Detection and Distinguishing of Uranium Particles and Plutonium Particles by Using Alpha Autoradiography

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Abstract. Tracks, which had been caused by alpha-particles in polycarbonate detector, are used for the detection of rare uranium and plutonium microparticles on the surfaces of different objects and for determination of alpha emitting component of particle. Prolongation of the tracks axis allows to implement first approximate localization of microparticle on the surface of investigated object with the uncertainty about 200 µm. Analysis of tracks geometry characteristics allows to determine, what is the the component of particle: uranium, plutonium or both together.

1. Introduction

As a rule unique alpha-emitted microparticles can not be investigated by using high sensitivity microbeam methods if such particles are located on the surface of relatively large or electrically nonconductive bearing objects: domestic appliances, clothing and other fabrics, etc. Therefore detection and extraction of such particles from bearing objects is necessary preliminary step before advanced and in-depth analyses.

Moreover preliminary information about the source of alpha emitting, plutonium or uranium, can be also useful for decision, is it necessary to extract concrete alpha-emitted particle or not. Further precise investigation of some particle after its very labor intensive extraction can not add useful information for prosecution.

The purpose of this paper is the demonstration of the developed analytical procedure for the detection of rare uranium and plutonium microparticles on the surfaces of different objects and for determination, is the detected particle uranium or plutonium. Detection of uranium and plutonium particles and determination of the particle component: uranium or plutonium, are based on the results of analysis of the orientation and of the shape of tracks, which had been caused by alpha-particles in polycarbonate detector. Besides the number of tracks allows to estimate the amount of uranium and/or plutonium in particle and consequently to estimate the size of particle.

2. Characteristics of uranium and plutonium particles and tracks

Clusters of tracks from uranium particles and from plutonium particles as well as from particles, which contain both of them, were investigated for experimental confirmation of validity of suggested approach. Both materials, original for microparticles: uranium and plutonium, were none monoisotopic. Uranium was HEU. Main alpha-emitter of that material is uranium-234. It emits alpha-particles with the energy about 4.8 MeV. The yield of alpha-particles from uranium-235 with the energy about 4.4 MeV could contain several percents. The yield of alpha-particles from uranium -238 could contain less than 1%.

Plutonium-239 and plutonium-240 were the main isotopes of the used plutonium, these isotopes provided alpha-particles with energies about 5.15 MeV. Minor, but much more alpha-radioactive plutonium-238 and americium-241 could provide no more than 20% of alpha-particles, the energies of these alpha-particles are about 5.5 MeV.

Track-detectors TASTRAK CR-39 (Track Analysis Systems Limited, UK) were used for registration of alpha-particles in this work. Typical track of alpha-particle has been flied into detector at an acute angle to the surface is shown on the fig. 1.

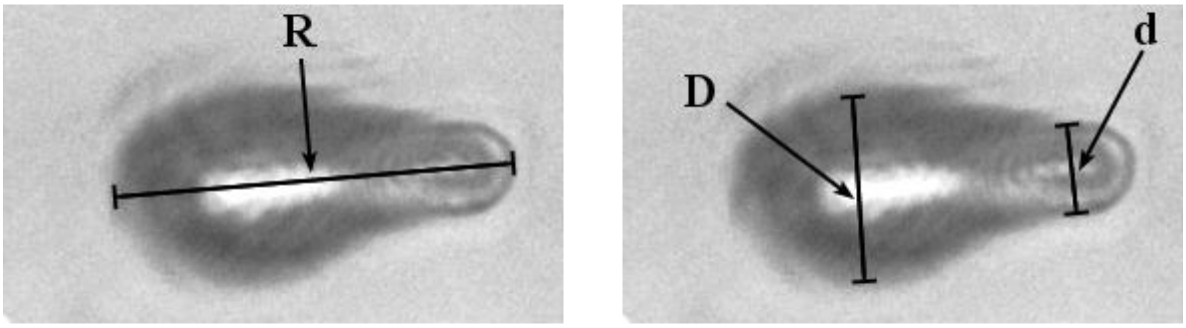

FIG. 1. Characteristics of individual alpha-track: length (large axis) R, diameter D of the input hole, diameter d of the curvature of cone top of the track.

For registration of alpha tracks the detectors were set on the distance about 200 µm above the investigated surface.

3. Distinguishing of alpha tracks from uranium and from plutonium microparticles

Shape and size characteristics of the track are the functions of the energy of the emitted alpha-particle [1, 2]. The study of the geometry parameters of alpha-tracks from thin modeling layers of uranium-235, plutonium-239 and americium-241 [2] has been shown that among all geometry parameters diameter d of the curvature of cone top of the track is most dependent on the energy of the alpha-particle.

Energies of alpha-particles of these isotopes and also uranium-234 as well as parameters of size distribution of the curvature of corresponding cone tops are presented in table 1. It can be seen, that these parameters allow to conclude that size distributions of the curvature of cone tops can identify alpha emissions of different isotopes. Therefore main attention in this work was paid to investigation of this characteristic of the tracks. The measurements of tracks geometry parameters in this work were implemented according to the technique [3].

