Morphologic and Chemical Characterization of Products from Hydrolysis of UF₆

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ABSTRACT: Characterization of the chemical speciation and morphologies of products formed from hydrolysis of uranium hexafluoride (UF₆) is important for predicting dispersion and contamination of released material, or health consequences from inhalation of air-borne particles. We report products of hydrolysis of UF₆ in which the quantity of water was insufficient for complete formation of UO₂F₂. Material was deposited onto carbon tape and aluminum. Scanning Electron Microscopy was employed to characterize textures and particle sizes, and powder X-ray diffraction analysis and μ -Fourier Transform Infrared Absorption spectroscopy were used to characterize chemical speciation. These results revealed that the ratio of H₂O to UF₆, depository substrate composition, and storage conditions must be considered when evaluating chemical speciation, morphologic textures and particles size of UF₆ hydrolysis products. LA-UR-15-23846.

KEYWORDS: hydrolysis; micro-Fourier Transform infrared spectroscopy; powder X-ray diffraction; Scanning Electron Microscopy; uranium hexafluoride; UOF₄

1. Introduction

Uranium hexafluoride (UF₆) is a ubiquitous material in the nuclear enterprise [1-3]. A grey crystalline solid with a high vapor pressure under standard temperature (T) and pressure, UF₆ is readily volatilized due to a low triple point at 64.05°C. This property, along with the fact that fluorine is mono-isotopic, qualifies UF₆ as a useful substrate for isotope enrichment.

Although UF₆ is inert to hydrolysis under dry air, a simple model suggests that UF₆ reacts with water as follows [4]:

Many studies have suggested that this reaction proceeds via a number of intermediates, including uranium oxy-tetrafluoride (UOF_4) and hydrogen fluoride (HF), followed by hydration and hydrofluorination to produce a mixture of uranyl fluorides and uranium oxides. Thus, it should be possible to isolate the UOF_4 intermediate in a reaction in which the quantity of water is insufficient for complete hydrolysis to UO_2F_2 [5,6]:

Theoretical studies have been carried out using relativistic density functional theory (DFT) to characterize mechanisms of UF_6 hydrolysis. These studies suggested a complex reaction pathway from UF_6 to UOF_4 through a UF_5OH intermediate, and reported binding energies of formation and vibrational frequencies of molecular fragments [7-9]. A subsequent study using DFT with a small-core, scalar relativistic pseudopotential proposed that trimolecular mechanisms are likely involved in formation of the UF_5OH intermediate [10]. While the structure and vibrational spectroscopy of UOF_4 has been reported, the UOF_4 intermediate has not been measured directly during hydrolysis of UF_6 in the presence of either excess or substoichiometric water concentrations [5,6 and refs therein].

A number of studies have attempted to fully characterize the hydrolysis products of UF_6 . Pickrell investigated morphologies of hydrolyzed UF_6 following gravimetric deposition onto Formar-coated electron microscope grids made of nickel [11-13]. A glass or metal sample holder with UF_6 was pressurized with heat, allowing the UF_6 to be released as a liquid. Analyses of the products formed indicated that aggregate particle morphologies and size distributions of the settled products were dependent upon relative humidity, temperature of the UF_6 , and time (hours)

after release. Powder X-ray diffraction (p-XRD) analyses identified formation of $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$, $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O} \cdot \text{HF}$, and other unidentified phases. Later, Kips reported similar observations regarding size and physical characteristics of materials generated from gaseous UF_6 material that settled onto graphite planchets [14,15]. In this latter study, UF_6 was contained in glass that was mechanically ruptured, allowing the compound to hydrolyze with air in a surrounding enclosure. Morphologic characterization revealed that chainlike agglomerates were made up of particles precipitated under conditions of 15% relative humidity, while non-chainlike agglomerates composed of irregularly-structured particles were formed under higher humidities.

