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SAMPLING AND CHARACTERIZATION OF AEROSOLS FORMED IN THE ATMOSPHERIC HYDROLYSIS  
OF UF<sub>6</sub>

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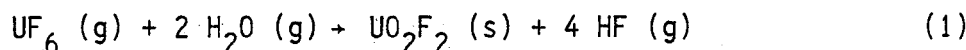
ABSTRACT

When gaseous UF<sub>6</sub> is released into the atmosphere, it rapidly reacts with ambient moisture to form an aerosol of uranyl fluoride and HF. As part of our Safety Analysis program, we have performed several experimental releases of UF<sub>6</sub> (from natural uranium) in contained volumes in order to investigate techniques for sampling and characterizing the aerosol materials. The aggregate particle morphology and size distribution have been found to be dependent upon several conditions, including the relative humidity at the time of the release and the elapsed time after the release. Aerosol composition and settling rate have been investigated using isokinetic samplers for the separate collection of UO<sub>2</sub>F<sub>2</sub> and HF, and via laser spectroscopic remote sensing (Mie scatter and infrared spectroscopy).

INTRODUCTION

Uranium hexafluoride (UF<sub>6</sub>) is the only uranium compound which is gaseous at moderate temperatures (boiling point ~56°C at 760 torr); as such, it finds large scale application in both the gaseous diffusion and centrifugation uranium isotope separation processes. The United States Department of Energy has sponsored a Safety Analysis effort to determine the fate of UF<sub>6</sub> which might be released into the environment. This communication summarizes some of our recent investigations on the sampling and characterization of the reaction products formed under conditions of a controlled release within an enclosed volume. Emphasis is upon those characteristics of the product which affect their dispersion and detection.

When it is released into the atmosphere, gaseous UF<sub>6</sub> is rapidly hydrolyzed by ambient moisture to form uranyl fluoride and HF:



"Anhydrous" UO<sub>2</sub>F<sub>2</sub> is hygroscopic (ref. 1), as is HF (ref. 2), hence, both species tend to become hydrated to some extent. The particulate UO<sub>2</sub>F<sub>2</sub> is readily visible as a white aerosol cloud or "smoke", which may rise and be dispersed into the environment.

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## PHYSICAL CHARACTERIZATION OF AIRBORNE PARTICULATE $UO_2F_2$

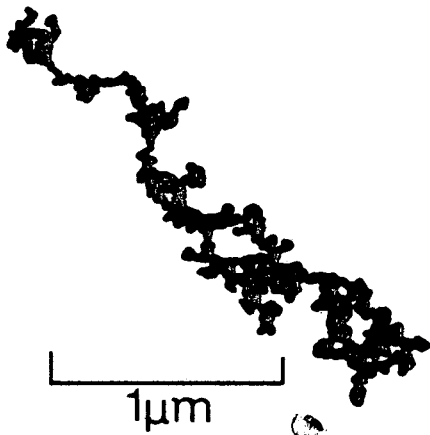
Particle size and morphology of airborne particulates are critical parameters in the dispersion of materials created in the atmospheric release of  $UF_6$  and in the detection of these materials by physical measurements such as light scatter or ionized smoke detection. Pickrell (ref. 3) has summarized the results for the experimental release of  $UF_6$  in a contained volume. Particle size and the degree of agglomeration were found to be dependent upon the temperature of the  $UF_6$  at the time of its release, the relative humidity (R.H.) of the air into which it is released, and the time elapsed after the release (Fig. 1). Materials formed in high humidity (e.g., > 85% R.H.) environments usually form solutions and, therefore, tend to be spheroidized (Fig. 1). When formed under "normal" conditions of humidity (e.g., 20 to 80% R.H.), the materials collected from the  $UO_2F_2$  "plume" tend to be chain-like agglomerates comprised of individual 0.1 to 0.2  $\mu m$  spheroids. These agglomerates may reach 5 to 10  $\mu m$  in greatest dimension, although most are smaller. Lux (ref. 4) has investigated the physical size distribution of fallout particulates formed under a variety of conditions, and found them to be concentrated in the lower end of the range 0.5 to 3.0  $\mu m$  (electron microscopy).

Samples collected from  $UO_2F_2$  plume and fallout have been examined by x-ray diffraction (XRD), (ref. 3). In general, these materials appear to be of variable composition, for which no standard data are available for comparison (ref. 1,3,5), although, on occasion, stable dihydrate or hydrogen fluoride hydrates of  $UO_2F_2$  have been identified in the fallout material.