Table 1. Energies of alpha-particles and parameters of size distribution of value d

Isotope	U-235	U-234	Pu-239+Pu-240	Pu-238+Am-241
Energy, MeV	4.4	4.8	5.15	5.5
Average d_{av}, µm	11.5	8.8	6	3.6
Std. deviation, µm	0.7	0.7	0.8	0.5

Images of typical small uranium and plutonium particles, track clusters, corresponding to these two particles and histograms of the size distributions of d for collection of four similar uranium particles and collection of two similar plutonium particles are presented on fig. 2. Tracks from several similar particles were processed for providing acceptable statistics.

Comparison of histograms for uranium and for plutonium particles allows to conclude, that alpha-autoradiography of suspicious objects can provide information not only about location of alpha-emitting microparticles on the surface of object, but also about the material of particle: HEU or plutonium.

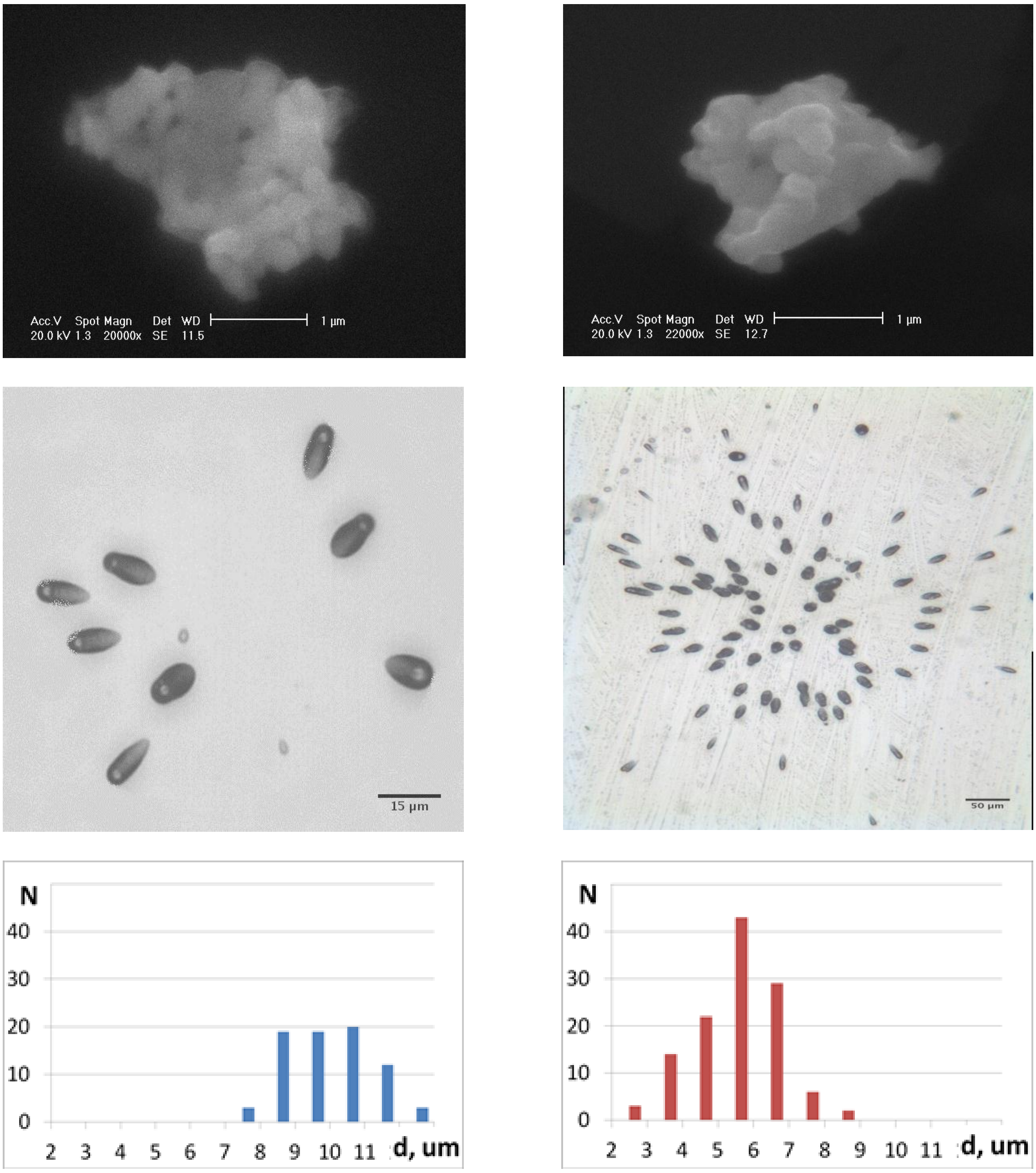

FIG. 2. Uranium (left) and plutonium (right) particles, corresponding alpha-track clusters and histograms of tracks distribution on values d for 4 uranium particles (blue) and 2 plutonium particles (red).