Vibrational spectroscopy has been an important probe of chemical speciation of reaction products of UF_6 hydrolysis. Micro-Raman spectroscopy was employed to measure UO_2F_2 from UF_6 “residue powder” from hot UF_6 released to static, humid room air conditions [16]. Kips noted that UO_2F_2 was present in UF_6 hydrolysis products after storage under UV light [14]. The dynamic relationships between UO_2F_2 , H_2O , HF , and $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O} \cdot y\text{HF}$ products in aerosols formed from release of hot, pressurized UF_6 gas into ambient air were probed by Fourier-Transform Infrared (FT-IR) spectroscopy [17]. However, UOF_4 was detected by FT-IR following hydrolysis of UF_6 conducted in an argon matrix, a potential trap for reaction intermediates, or in solid films of $\text{UF}_6/\text{H}_2\text{O}$ mixtures prepared at 12 K and slowly annealed to 242 K [5,18]. Raman spectra collected from UF_6 hydrolysis products on stainless silver foil, stainless steel, or gold-coated silicon wafers revealed that the signals from UO_2F_2 products were enhanced compared to the signals from UO_2F_2 products deposited on graphite [19].

The method described herein differs from previous work in that we produced uranium oxy-fluoride material following introduction of ambient atmosphere into the UF_6 vapor under reduced pressure. This route is possible in a fracture from any UF_6 storage containment permitting air to

leak *into* the vessel such that the air is substoichiometric with respect to the UF_6 . Likewise, a large environmental release of UF_6 would induce a hypoxic environment on the interior of the cloud, favoring partial hydrolysis of UF_6 . We stored the deposited material under controlled conditions of temperature and relative humidity to evaluate changes in morphologic texture and chemical composition over time. We employed Scanning Electron Microscopy (SEM), μ -Fourier Transform Infrared Absorption Spectroscopy (μ -FTIR), and powder X-ray diffraction (p-XRD) analysis to characterize the products.

2. Experimental

Materials. The uranium hexafluoride (depleted) used in each experiment came from a single source. The temperature and relative humidity of the laboratory air was measured by a Fisher ScientificTM TraceableTM Radio-Signal hygrometer/thermometer. Double sided carbon conductive tape (acrylic adhesive bound carbon black) and aluminum conductive tape were purchased from Ted Pella, Inc. The bench-scale reaction chamber was built in-house from stainless steel parts [20,21]. Lithium iodide and potassium nitrate were purchased from Fisher Scientific. Calculation of pressure was conducted using standard formulas.

Uranium oxyfluoride products. A bench-scale reaction chamber was fabricated from stainless steel Swagelok fittings [20,21]. A labelled photograph, and cross sectional photograph are shown in Figure 1. The reaction chamber, which has a volume of 898 cm^3 , was evacuated to a pressure of 133 torr, as measured with a thermocouple vacuum gauge, at 25°C . The chamber was backfilled with UF_6 to a pressure of either 5 torr (0.3 mmol), 50 torr (3.5 mmol) or 55 torr (3.8 mmol UF_6). To form uranium oxy-fluoride particles, laboratory air at 17-19% relative humidity (0.10-0.13 mmol water vapor) was introduced into the chamber through a needle valve at a

sufficient rate to equilibrate to atmospheric pressure (579 torr at Los Alamos altitude of 2,230 m) over 15-30 minutes, allowing the water vapor in the air to react with the UF_6 . These amounts were insufficient to support either complete hydrolysis to UO_2F_2 (eq 1) (5 torr of UF_6 requires 0.6 mmol of water vapor, 50 torr of UF_6 requires 7.0 mmol of water vapor, 55 torr of UF_6 requires 7.6 mmol of water vapor) or partial hydrolysis (eq 2) (5 torr of UF_6 requires 0.3 mmol of water vapor, 50 torr of UF_6 requires 3.5 mmol of water vapor, 55 torr of UF_6 requires 3.8 mmol of water vapor). (See Table 1) Following hydrolysis, particles collected on carbon conductive tape or conductive aluminum tape on SEM stubs that were inserted into a 6 cm long strip situated in front of the air inlet, allowing particles to be collected 1-6 cm from the nozzle. After approximately 5 minutes, the reaction chamber was opened and the samples were removed for initial analyses and aging experiments.

Experiment number	Relative humidity (%)	H_2O (mmol)	UF_6 (mmol)	$\text{H}_2\text{O}/\text{UF}_6$	Collection substrate
1	19	0.13	0.3	0.43	Carbon tape
2	19	0.12	3.8	0.03	Carbon tape
3	17	0.10	3.5	0.03	Aluminum tape

Table 1. Relative humidity, quantity of water and UF_6 , ratio of water to UF_6 , and collection substrate for UF_6 hydrolysis experiments 1-3.

