



# Nuclear forensics investigation of morphological signatures in the thermal decomposition of uranyl peroxide

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## ABSTRACT

The analytical techniques typically utilized in a nuclear forensic investigation often provide limited information regarding the process history and production conditions of interdicted nuclear material. In this study, scanning electron microscopy (SEM) analysis of the surface morphology of amorphous- $\text{UO}_3$  samples calcined at 250, 300, 350, 400, and 450 °C from uranyl peroxide was performed to determine if the morphology was indicative of the synthesis route and thermal history for the samples. Thermogravimetric analysis-mass spectrometry (TGA-MS) and differential scanning calorimetry (DSC) were used to correlate transitions in the calcined material to morphological transformations. The high-resolution SEM images were processed using the Morphological Analysis for Material Attribution (MAMA) software. Morphological attributes, particle area and circularity, indicated significant trends as a result of calcination temperature. The quantitative morphological analysis was able to track the process of particle fragmentation and subsequent sintering as calcination temperature was increased. At the 90% confidence interval, with 1000 segmented particles, the use of Kolmogorov-Smirnov statistical comparisons allowed discernment between all calcination temperatures for the uranyl peroxide route.

## 1. Introduction

For interdicted nuclear materials, there is an increasing reliance on nuclear forensics for the identification of the nuclear material's source and route of diversion in order to mitigate the potential for additional illicit trafficking. Nuclear forensic analysis utilizes elemental, isotopic, chemical, and physical signatures to provide technical insight into the provenance (synthesis methods and procedures), and history of nuclear materials of an unknown origin [1]. These signatures can be the result of multiple factors including the starting materials, chemical synthesis and conversion conditions, neutron irradiation, physical processing (milling and grinding), and aging conditions. Understanding the impact of these parameters on the resulting product can improve the accuracy of nuclear attribution. Among the most important nuclear materials requiring well characterized forensic signatures is uranium and its associated oxide species.

The nuclear fuel cycle is initiated with the extraction of uranium-bearing ore from a mine. The uranium is recovered from the ore through leaching (acidic, basic, and/or in-situ), purified via solvent extraction or column chromatography, and precipitated through the addition of ammonia, magnesium, sodium hydroxide, ammonium hydro-

xide, or by the formation of  $(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$  using hydrogen peroxide [2–4]. The precipitation of ammonium di-uranate (ADU) with gaseous ammonia or ammonium hydroxide was frequently used, but is now discouraged due to environmental concerns [5]. As a result of ammonia's environmental hazards, the increasing demand for higher purity uranium product, and the need to reduce contaminants from lower grade ores, there has been great interest in utilizing the hydrogen peroxide precipitation process. Several commercial plants have utilized the peroxide route since the 1960's, including the Rabbit Lake Uranium Mill in Canada [5], the Uranium Corporation of India Limited at Jaduguda Mines [6], and Atlas Minerals of Moab, UT [7].

The resulting precipitates may then be calcined to  $\text{UO}_3$  or  $\text{U}_3\text{O}_8$ , or be directly reduced to  $\text{UO}_2$ . Commercially, the calcination of uranyl peroxide to  $\text{UO}_3$  or  $\text{U}_3\text{O}_8$  is often performed to increase product stability, improve product purity, and reduce shipping costs [8]. The calcination of uranyl peroxide to  $\text{UO}_3$  occurs commercially at temperatures ranging from 260 to 450 °C, and for the calcination to  $\text{U}_3\text{O}_8$  at temperatures of 700–800 °C [5,9–13]. To complicate matters further, depending upon the source material and the calcination temperature, the resulting  $\text{UO}_3$  can consist of various crystalline polymorphs [14]. To this end, in this study, the morphology of a common polymorph

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from the uranyl peroxide route, amorphous- $\text{UO}_3$  (am- $\text{UO}_3$ ), was evaluated as a forensics identifier of the material's processing. In 1963, Cordfunke et al. synthesized am- $\text{UO}_3$  via the uranyl peroxide route from a uranyl nitrate solution [15]. They found that if the uranyl peroxide precipitate,  $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ , was washed of any residual nitrates, and dried at 80 °C to form  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ , no apparent change in morphology occurred. Upon calcination at 425 °C, am- $\text{UO}_3$  was formed, and retained the morphology of the initial uranyl peroxide. Through additional heating to 500 °C,  $\alpha$ - $\text{UO}_3$  would be formed. In contrast, if the residual nitrates were not washed from the uranyl peroxide precipitate, the drying process resulted in  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$  with a radically different morphology. Further calcination at 425 °C would produce  $\alpha$ - $\text{UO}_3$ , with no apparent change in morphology from the previously dried  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ . While the final product of both the washed and unwashed uranyl peroxide can be  $\alpha$ - $\text{UO}_3$ , Cordfunke et al. noted that the morphology of the resulting  $\alpha$ - $\text{UO}_3$  can be drastically different [15]. From a nuclear forensic analysis viewpoint, this work indicates an analysis of surface morphology could narrow the source of a  $\text{UO}_3$  material of unknown origin to a producer that does, or does not, wash their uranyl peroxide precipitates. In this study, the morphology of am- $\text{UO}_3$  from washing uranyl peroxide was quantified for the first time to assess the feasibility of this signature.

Historically, optical and electron microscopy have been used in the nuclear forensics community to gain qualitative insight about a sample, without compromising the sample's integrity. Examples of this form of qualitative morphological analysis can be seen in the work of Tamasi et al. [16–19], and Keegan et al. [20]. Ray et al. have advocated for the development of “microstructural fingerprints”, which are a set of qualitative and quantitative signatures developed through microscopic analysis of powder nuclear materials that are indicative of thermal and process history [21]. There is a major need for quantitative parameters that can rapidly determine whether differences between an unknown sample and a reference standard are statistically significant. It would be even more beneficial if these parameters could elucidate not just the starting material speciation, but the processing conditions experienced by the sample.