4. Detection and extraction of alpha-emitted particles

Particles of HEU and particles of mixture of HEU and plutonium were used for validation of the developed techniques. Special samples were prepared by putting of these particles on the surface of cotton fabric. Fabric surface was processed by 0.4% solution of polyisobutylene in the heptane after this putting for fixing of particles on the surface.

Duration of exposition of the detectors above the sample was 48 hours. Such duration provides registration of tracks from HEU particles with sizes about 2 µm and more, as well as from plutonium particles with sizes about 0.2 µm and more. Etching of exposed detectors was implemented in 6M solution of NaOH during 4 hours under 80ºC. Clusters of the developed tracks used for some characterization of particles.

Prolongation of the axis R of the track reconstructs the trajectory of emitted alpha-particle from the surface of the alpha-emitting microparticle. The crossing of the several tracks trajectories of the same cluster allows to localize microparticle on the surface of investigated subject. Fig. 3 illustrates the process of determination of the area of the tracks crossing.

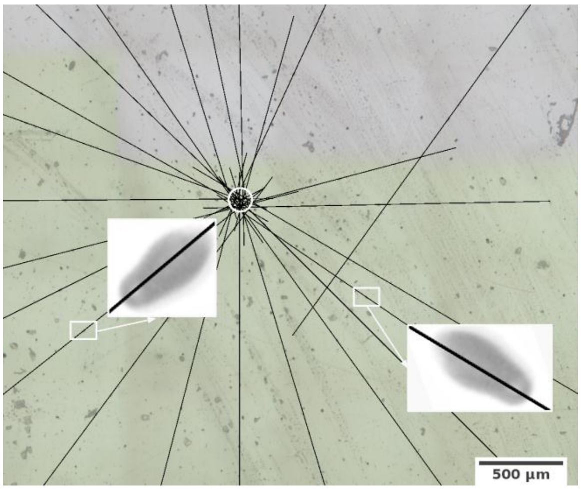

FIG. 3. Determination of the center of tracks cluster.

Specially manufactured template with coordinated grid is used for correct re-alignment of developed detector and the investigated sample. The using of this template allows to provide the accuracy of localization of particles on the fabric surface (150 … 200) µm. The punch was manufactured for cutting of the fabric fragments, which contain alpha emitting particle. Diameter of cut fragment is 5 mm (fig.4). This size guaranteed presence of sought-for particle on the cut piece of fabric and provides convenient further manipulations with the fragment. Assurance about this presence is reached by repeat expositions of cut fragments.

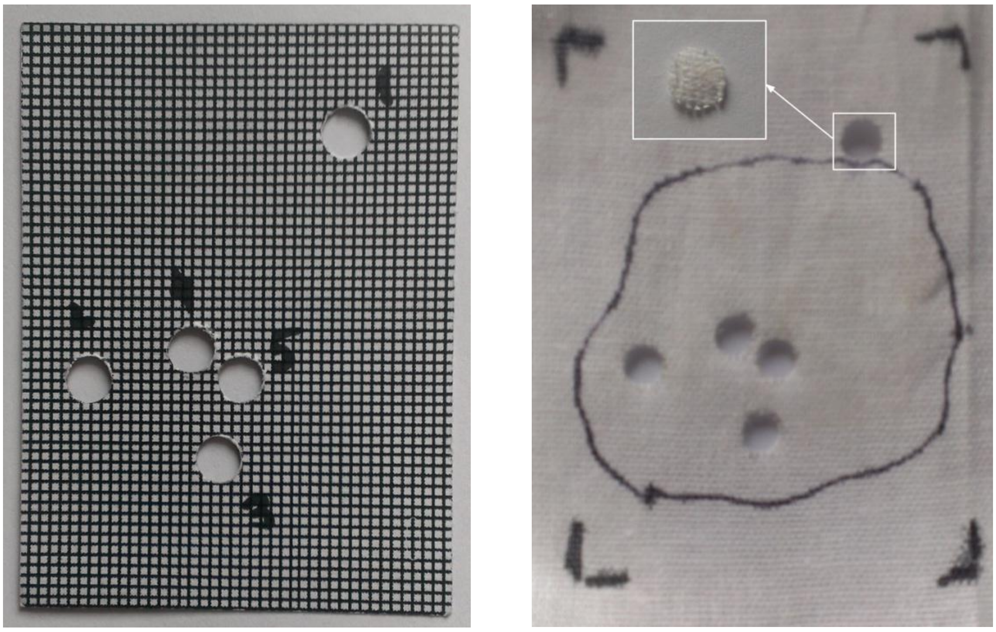

FIG. 4. Girded template (left) and fabric (right) with holes from 5 cut fragments and with one cut fragment.

5. Information about composition and size of alpha-emitting microparticles

Preliminary information about composition and size of alpha-emitting microparticles is important if not all particles can provide prosecution with useful information. The time and efforts can be saved for useful work. The possibility of obtaining of the correct preliminary information is checked by the comparison of the results of alpha autoradiography with the results of ICP mass spectrometry of 2 cut fragments (fig. 4). ICP MS was applied for much more accurate measuring of amount of uranium and plutonium in 2 cut fragments (in 2 particles) and for confirmation or disavowal of the alpha autoradiography results. The results of analysis of two particles with different elemental compositions are discussed in this paper.

