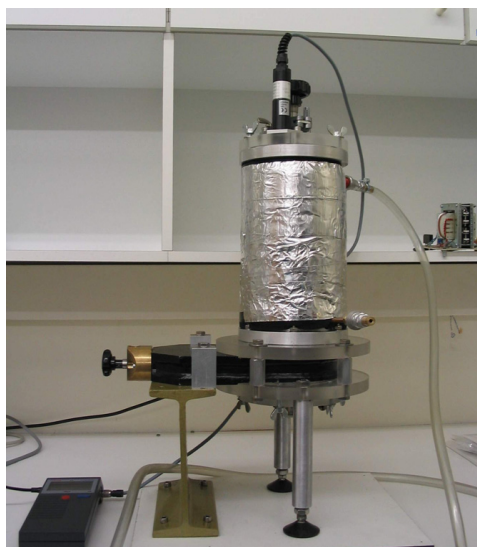
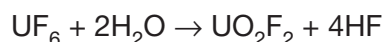
In this study, we investigated whether the analysis of fluorine in  $UO_2F_2$  particles could be used to supplement information on the uranium isotopic composition. In particular, if a correlation could be found between the amount of fluorine and the age of the particle, the measurement of fluorine in particles would not only provide information on the likely source of the particles, i.e. enrichment activities, but also on their history.

The particles formed from uranium hexafluoride are highly hygroscopic, and little is known about their long-term stability. Before being collected on swipes they may have been exposed to high temperatures, a high humidity or sunlight. All of these factors could have altered their morphology and composition and, more specifically, their fluorine content. Any study of the fluorine content of particles originating from  $UF_6$  must therefore take into account the environmental parameters that influence the amount of fluorine. In this work, the effects of ultraviolet light and storage time on the fluorine content of particles

prepared under controlled conditions were examined.

## 2. Materials and Methods

$\text{UO}_2\text{F}_2$  particles were prepared using an aerosol deposition chamber developed at the Institute for Reference Materials and Measurements (EC-JRC-IRMM) (Fig.1). When released into the aerosol deposition chamber, the  $\text{UF}_6$  reacts with the atmospheric moisture to form hydrogen fluoride (HF) and  $\text{UO}_2\text{F}_2$  particles [4]:

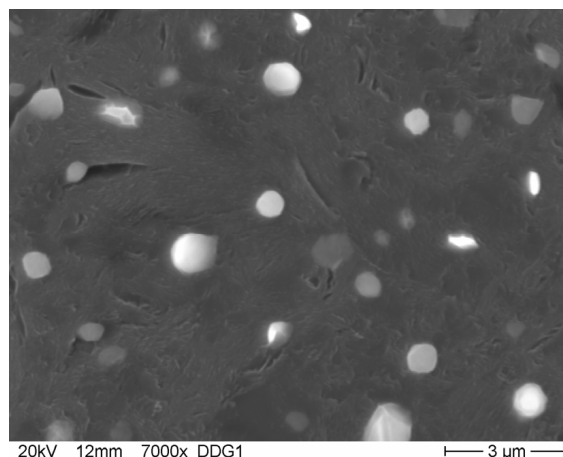


**Figure 1:** Aerosol deposition chamber designed at the IRMM for the preparation of  $\text{UO}_2\text{F}_2$  particles from the controlled hydrolysis of  $\text{UF}_6$ .

The  $\text{UO}_2\text{F}_2$  particles were collected on graphite planchets of 25 mm diameter (Schunk, Germany) at the base of the deposition chamber. It has been demonstrated that the humidity of the air inside the deposition chamber is a determining factor for the particle morphology [4-6]. A dry atmosphere, of less than 15 % relative humidity, results in submicron particles that agglomerate to larger structures of up to 100 micrometers. In contrast, when the relative humidity of the air exceeds 60 %, the particles become more spherical and the degree of agglomeration is lower. Using a high humidity to limit agglomeration, particles of diameters between a few hundred nanometers and 2.5 micrometers were collected, with individual particles separated by a few micrometers (Fig. 2). Such particles were well-suited for direct analysis.

As part of the original preparation procedure, the particles were heated for at least 6 hours in an open furnace at 350 °C to remove excess water and other

volatile elements. This heat treatment inevitably removes most of the fluorine in the particles. As a consequence, any existing information between the amount of fluorine and the age of a particle is lost. The heat treatment was therefore omitted from the preparation procedure and freshly prepared particles were measured directly after preparation by SEM-EDX.