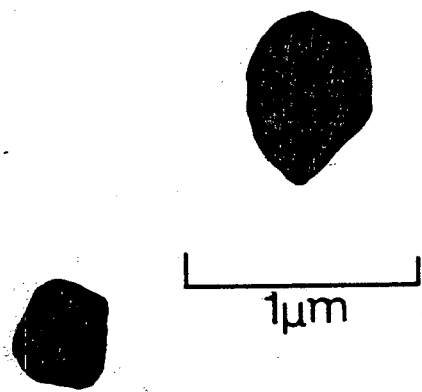
Fallout material from a typical  $UF_6$ -release experiment was determined to have a density of 4.13  $g/cm^3$ , and a refractive index of  $\sim 1.54$ .

## ISOKINETIC SAMPLING

Isokinetic samplers have application in aerosol measurements for health physics and in dispersion modeling due to their relative simplicity and low cost, and for the possible specific physical or chemical examination of the collected sample. Particulates, such as  $UO_2F_2$ , can be collected on a small pore size (e.g., 1  $\mu m$ ) membrane prefilter. Uranium may then be extracted and measured via spectroscopy or (if isotopically-enriched material is used) via alpha-radiation counting. HF vapor may be collected via chemisorption onto treated filters (ref. 6) or by impinging the vapor into a trapping solution (the former collection mode yields an integrated response over the sampling interval, whereas, the latter collection mode may be used for either integrated or continuous measurement). Fluoride ion is conveniently determined with use of an ion-selective electrode (ref. 6). Ishida and co-workers (ref. 7) have judged the sensitivity and response performance of the potentiometric measurement of fluoride ion (continuous mode) to be superior to that of an alpha dust

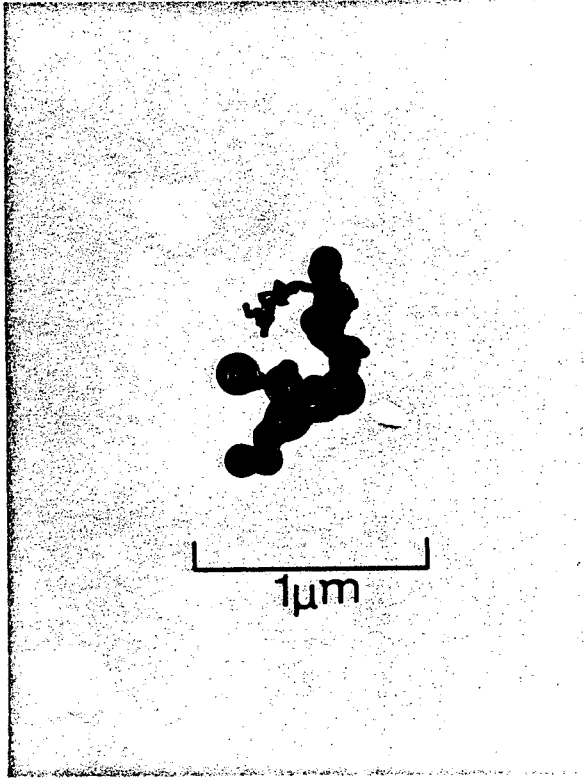


R.H. <2%

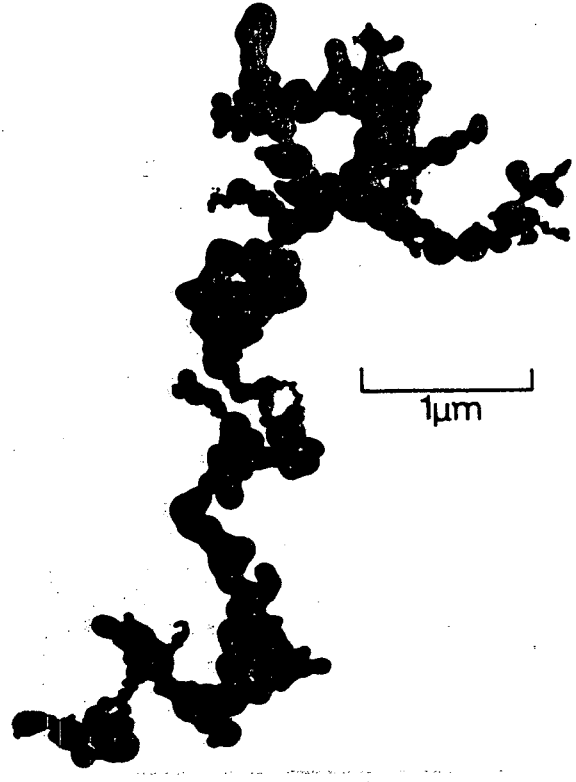


R.H. ~100%

Effect of relative humidity (R.H.) on particle size and shape.