Figure 1. Labelled photographs of the reaction chamber for hydrolysis of UF_6 .

Aging of products under controlled temperature and humidity. Aging vessels fabricated from Swagelok fittings were described elsewhere [20,21]. The volume in the aging vessel was 7.8 mL, and the water vapor was circulated by natural convection. Four storage conditions of temperature and relative humidity included: Condition 1 (5°C, 25% relative humidity), Condition 2 (37°C, 15% relative humidity), Condition 3 (5°C, 97% relative humidity), and Condition 4 (37°C, 89% relative humidity), and are given in Table 2 along with respective water vapor densities.

Saturated lithium iodide aqueous solution was used to achieve lower relative humidities, and saturated potassium nitrate aqueous solution was used to establish higher relative humidities [21,22]. Time 0 was defined as the time at which the initial SEM measurements were collected. Average conditions in our laboratory were ~ 20°C and 20% relative humidity.

Condition	Temperature (°C)	Relative humidity (%)	Water vapor density (g/cm ³)
1	5	25	1.7 x10 ⁻⁶
2	37	15	6.6 x10 ⁻⁶
3	5	97	6.7 x10 ⁻⁶
4	37	89	39 x10 ⁻⁶

Table 2. Conditions (temperature, relative humidity) and resultant water vapor density used for storage of materials.

Crystallographic Measurements. Powder X-ray Diffraction (p-XRD) Analysis. Powder patterns were collected on a Bruker D8 Advance, with Lynxeye D silicon strip detector and unconditioned CuK_α X-rays. Qualitative analyses were performed using JADE 9.0 search/matching and the PDF-4+2013 database from the International Center for Diffraction Data.

Fourier Transform Infrared (FTIR) absorption spectroscopy. Infrared spectra were acquired using a Varian FTS7000 FTIR bench coupled to a UMA600 Infrared microscope. The samples were measured in reflection mode using a Ge attenuated total reflection objective accessory. The data were acquired at 4 cm⁻¹ resolution over 128 scan at 20 kHz using a liquid nitrogen cooled HgCdTe detector.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDS) Analysis. Images were collected on a FEI Quanta 200F Field Emission Scanning Electron Microscopy (SEM) using accelerating voltages of 15 – 30 kV. The SEM system was equipped with an EDAX Apollo

40 Energy Dispersive Spectrometer (EDS) detector that was used to qualitatively identify elements in the material. Gold-coating was carried out on selected samples to inhibit charging, as indicated in the Figure captions.

3. Results and Discussion

Prior experimental studies reported products of UF_6 hydrolysis under an excess of water [4]. However, partial hydrolysis is a relevant component in hypoxic conditions of leaking containment vessels or a reaction plume [5,6]. Equally important is understanding physical and chemical changes in these products as a function of controlled storage conditions of temperature and relative humidity [14,20].

3.1 Hydrolysis products deposited onto a carbon conductive tape

After filling the reaction chamber with 5 torr of UF_6 (0.3 mmol), the system was allowed to come to atmospheric pressure over 30 minutes with 19% humidified air (0.24 mmol) (see Table 1, Experiment 1). Immediate formation of a mist was observed through a glass window, and particles formed and gravimetrically deposited onto carbon tape mounted on aluminum SEM stubs. The chamber was evacuated and then backfilled to ambient pressure with laboratory air. Within two days, the stubs were imaged by SEM. Images revealed formation of spherical particulates $\sim 0.2\text{-}2\ \mu\text{m}$ in diameter (Figure 2). The SEM-EDS spectra indicated that the major elemental constituents were uranium, oxygen and fluorine (Supplemental Information Figure S-1). The shapes of the particulates were homogeneous, and some particulates were connected into agglomerates. A descriptor of the particulate morphology is given in Table 3 [23]. No differences in morphology or particle load were observed between samples collected at 1 cm versus 6 cm from the air inlet.

Figure 2. SEM images of material produced from 5 torr of UF_6 hydrolyzed under 19% relative humidity, and deposited onto carbon tape.