**Figure 2:** Scanning electron image in secondary electron mode showing uranium particles (white dots) produced in high humidity conditions (> 60 %) on a graphite planchet.

A FEI Quanta 200 3D scanning electron microscope equipped with an Oxford Si(Li) energy-dispersive X-ray detector (SEM-EDX) was used to locate the uranium particles and to determine their elemental composition. The electron acceleration voltage was set to 10 kV.

SIMS ion-microprobe measurements were carried out to assess the effect of ultraviolet light and storage time on the relative amount of fluorine on a set of 14 particle samples. For every sample, SIMS ion-microprobe measurements were applied to between 4 and 7 particles. All but one sample contained  $\text{UO}_2\text{F}_2$  particles: one sample contained  $\text{UF}_4$  particles stored in a laboratory environment for more than 2 years. This  $\text{UF}_4$  sample was used to test the repeatability of SIMS  $\text{UF}_4$  spectra and their quantitative distinctiveness from  $\text{UO}_2\text{F}_2$ . The storage time for the  $\text{UO}_2\text{F}_2$  particle samples varied between 2 weeks and 29 months. One sample was exposed to ultraviolet light for 3 weeks.

At QinetiQ in Malvern (UK), a Cameca IMS 4f SIMS spectrometer was used with 8.5 keV  $\text{O}_2^+$  primary ion bombardment at a current of 2 nA in a focused spot (estimated diameter 10  $\mu\text{m}$ ). The data were obtained by cycling the masses 238 (U), 239 (UH), 254 (UO), 257 (UF), 270 ( $\text{UO}_2$ ), 273 (UOF) and 276 ( $\text{UF}_2$ ) 10 times each to reveal any ratio variations with sput-

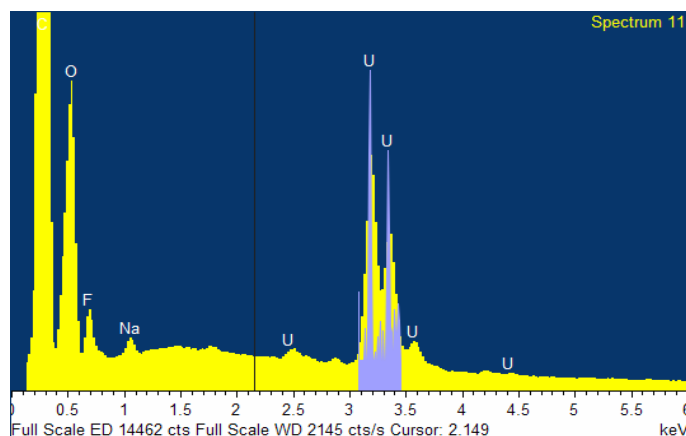
tering. The mean values of these ion intensity measurements were evaluated relative to the intensity at mass 238 (U).

### 3. Results

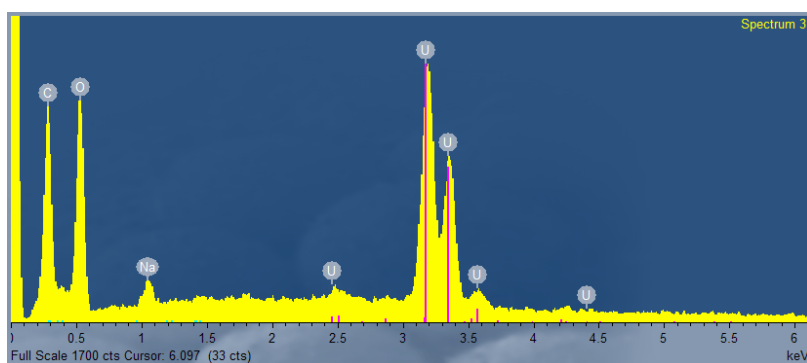
The signature of freshly prepared particles was recorded using EDX, to serve as a reference level. Spectra of these freshly prepared particles clearly showed the fluorine  $K_{\alpha}$  line at 0.677 keV, in addition to the U  $M_{\alpha}$  (3.17 keV) and  $M_{\beta}$  (3.34 keV) X-ray lines (Fig. 3). The fluorine  $K_{\alpha}$  line was still detected in the EDX spectrum after 3 weeks of ultraviolet light exposure. In contrast, particles subject to a heat treatment of 350 °C for 6 hours, as originally foreseen in the particle preparation procedure, did not show the characteristic fluorine  $K_{\alpha}$  line (Fig. 4). Carbon and oxygen were detected in all EDX spectra. The carbon peak was attributed to the graphite planchet substrate, whereas the oxygen peak was partially attributed to the particles, partially to surface contamination and residual gases in the specimen's chamber.