Loss of energy of the alpha particle during the moving through the solid of microparticle should be taken into consideration for the correct interpretation of the histograms with size distribution of the curvature of corresponding cone tops. The energy loss determines increasing of the diameter d of the curvature of cone top corresponding to that alpha particle. Accordingly the distribution will be expanded to the direction of the larger values of diameter d and maximum of distribution will be shifted in the same direction.

Energy losses are significant in the high density particles of uranium oxides with sizes beyond 3 µm and particles of plutonium oxides with sizes beyond 5 µm [4]. Alpha particles, which are emitted by nucleus of uranium-234 from the microparticle depth layer of 2 µm, will form tracks corresponding to alpha particles, which are emitted from the surface of microparticle by nucleus of uranium-235. Alpha particles, which are emitted by nucleus of uranium-234 from the microparticle depth layer of 3 µm, will form tracks corresponding to alpha particles, which are emitted from the surface of microparticle by nucleus of uranium-238.

Size distribution of diameter d for particle 1 is shown on fig. 5. Total amount of tracks is 347. Maximum of distribution about d = 6 µm confirm the presence of plutonium. Expanding of the size distribution to the direction of larger values d can be explained by the presence of uranium as well as by a relatively large size of the plutonium microparticle and accordingly by majority of alpha particles, which have lost its energy inside the solid of microparticle.

But total amount of tracks and accordingly common alpha radioactivity of the microparticle does not correspond to relatively large plutonium microparticle. It corresponds to the diameter of spherical plutonium particle of about 0.5 µm. No energy loss can be noted under such a size. Therefore it may be concluded, that both: plutonium and HEU present in microparticle.

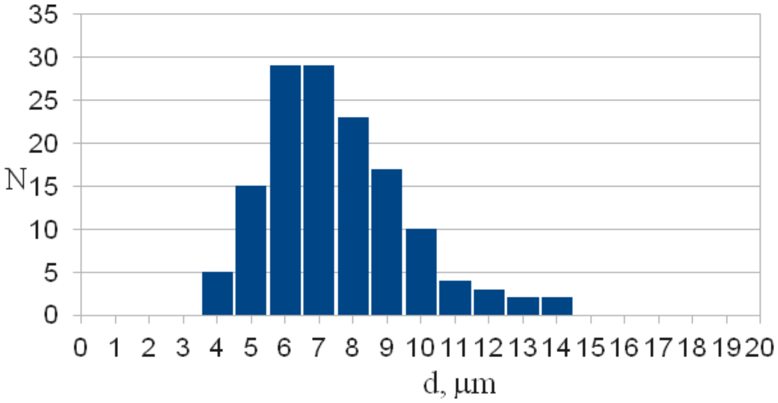

FIG. 5. Size distribution of diameter d for fragment 1 (particle 1).

Tracks with d = 14 µm can be formed by alpha particles emitted by the uranium-234 nucleus and flown about 3 µm inside the solid of microparticle.

Amounts of plutonium and HEU can be estimated by dividing the size distribution of d in correspondence with modeling size distributions for plutonium-239 and plutonium-240 together and for uranium-234 separately. Selecting the altitudes of distributions, summarizing these modeling distributions and inscribing of the sum of two modeling distributions into experimental distribution allow to obtain two approximate distributions. Two such distributions for particle 1 are shown on the fig. 6.

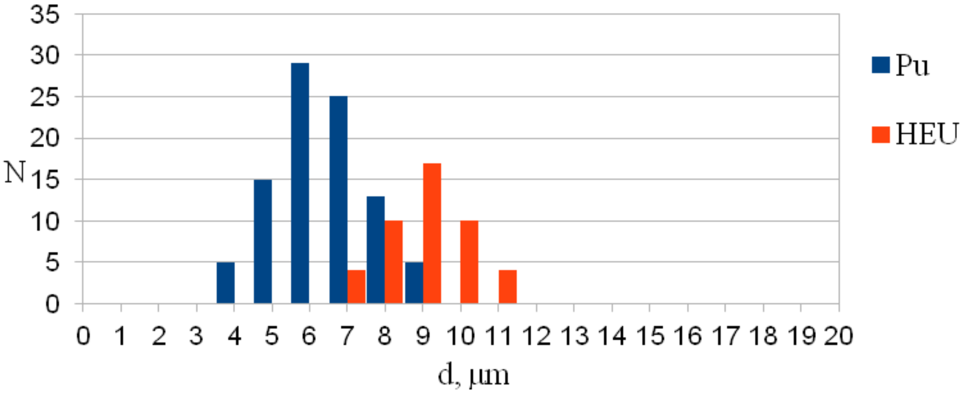

FIG. 6. Dividing of size d distribution of fig. 5 on two modeling distributions: "^{239}Pu + ^{240}Pu distribution" (blue) and "^{234}U-distribution" (red).

This dividing together with the total amount of tracks determines the size of HEU particle about 4 µm, and the size of plutonium particle – about 0.4 µm. It means that the size of single particle is about 4 µm.