Experiment number	Substrate	Morphologic descriptor ²³
1	Carbon tape	Spherical particulates ($\sim 0.2\text{-}2\ \mu\text{m}$)
2	Carbon tape	Spherical particulates ($\sim 1\text{-}2\ \mu\text{m}$)
3	Aluminum tape	Divergent/radiating fibers

Table 3. Substrate and morphologic descriptor for material produced after each experiment.

The experiment was repeated with 55 torr of UF_6 (3.8 mmol) (see Table 1, Experiment 2). The SEM images revealed that a larger number of particulates formed, and that the average diameter of the spherical particulates was $\sim 1\text{-}2\ \mu\text{m}$ in diameter (Figure 3 and Table 3). Some agglomeration into short chains was observed [24]. As observed in Experiment 1, no differences in morphology or particle load were observed between samples collected at 1 cm versus 6 cm from the air inlet. SEM-EDS spectra indicated that the major elemental constituents were uranium, oxygen and fluorine (Supporting Information Figure S-2).

Figure 3. SEM images of material produced from 55 torr of UF_6 hydrolyzed under 19% relative humidity, and deposited onto carbon tape.

In contrast, Pickrell observed formation of $\sim 10 \mu\text{m}$ agglomerates made of discrete spheroids on the order of $0.1 \mu\text{m}$ in diameter following release of liquid UF_6 to excess water, and suggested that agglomeration of particles over time was likely due to charging [11,12]. Kips reported an increase in the average particle diameter with increased relative humidity [15]. Because the morphologic shapes of the materials deposited onto a carbon conductive surface were consistent with these prior experimental measurements and analyses, we chose not to store these samples under controlled conditions.

3.2 Hydrolysis products deposited onto conductive aluminum tape

We then examined the morphology and chemical speciation of hydrolyzed UF_6 particles deposited onto aluminum conductive tape. After filling the reaction chamber with 50 torr of UF_6 (3.5 mmol), the system was allowed to come to atmospheric pressure over 15 minutes under 17% humidified air (0.21 mmol) (see Table 1, Experiment 3). Particles formed and gravimetrically deposited onto conductive aluminum tape mounted to aluminum SEM stubs. The stubs were removed and the tape was imaged with SEM within two days. The SEM images revealed a different texture that is described as divergent/radiating fibers that are $\sim 5 \mu\text{m}$ in diameter (See

Figure 4 and Table 3). No difference in morphology or particle load was observed between samples collected at 1 cm versus 6 cm from the air inlet. The variation between morphologies of the materials released onto carbon tape versus aluminum may have been related to the differences between captive moisture in the substrates. Aluminum may also be etched by hydrogen fluoride. We found no other data, either from our experiments or those of other authors, to support conjecture regarding the effect of substrate composition on the morphology of hydrolysis products observed in this study [25].

Figure 4. SEM images and SEM-EDS spectrum of material produced from 50 torr of UF_6 hydrolyzed under 17% relative humidity, and deposited onto conductive aluminum tape.

3.3 Storage of hydrolysis products on conductive aluminum tape under controlled conditions

The aluminum tape used as a depository surface was cut into four sections. Each section was placed in an aging vessel under the controlled conditions provided in Table 2. After one week, a small portion of each sample was removed for imaging (See figure 5 and Table 4), and the remainder was returned to the appropriate aging vessel. Little change in the texture was perceptible in the material after storage under low relative humidity (Conditions 1 and 2) for 1 week. A cracked smooth surface formed after storage under Condition 3, indicative of

deliquescence. After storage under Condition 4, there was obvious formation of a more granular texture described as an agglomerate of acicular particles, which perhaps formed following from crystallization after rapid absorption and desorption of water. The SEM-EDS spectra indicated that uranium, oxygen and fluorine were the major elemental constituents (Supporting Information Figure S-3).

Condition number	Age (weeks)	Morphologic descriptor ²³
1	1	Divergent/radiating fibers
2	1	Divergent/radiating fibers
3	1	Smooth cracked surface
4	1	Agglomerate of acicular particles
1	7	Rounded/sub-rounded particles
2	7	Rounded/sub-rounded particles
3	7	Cracked agglomerate of layered platy particles
4	7	Cracked agglomerate of

		blocky/stubby particles
1	78	Divergent/radiating fibers
2	78	Divergent/radiating fibers
3	78	Cracked agglomerate of acicular particles
4	78	Agglomerate of acicular particles

Table 4. Summary of the descriptors for morphologic textures of material produced from 50 torr of hydrolyzed UF₆ under 17% relative humidity and deposited onto conductive aluminum tape after storage 1 week, 7 weeks, and 78 weeks (1.5 years) under Conditions 1-4.