SIMS ion-microprobe measurements were carried out, providing greater sensitivity than EDX in measuring fluorine, in a range of samples subjected to various exposure and storage conditions. The 254 (UO) signals were inherently strong for all samples due to the oxygen primary ion beam that was used. In general, the  $^{254}(\text{UO})/^{238}\text{U}$  ion ratio measurements were fairly reproducible, with a variation of a factor 3 between samples. The  $^{270}(\text{UO}_2)/^{238}\text{U}$  ratio generally tracked the  $^{254}(\text{UO})/^{238}\text{U}$  ratio.

In contrast to the uranium oxide ions, the fluorine-containing uranium ions did show significant differences between the sample types, the storage times and the degree of exposure to ultraviolet light [7]. For samples stored in the laboratory for between 11 and 16 months, the  $^{257}(\text{UF})/^{238}\text{U}$  ratio was about 10 times lower than for samples that were only 2 months old. Similar decreases were observed for the  $^{273}(\text{UOF})/^{238}\text{U}$  and  $^{276}(\text{UF}_2)/^{238}\text{U}$  ratios, which generally tracked the  $^{257}(\text{UF})/^{238}\text{U}$  ratio, although the variations in the  $^{276}(\text{UF}_2)/^{238}\text{U}$  ratio were much more pronounced.



**Figure 3:** Energy-dispersive X-ray spectrum of a uranium-bearing particle prepared by the aerosol deposition chamber showing the U  $M_{\alpha}$  (3.17 keV) and  $M_{\beta}$  (3.34 keV) X-ray lines, in addition to the fluorine  $K_{\alpha}$  line at 0.677 keV. The other peaks in the spectrum were attributed to oxygen, carbon and sodium.



**Figure 4:** Energy-dispersive X-ray spectrum of a uranium-bearing particle prepared by the aerosol deposition chamber and heat-treated at 350 °C for 6 hours showing the U  $M_{\alpha}$  (3.17 keV) and  $M_{\beta}$  (3.34 keV) X-ray lines, in addition to carbon, oxygen and sodium. The fluorine  $K_{\alpha}$  line at 0.677 keV line could no longer be detected in this spectrum.

To assess the reduction in the level of fluorine due to exposure to ultraviolet light, particles on a graphite planchet were exposed to ultraviolet light for 3 weeks. Although the sample was only 2 months old at the time of measurement, the  $^{257}\text{UF}/^{238}\text{U}$  ratio had fallen to the level observed for particles that were stored for almost 1 year. This demonstrated that exposure to ultraviolet light significantly accelerated the particle ageing process.

Although the SIMS measurements showed distinct differences between samples with different storage or exposure conditions, large particle-to-particle variations within the same sample were also observed. These were attributed either to variations in the particle morphology or to SIMS measurement effects related to the ionisation and detection efficiencies. In some cases, a uniform film of uranium was detected instead of particles. The fact that the  $\text{UO}_2\text{F}_2$  particles are highly hygroscopic could explain this observation.

## 5. Conclusion and outlook

The aerosol deposition chamber produces micrometer-sized uranium oxyfluoride particles from the controlled hydrolysis of  $\text{UF}_6$ . These were used to study the effect of storage time and ultraviolet light exposure on the relative amount of fluorine in particles. A link between the relative amount of fluorine and the age of a particle was established, although large particle-to-particle variations within the same sample did occur. Planned transmission electron microscopy (TEM) and Raman measurements will give us more insights into the particle ageing processes. The results of a further study will be reported elsewhere [7].

The observation that the relative amount of fluorine in single particles is an indicator of the time since deposition, and possibly of the environmental influences, could be important in interpreting the data obtained from analysis of particles collected during safeguards inspections.

## 6. Acknowledgements

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