ICP MS results confirm the presence of both: plutonium and HEU in this microparticle. Measured amount of plutonium and uranium correspond to spherical microparticle of plutonium with diameter 0.51 µm and spherical microparticle of HEU with diameter 2.6 µm. It means that ICP MS results also confirm the approximate estimation of microparticle size.

Size distribution of diameter d for autoradiography results of particle 2 is presented on fig. 6.

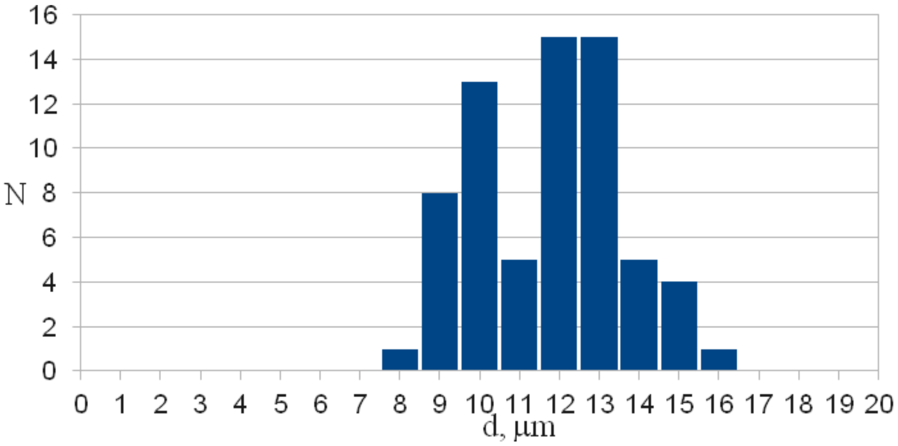

FIG. 6. Size distribution of diameter d for fragment 2 (particle 2).

Total amount of tracks is 183, what determines some worse statistics parameters in comparison with the particle 1. Minimum value of diameter d is about 8 µm. It means that microparticle does not contain plutonium and contains HEU only. Maximum value of diameter d is about 16 µm.

It determines the flying distance about 6 µm inside the solid of microparticle for alpha particle emitted by the nucleus of uranium-234. Total amount of tracks approximately correspond to such size of HEU microparticle.

ICP MS results confirm the presence only of HEU in this microparticle. Measured amount of HEU correspond to spherical microparticle of HEU with diameter 7.2 µm, what is relatively close to 6 µm had been determined by alpha autoradiography method.

6. Conclusions

1. The results of alpha autoradiography allow to distinguish HEU particles and plutonium particles by the comparison of size distributions of the curvature of corresponding alpha track cone tops.

2. Accuracy of the localization of alpha emitting particle on the first step of its proceeding is about 200 µm.

3. Analysis of the size distribution of the curvature of the alpha track cone tops allows not only to distinguish HEU microparticles and plutonium microparticles, but to determine the presence of both elements in microparticle, to estimate amounts of uranium and plutonium in particle and even to estimate the size of particle with relative uncertainty about 20%.

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Probing Forensic Signatures of Nuclear Materials

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Abstract. Processes conducted to purify uranium-bearing materials are chemical in nature. These activities provide the opportunity for chemical reagents or reaction intermediates to carry over into uranium end-products. Measurements of the chemical species in uranium oxide conversion materials may provide information important to forensic analyses, and signatures of the detectable chemical species may transform over time. To better evaluate detectable process signatures from conversion materials, we have initiated an effort to measure chemical speciation and to monitor temporal changes in materials subjected to controlled temperatures and relative humidities.

1. Introduction

It has been reported that new analytical approaches are needed for the field of nuclear forensic science, and that there is interest in developing tools that are sensitive to chemical speciation for forensic analyses [1-2]. The range of chemical compositions of uranium oxides is considerable and complicated, providing challenges to measurement and interpretation, particularly in non-crystalline materials [3]. Previous work conducted by our research team to study environmental samples containing uranium revealed the value of synchrotron-based X-ray Absorption Spectroscopy for probing chemical speciation of non-crystalline materials containing actinides [4]. We explored the use of synchrotron-based micro-X-ray absorption techniques developed at the Stanford Synchrotron Radiation Lightsource (SSRL) Beam Line 2-3 to image elemental compositions and chemical speciation of environmental samples containing actinide oxide materials with the intent of understanding future transport and fate of actinides in the environment.

One component of forensic analyses of interdicted materials is characterization of morphologies. Identification of chemical speciation of both major and minor components in a sample may be correlated with process history [5-9]. Both classes of signatures may be impacted over time by temperature and relative humidity. We employ powder X-ray diffraction (pXRD) analysis and synchrotron-based extended X-ray absorption fine structure (EXAFS) spectroscopy to characterize chemical speciation in uranium oxide powder samples, and to probe temporal changes in the valence

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states and chemical speciation following storage under controlled conditions of temperature and relative humidity. These tools provide complementary means for characterizing subtle changes in the material.