Figure 5. SEM images of material produced from 50 torr of UF_6 hydrolyzed under 17% relative humidity, deposited onto conductive aluminum tape, and stored one week under Conditions 1-4.

The aluminum strips were returned to the aging vessels. After further storage for a total of 7 weeks, another small portion of each sample was removed for SEM analysis, and the remainder of each sample was returned to the appropriate aging vessel. The morphologic images of materials stored under low relative humidity (Conditions 1 and 2) revealed loss in definition of the edges to form round/sub-rounded particles $< 10 \mu\text{m}$ in diameter (Figure 6). Desorption after

storage under low relative humidity may have led to formation of divergent/radiating fiber-like structure to rounded/sub-rounded particles. Materials stored under Conditions 3 and 4 (high relative humidity) showed an increase in surface roughness, and formed cracked agglomerates of layered platy particles and block/stubby particles, respectively (Table 4). Following exposure to Conditions 1 through 4 for a total of 1.5 years (78 weeks), images were collected. Interestingly, the materials on sections stored under low relative humidity (Conditions 1 and 2) took on a different structure no longer composed of rounded/sub-rounded particles, but rather agglomerates that looked like divergent/radiating fibers (see Table 4). The images collected from the samples stored under Conditions 3 or 4 did not reveal significant textural changes. The major elemental constituents in each material were uranium, fluorine and oxygen, as recorded in the SEM-EDS spectra (Supporting Information Figure S-4).

Figure 6. SEM images of material produced from 50 torr of UF_6 hydrolyzed under 17% relative humidity, deposited onto conductive aluminum tape, and stored seven weeks under Conditions 1-4.

Figure 7. SEM images of material produced from 50 torr of UF_6 hydrolyzed under 17% relative humidity, deposited onto conductive aluminum tape, and stored 1.5 years (78 weeks) under Conditions 1-4. It was necessary to gold-coat these surfaces to inhibit charging.

Powder-XRD patterns from the material deposited onto the aluminum conductive surface that had been stored for 1.5 years (78 months) (Figure 8). Analyses of material stored under LANL conditions revealed (011), (022) and (033) reflections from UOF_4 , that likely formed as a reaction intermediate in the hydrolysis of UF_6 and remained during storage of the material. The

intensities of the reflections stored under Conditions 1-4 were quite weak against the aluminum background. Uranium oxide tetrafluoride (UOF_4) was measured only in materials stored under low temperature, low relative humidity, but no chemical species were identified in the material stored under Condition 2. The p-XRD patterns collected from materials stored under Conditions 3 and 4 revealed reflections from $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$, and a schoepite-species that was likely an admixture of schoepite ($\text{UO}_3 \cdot 2.25\text{H}_2\text{O}$) and metaschoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), was present in material stored under Condition 4, a result consistent with storage of U_3O_8 under high relative humidity conditions [20].

Figure 8. Powder-XRD patterns of material produced from 50 torr of hydrolyzed UF_6 hydrolyzed under 17% relative humidity, deposited onto conductive aluminum tape, and stored 1.5 years (58 months) under Conditions 1-4 and laboratory conditions at LANL, along with patterns of background aluminum (bottom). (+ = 011, 022 and 033 reflections from UOF_4 ; # = reflections from $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$; * = $\text{UO}_3 \cdot x\text{H}_2\text{O}$)

While p-XRD analysis is sensitive to long range order of the lattice, FT-IR spectroscopy provides information on both crystalline and non-crystalline chemical species in the material. A number of publications reported the energy of the infrared active asymmetric stretch of uranium oxy-fluoride compounds [1]. The infrared-active asymmetric stretch of uranyl, ν_3 , lies at $\sim 990\text{-}1000\text{ cm}^{-1}$ for anhydrous UO_2F_2 , and at $\sim 935\text{ cm}^{-1}$ for $\text{UO}_2\text{F}_2 \cdot \text{H}_2\text{O}$ [17,26,27]. A separate report suggested that an increase in level of hydration results in a decrease in the energy of ν_3 from 966 cm^{-1} ($\text{UO}_2\text{F}_2 \cdot \text{H}_2\text{O}$) to 945 cm^{-1} ($\text{UO}_2\text{F}_2 \cdot 4\text{H}_2\text{O}$) [28]. The energy of the U-O bond of UOF_4 was reported at 891 cm^{-1} in the infrared [6].