R.H. = 47%  
 $\Delta t$  = 3 min.



R.H. = 47%  
 $\Delta t$  = 2h

Effect of elapsed time ( $\Delta t$ ) on particle agglomeration.

Figure 1

monitor or an ionized smoke detector for  $UF_6$ -release aerosols.

Our sampling system includes two membranes stacked together in a 47-mm filter holder made of hydrophobic polypropylene (Millipore Corp.); a 1- $\mu$ m pore Teflon membrane is used as the prefilter, and a 5- $\mu$ m pore formate-impregnated cellulose ester membrane (ref. 6) is used for HF recovery. In an  $UF_6$ -release experiment, 99.92% of the uranium drawn into the filter assembly was recovered on the prefilter. In a separate experiment, anhydrous HF (from a permeation tube apparatus, similar to that described in ref. 6) was metered into the filter assembly; recovery of HF was  $\sim 0.003\%$  on the prefilter and  $>97\%$  on the treated membrane.

The data presented in Fig. 2 represent analytical results obtained following the release of  $\sim 1$  g  $UF_6$  within an acrylic-walled test chamber with total volume  $\sim 0.2$  m<sup>3</sup>. A miniature diaphragm pump is used to pull an aerosol sample through the filter assembly and to return the remainder of the sample to the test chamber. Note in Figure 2A that both  $UO_2F_2$  and hydrated HF are progressively lost from the gas-phase due to sedimentation.

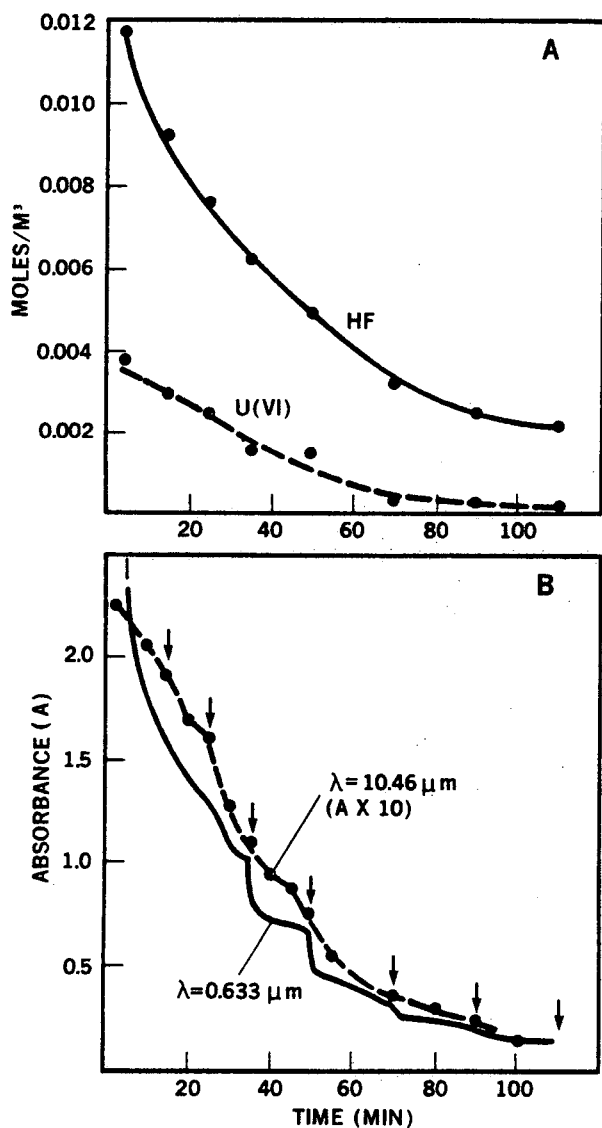


Figure 2. Aerosol measurement following the atmospheric release of  $UF_6$  ( $\sim 1$  g in a contained volume of  $\sim 0.2$  m<sup>3</sup>). (A) Results from the chemical analysis of materials collected on membrane filters using an isokinetic sampling system. Particulate  $UO_2F_2$  is collected on a 1- $\mu$ m pore Teflon prefilter, and HF is chemisorbed on a formate-impregnated cellulose acetate membrane. (B) Absorbance measurements ( $\sim 60$  cm pathlength), as performed with use of (1) a HeNe laser (solid line;  $\lambda = 0.633$   $\mu$ m), representing Mie scatter, and (2) a CO<sub>2</sub> laser (broken line;  $\lambda = 10.46$   $\mu$ m), representing uranyl ion concentration. CsI windows were inserted into the test chamber to permit transmission of the IR radiation. Arrows indicate times at which samples were withdrawn for chemical analysis (see Figure 2A).