2. Experimental

The cornerstone of this work is the ability to synthesize and analyze high-purity uranium oxides samples from U960, a NIST Standard Reference material, for eventual comparison with uranium oxides prepared using common conversion processes. We prepared U_3O_8 by dissolution of U metal in $HCl_{[conc]}$, followed by precipitation of uranyl peroxide hydrate [3]. The $UO_2(O_2)$ was heated in air to 500ºC for 8 hours to form amorphous uranium trioxide (A-UO_3). The orange A-UO_3 was then ground using a mortar and pestle, returned to the ceramic boat, and heated at 800ºC under air for 20 hours. The product is a dark black powder. The phase was confirmed by powder X-ray diffraction analysis.

Subsamples were subjected to controlled temperatures and relative humidities (LTLH: 5ºC and 25% relative humidity; HTLH: 37ºC, 15% relative humidity; LTHH: 5ºC and 97% relative humidity; HTHH: 37ºC, 89% relative humidity) in order to measure and compare potential changes in morphology versus chemical speciation as a function of time. Aging vessels consisting of modified Swagelok fittings are described elsewhere [10]. Lithium iodide and potassium nitrate salt solutions were used to control relative humidities within the aging vessels [11].

Powder X-ray diffraction measurements were collected on either a Bruker D8 Discover diffractometer quipped with either a Hi-Star area detector or a NiI scintillation detector, and monochromatized Cu K_α X-rays, or on a Bruker D8 Advance diffractometer equipped with a Lynxeye 1-3 silicon strip detector and unconditioned Cu K_α X-rays. Samples for EXAFS measurements were prepared by diluting the uranium oxide analyte with boron nitride and then finely grinding the mixture with a Wig-L-Bug. Each mixture was loaded into nested aluminum sample holder equipped with Kapton windows and sealed with indium wire. Measurements were conducted at SSRL on end stations 10-2 and 11-2 under dedicated operating conditions (3.0 GeV, 5%, 450 mA) using a Si[220] (ϕ = 90) double-crystal monochromator. Morphologic images of materials were collected on an FEI Quanta 200F Field Emission Scanning Electron Microscopy (SEM).

3. Results

The pXRD analysis of high purity U_3O_8 material reveals pure α-U_3O_8, as shown in Figure 1. The purity of this material contrasts the compositions of legacy materials of known pedigree but prepared using synthetic routes common to commercial processing of uranium oxides. In these legacy materials, it was possible to measure chemical precursors, such as uranyl fluoride hydrate, uranyl peroxide hydrates, or ammonium diuranate [3].