FT-IR absorption spectroscopy was employed to characterize these same samples (Figure 9). The material stored under Condition 3 was characterized by a sharp peak that is lower in energy (1009 cm^{-1}), which was assigned to the uranyl stretch anhydrous UO_2F_2 , and a peak at 893 cm^{-1} , which we assigned to the U-O vibration of UOF_4 . This peak was characterized by a shoulder to higher energy at 924 cm^{-1} , likely due to $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$ [6,17,26-28]. We assigned the peaks measured at $924\text{-}928\text{ cm}^{-1}$ to the asymmetric stretch of uranyl in $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$ [28]. These latter peaks were characterized by unresolved shoulders to lower energy, likely due to UOF_4 . Based upon the p-XRD data and the infrared spectra, it is most likely that each of the materials stored under Conditions 1, 2 and 4 contained both UOF_4 and $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$. In comparison, material

stored under Condition 3 retained a more significant amount of UOF_4 , as well as both anhydrous UO_2F_2 and $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$.

Figure 9. FT-IR spectra of material produced from 50 torr of hydrolyzed UF_6 under 17% relative humidity, directly deposited onto conductive aluminum tape, and stored under Conditions 1-4 (Condition 1, pink; Condition 2, green; Condition 3, purple; Condition 4, red) for 1.5 years (78 weeks).

4. Conclusions

Effective strategies for predicting the physical and chemical stabilities of materials, evaluating the dispersive properties of airborne particles, managing the fate of potential contamination, and assessing the health consequences of inhaled contaminants depend upon the ability to characterize physical and chemical transformations of products as a function of both storage conditions and time. Here, we developed a method to conduct water deficient hydrolysis of UF_6 in the gas phase. We observed different morphologies from material products formed on carbon tape versus aluminum. Substrate effects on particle morphology warrant future investigation. We measured changes in morphologies and chemical speciation in material released onto aluminum after storage under controlled conditions for 1 week and over longer periods of time. These analyses revealed that the ratio of H_2O to UF_6 , depository substrate composition, and storage conditions over time must be considered in evaluation of the chemical speciation, morphologic texture and particle size of UF_6 hydrolysis products for use in a number of applications.

ASSOCIATED CONTENT

Supporting Information

Supporting Information includes SEM-EDS spectra.

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Notes

The authors declare no competing financial interests.

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REFERENCES

1. I. Grenthe, J. Drożdżyński, T. Fujino, E. C. Buck, T. E. Albrecht-Schmidt, S. F. Wolf Uranium. In *The Chemistry of the Actinide and Transactinide Elements*; Morrs, L. R., Edelstein, N. M., Fuger, J., Katz, J. J., Eds; Springer: Dordrecht, The Netherlands, 2011; pp 557-567.
2. W. Bacher, W., E. Jacob, E. Uranium Hexafluoride. In *Handbook on the Physics and Chemistry of the Actinide*; Freeman, A. J., Keller, C., Eds; Elsevier Science Publishers, 1986; 1-38.
3. J. J. Katz, E. Rabinowitch Uranium Hexafluoride. In *The Chemistry of Uranium*, Part 1, The Element, Its Binary and Related Compounds; McGraw-Hill Book Company, Inc., 1951; 396-449.
4. W. D. Bostick, W. H. McCulla, P. W. Pickrell, J. Environ. Sci. Health A20(3) (1985) 369-393.