## REMOTE SENSING OF PARTICULATE $UO_2F_2$ VIA SPECTROSCOPY

Remote sensing of aerosols would be advantageous in providing a real-time alarm to accidental releases of  $UF_6$ . Potentially, remote sensing devices could be employed to determine both the magnitude and the propagation of the aerosol.

Light-scattering is an obvious candidate for the remote sensing of particulates. Parameters which influence the intensity of light-scatter include the difference in refractive indices between the particulate material and the surrounding medium, the particle size distribution, and the radiation wavelength. The wavelength of visible radiation (0.4 to 0.7  $\mu m$ ) is comparable in magnitude to the particle sizes in the  $UO_2F_2$  aerosol, and thus the scattered light is strongly concentrated in the forward direction (Mie scattering).

The change in absorbance (turbidity) following a release of  $UF_6$  is shown in Fig. 2B, using a HeNe laser source ( $\lambda = 0.633 \mu m$ ). Comparison with the data obtained with use of the isokinetic sampling system (Fig. 2A) indicates that light-scatter is a sensitive index to the aerosol composition. (Also note the perturbation in light-scatter signal that occurs when a volume of gas-phase [1 to 8% of total] is sampled.)

Although light-scatter is a sensitive means for the detection of the aerosol, it is inherently nonspecific. Techniques related to light-scatter, but which can provide specific chemical information, include fluorescence and Raman spectroscopy. Many uranyl salts are fluorescent; however, we noted little fluorescence response for solid-phase  $UO_2F_2$  fallout material (i.e., only  $\sim 0.3\%$  of the response measured for  $UO_2[NO_3]_2 \cdot 6H_2O$ ). The fluorescence of solid-phase uranyl salts appears to be strongly affected by crystal properties and the extent of hydration (ref. 8).

A sample of  $\alpha-UO_2F_2 \cdot 1.5H_2O$  (ref. 5, card 24-1151), with relatively large crystals, produced an intense Raman peak at  $868 \text{ cm}^{-1}$ , attributable to the symmetric stretching frequency of the uranyl ion. Unfortunately, the very small particles from  $UF_6$ -release fallout failed to give a Raman signal which was distinguishable from background (argon-ion laser excitation,  $\lambda = 0.514 \mu m$ ).

Particulate material from the plume produced in the release of  $UF_6$  was collected onto a polyvinylchloride membrane filter using the isokinetic sampling system. The filter was then scanned directly in an infrared (IR) spectrophotometer. A strong absorption was evidenced at  $\sim 955 \text{ cm}^{-1}$  ( $\sim 10.5 \mu m$ ), due to the asymmetric stretching frequency of the uranyl ion. (This wavelength is long relative to the average particle size, minimizing scattering effects.) An additional absorption band was observed at  $\sim 1625 \text{ cm}^{-1}$ , attributed to hydrated water.

The 10P6 transition of a  $CO_2$  laser ( $\lambda = 10.46 \mu m$ ) is ideal for the specific detection of uranyl species in the aerosol. As shown in Fig. 2B, the absorption at this wavelength closely parallels the Mie scatter, but the

sensitivity is reduced by an order of magnitude. The absorbance cross-section for uranium in the aerosol can be estimated using the expression:  $A = 0.434\sigma nl$ , where  $A$  is the absorbance at  $10.46 \mu\text{m}$ ,  $n$  is the concentration of U(VI) in the aerosol (molecules/cm<sup>3</sup>), and  $l$  is the absorption pathlength (cm); the cross-section  $\sigma$  is thus estimated to be  $\sim 4 \times 10^{-21} \text{ cm}^2$  (a moderately strong IR absorption).

## CONCLUSIONS

The most salient characteristic of the aerosol produced in the atmospheric hydrolysis of  $\text{UF}_6$  is the small particle size of the  $\text{UO}_2\text{F}_2$  which is formed. Uranyl fluoride and HF components of the aerosol may be separately collected with the use of membrane filters in an isokinetic sampling system. The collected samples are in a stable, concentrated form from which they may be subsequently assayed using sensitive and selective wet chemical procedures. Alternately, remote sensing of the aerosol is possible using Mie scatter (which is sensitive, but inherently nonspecific) or by selective (but modestly sensitive) IR detection.

## ACKNOWLEDGEMENT

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