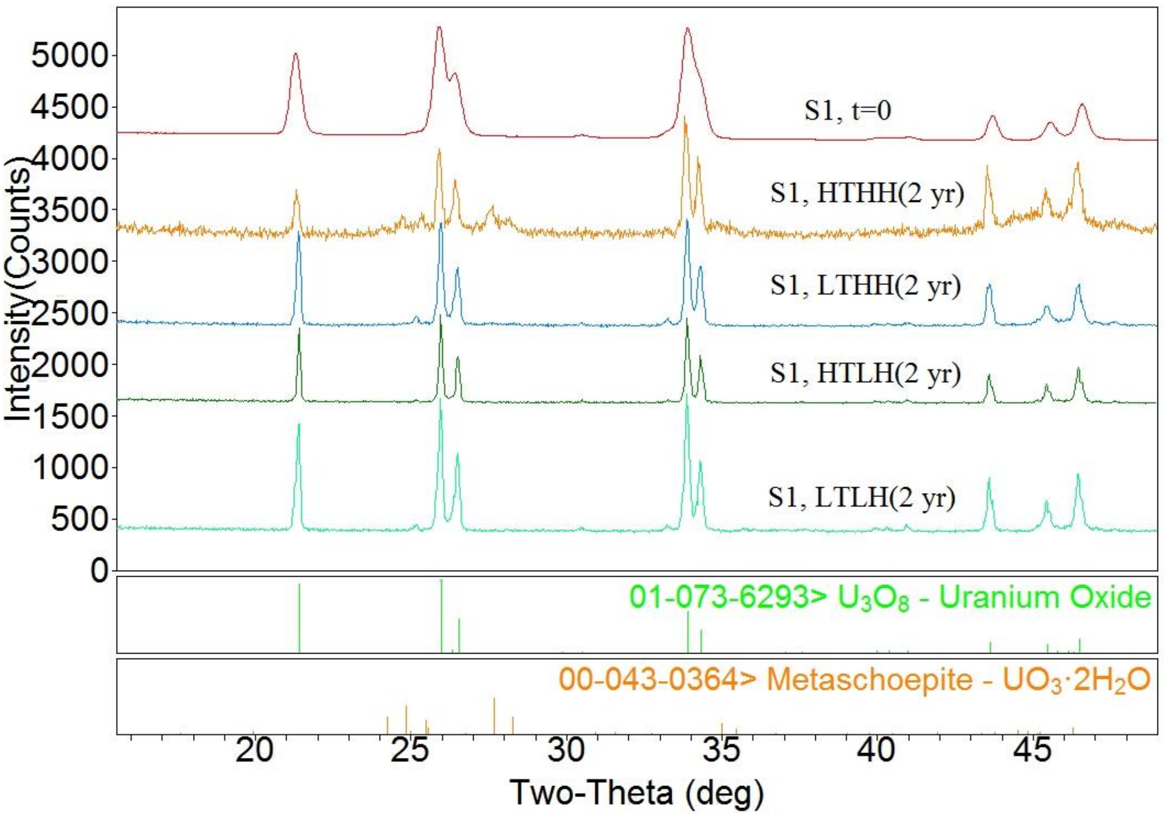

FIG. 1. Powder X-ray diffraction patterns of U_3O_8 measured following synthesis of the material (time = 0), and after storage for 2 years under the following conditions: High Temperature High Relative Humidity (HTHH), Low Temperature High Relative Humidity (LTHH), High Temperature Low Relative Humidity (HTLH), and Low Temperature Low Relative Humidity (LTLH).

The EXAFS spectrum for high purity U_3O_8 is shown in Figure 2. The U-O and U-U scattering paths calculated from α-U_3O_8 were used to model the EXAFS data sets.

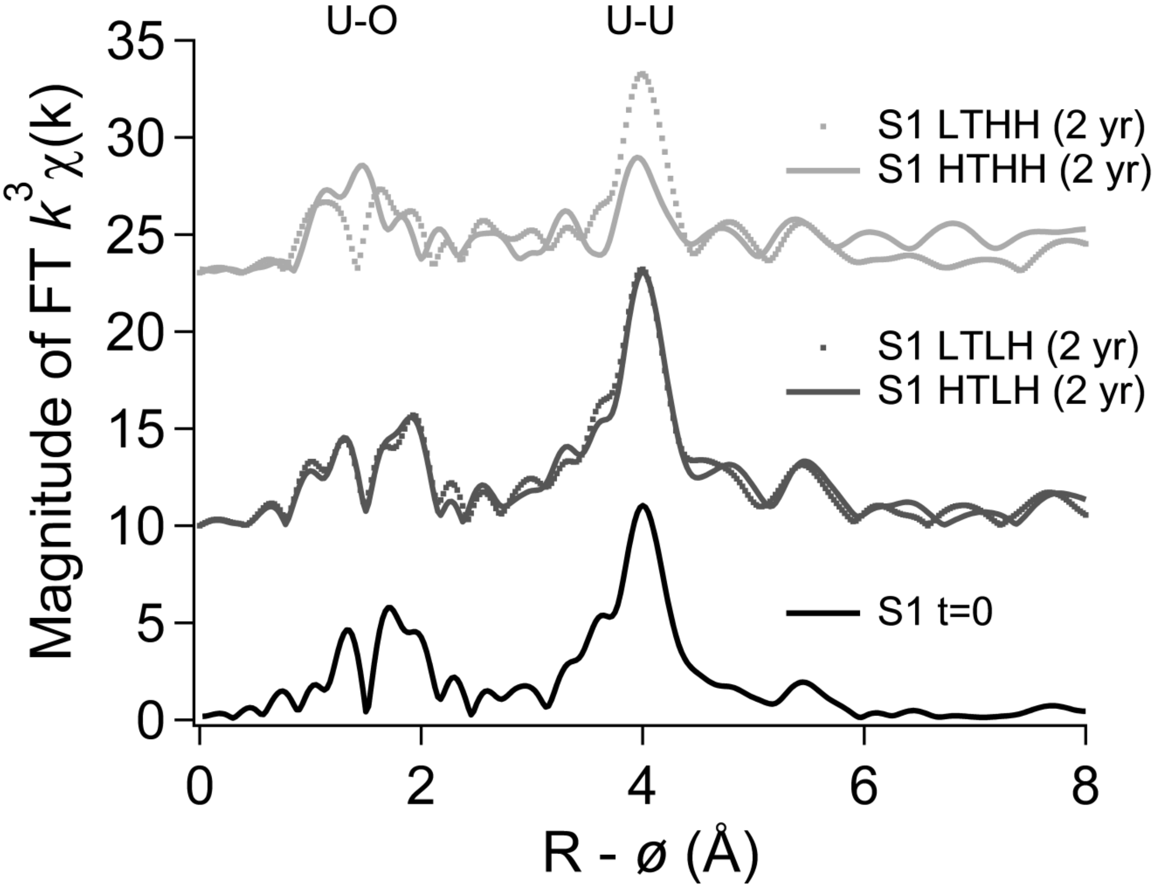

FIG. 2. Fourier Transforms of U L_{III} *EXAFS data of* U_3O_8 *measured following synthesis of the material (time = 0), and after storage for two years under the following conditions: High Temperature High Relative Humidity (HTHH), Low Temperature High Relative Humidity (LTHH), High Temperature Low Relative Humidity (HTLH), and Low Temperature Low Relative Humidity (LTLH).*

An SEM image reveals that the material is composed of fairly spherical granules approximately 2 µm in diameter (Figure 3), which is comparable with the morphology measured from the uranyl peroxide precursor.