5. S. A. Sherrow, R. D. Hunt, *J. Phys. Chem.* 96 (1992) 1095-1099.
6. R. T. Paine, R. R. Ryan, R. L. B. Asprey, *Inorg. Chem.* 14(5) (1975) 1113-1117.
7. S.-W. Hu, H. Lin, X.-Y. Wang, T.-W. Chu, *J. Mol. Struct.* 1062 (2014) 29-34.
8. S.-W. Hu, X.-Y. Wang, T.-W. Chu, X.-Q. Liu, *J. Phys. Chem. A* 113 (2009) 9243-9248.
9. S.-W. Hu, X.-Y. Wang, T.-W. Chu, X.-Q. Liu, *J. Phys. Chem. A* 112 (2008) 8877-8883.
10. M. C. Lind, W. L.; Garrison, J. M. Becnel, *J. Phys. Chem.* 114 (2010) 4641-4646.
11. P. W. Pickrell, Characterization of the Solid, Airborne Materials Created when UF_6 Reacts with Moist Air Flowing in Single-Pass Mode. 1985, Oak Ridge National Laboratory, 1985; Report K/PS—1134.
12. P. W. Pickrell, Characterization of the Solid, Airborne Materials Created by the Interaction of UF_6 with Atmospheric Moisture in a Contained Volume; Technical Report No. K/PS-144; Union Carbide Corporation, Oak Ridge Gaseous Diffusion Plant: Oak Ridge, TN, April 1982.
13. W. D. Bostick, W. H. McCulla, P. W. Pickrell, D. A. Branam, Sampling and Characterization of Aerosols Formed in the Atmospheric Hydrolysis of UF_6 Oak Ridge National Laboratory, 2006; Report K/PS—5027.
14. R. Kips, A. J. Pidduck, M. R. Houlton, A. Leenaers, J. D. Mace, O. Marie, R. Pointurier, E. A., Stefaniak, P. D. P. Taylor, S. Van den Berghe, P. Van Espen, R. Van Grieken, R. Wellum, *Spectrochim. Acta, Part B* 64 (2009) 199-207.
15. R. Kips, A. Leenaers, G. Tamborini, M. Betti, S. Van den Berghe, R. Wellum, P. Taylor, *Microscopy and Microanalysis* 13 (2007) 156-164.
16. D. P. Armstrong, R. J. Jarabek, W. H. Fletcher, *Appl. Spectrosc.* 43(3) (1989) 461-468.

17. D. P. Armstrong, W. D. Bostick, W. H. Fletcher, *Appl. Spectrosc.* 45(6) (1991) 1008-1016.
18. P. F. Souter, L. Andrews *J. Mol. Struct.* 1997, 412, 161-167.
19. E. A. Stefaniak, L. Darchuk, D. Sapundjiev, R. Kips, Y. Aregbe, R. Van Grieken, *J. Mol. Struct.* 1040 (2013) 206-212.
20. A. L. Tamasi, K. S. Boland, J. C. Czerwinski, J. C. Ellis, S. A. Kozimor, R. L. Martin, A. L. Pugmire, D. Reilly, B. L. Scott, A. D. Sutton, G. L. Wagner, J. R. Walensky, M. P. Wilkerson, *Anal. Chem.* (Washington DC) 87 (2015) 4210-4217.
21. L. M. Anovitz, L.R. Riciputi, C. R. Cole, M. S. Gruszkiewicz, J. M. Elam *J. Non-Cryst. Solids* 352 (2006) 5652-5662.
22. ASTM Standard E104; ASTM International, West Conshohocken, PA, 2012.
23. A. L. Tamasi, L. J. Cash, C. Eley, R. B. Porter, D. L. Pugmire, A. R. Ross, C. E. Ruggiero, L. Tandon, G. L. Wagner, J. R. Walensky, A. D. Wall, M. P. Wilkerson. Manuscript submitted.
24. G. L. Wagner, M. T. Paffett, B. L. Scott, M. P. Wilkerson. In the Proceedings of the Plutonium Futures – The Science 2014 Conference, Las Vegas, NV, 7-12 September 2014.
25. Pitton, O.; Jørgensen, C. K.; Berthou, H. *Chem. Phys. Lett.* 40(3) (1976) 357-316.
26. K. Ohwada, *J. Inorg. Nucl. Chem.* 33 (1971) 1615-1623.
27. H. R. Hoekstra, *Inorg. Chem.* 2(3) (1963) 492-495.
28. A. A. Tsvetkov, V. P. Seleznev, B. N. Sudarikov, B. V. Gromov, *Russ. J. Inorg. Chem.* (Engl. Transl.) 18(3) (1973) 411-412.