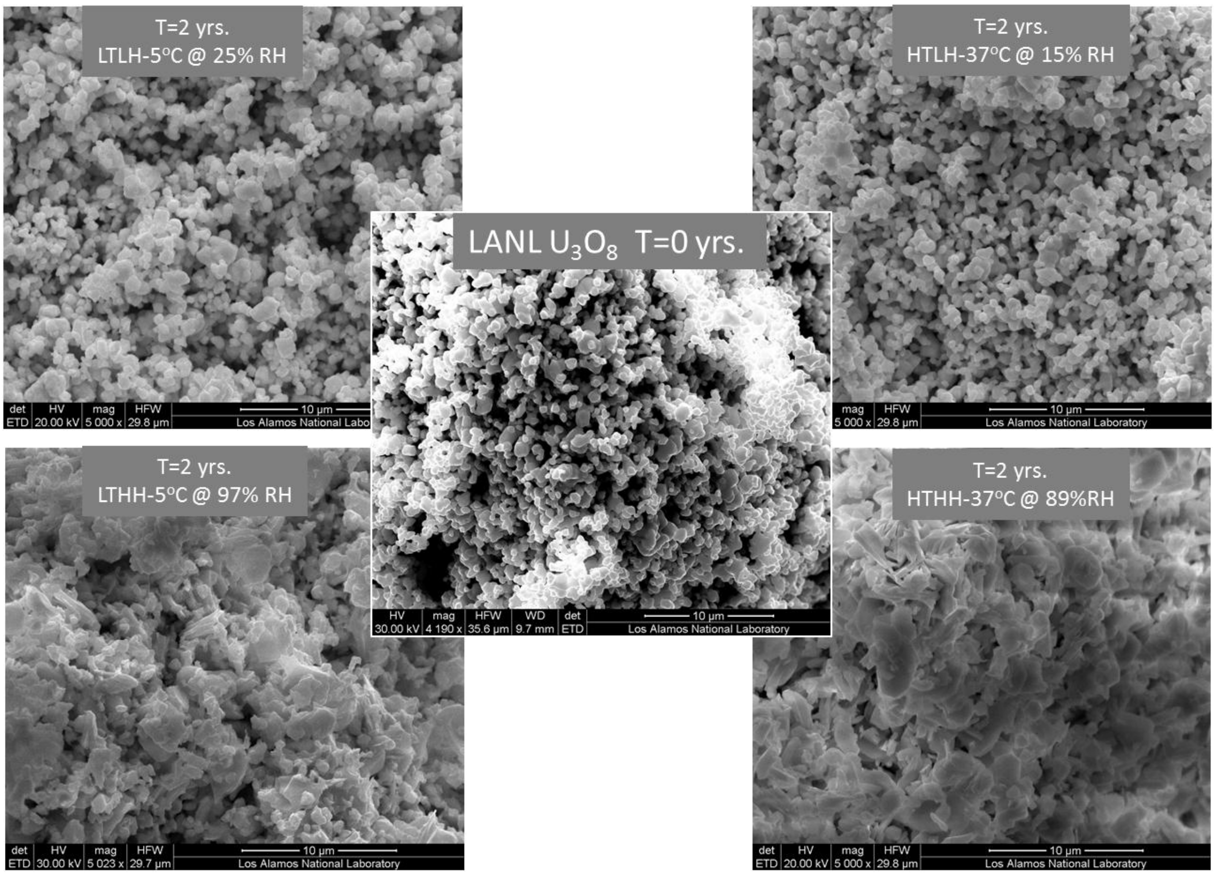

FIG. 3. SEM images at 5000X of U_3O_8 measured following synthesis of the material (time = 0), and after storage for two years under the following conditions: High Temperature High Relative Humidity (HTHH), Low Temperature High Relative Humidity (LTHH), High Temperature Low Relative Humidity (HTLH), and Low Temperature Low Relative Humidity (LTLH).

Ingrowth of metaschoepite ($UO_3\cdot 2H_2O$) is measured following exposure of U_3O_8 to controlled relative humidity and temperature over two years. Comparison of X-ray diffraction patterns with reference lines reported in the Cambridge Crystallographic Database reveals both U_3O_8 and $UO_3\cdot 2H_2O$ in the subsamples stored under high temperature and high humidity after two years (Figure 1). Significant changes are observed in the Fourier Transforms (FT) of the samples stored under high humidity conditions in terms of reduced amplitude in the U-U region, and changes in the number and position of peaks in the U-O region, particularly at high temperature. The FTs of the EXAFS data are not significantly altered in terms of the U-O local structure after exposure to low humidity conditions after two years (Figure 2). While the subsamples stored at low relative humidities maintain a similar shape after two years of storage, images of the two samples stored under high relative humidity conditions reveal visible flattening and loss of granule definition (Figure 3).

4. Conclusions

Our studies show that chemical signatures indicative of reaction history are measurable, and that chemical signatures may change under certain conditions. Further work is being conducted to exploit the rich, albeit complex, information from these complimentary probes to support the reconstruction of a sample's process history.

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