Recently, Olsen et al. demonstrated the ability to perform quantitative morphological analysis of SEM images to identify the calcination history of  $\alpha$ - $\text{U}_3\text{O}_8$  [22]. The following study builds upon this progress, demonstrating the quantitative morphological analysis of am- $\text{UO}_3$  as a function of calcination temperature. Differential scanning calorimetry (DSC), thermogravimetric analysis-mass spectrometry (TGA-MS), and powder X-ray diffractometry (p-XRD) were used to correlate morphological differences with chemical transitions.

## 2. Experimental methods

### 2.1. Materials and synthesis

The  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (International Bio-Analytical Industries, Inc., 99.9%) used in this study was first dissolved in 1%  $\text{HNO}_3$  solution to make a 1.0 M uranyl nitrate solution. The synthesis of studtite,  $(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ , from  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 30%  $\text{H}_2\text{O}_2$  (EMD Millipore, Suprapur™ grade) was described in detail previously [22]. The filtered and washed studtite was allowed to dry at room temperature overnight. Subsequently, metastudtite,  $(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2$ , was prepared by dehydrating the studtite for 24 h at 80 °C. The metastudtite was ground in a high-purity aluminum oxide mortar and pestle. Powder X-ray diffractometry (p-XRD) confirmed the purity of the resulting metastudtite. Approximately 100 mg of metastudtite was placed in 5 mL platinum crucibles for calcination in an atmosphere-controlled furnace. Amorphous- $\text{UO}_x$  ( $3 \leq x \leq 3.5$ ) was synthesized from the metastudtite material at calcination temperatures of 250, 300, 350, 400, and 450 °C in triplicate under a flow of 500 mL/min of purified air. The furnace was ramped to temperature at a rate of 2.5 °C/min., held at the target calcination temperature for 8.25 h., then ramped

down at a rate of 0.625 °C/min. While not undergoing processing or analysis, the samples were stored at room temperature in a vacuum chamber at 20kPa.

### 2.2. Powder X-ray diffraction (p-XRD) analysis

Powder XRD patterns of the starting material and various calcination products were collected at room temperature on a Philips Panalytical X'Pert diffractometer using  $\text{Cu K}\alpha$  X-rays ( $\lambda=1.5418 \text{ \AA}$ ) operating at 40 kV and 40 mA. Continuous scans were performed over the range of 15–90° 2 $\theta$  with a step size of 0.020° and a scan speed of 0.04°/second. All samples consisted of 70–90 mg of U-oxide, and they were characterized on quartz slides with a limited background.

### 2.3. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 3500 Sirius. A baseline was acquired using an empty aluminum pan within 12 h of running the metastudtite samples. Metastudtite samples of ca. 20 mg were placed in aluminum pans with pierced lids, and heated at a rate of 10 °C/min from 20 °C to 600 °C. At a rate of 40 mL/min, dry nitrogen was flowed over the aluminum pans. The large sample size allows for an increased sensitivity to transitions, but at the expense of decreased resolution, due to increased thermal lag. Empty aluminum pans with pierced lids were utilized as a reference signal for each run.

### 2.4. Thermogravimetric Analysis-Mass Spectrometry (TGA-MS)

Thermogravimetric analysis combined with online mass spectrometry (TGA-MS) was performed using a TA Instruments SDT Q600 coupled with a Pfeiffer ThermoStar GSD 320 T3 that contains a PrismaPlus mass spectrometer. Metastudtite samples of ca. 60 mg were placed in alumina crucibles, and purged in the TGA furnace with helium (100 mL/min) for 60 min at room temperature to reduce any atmospheric air signatures in the mass spectrometer. The samples were then heated at a rate of 10 °C/min from 25 °C to 600 °C, and held at 600 °C for 1 h, in a flowing atmosphere of 100 mL/min high-purity helium. The decomposition product gases were fed through a heated capillary column (150 °C) into the mass spectrometer. The mass spectrometer was operated in a selected ion mode targeting the following ions:  $m/z=14$  ( $\text{N}^+$ ), 16 ( $\text{O}^+$ ), 17 ( $\text{OH}^+$ ), 18 ( $\text{H}_2\text{O}^+$ ), 30 ( $\text{NO}^+$ ), 32 ( $\text{O}_2^+$ ), and 46 ( $\text{NO}_2^+$ ).

### 2.5. Scanning Electron Microscopy (SEM)

The initial metastudtite and the 15 am- $\text{UO}_x$  samples were prepared for SEM by dusting 5–10 mg of each sample on top of a 12 mm conductive carbon tab that was adhered to a 12.7 mm aluminum pin stub mount. Loosely held sample was removed by firmly tapping the side of the SEM stub mounts. Using a Gatan 682 Precision Etching and Coating System (PECS) the samples were sputter coated with  $20.2 \pm 0.1$  nm of Au/Pd film to reduce charging. Images of the samples were collected with a FEI Quanta 600 FEG scanning electron microscope at an accelerating voltage of 12 kV. Images were acquired using both the Everhart-Thornley secondary electron (SE) and solid-state diode back scattered electron (BSE) detectors. The BSE detector provided Z-contrast for the sample images. The SE detector was more sensitive to surface-generated secondary electrons and provided images of the surface topography with high resolution. Within each sample, 3–4 macro-particles were selected for thorough examination. For each macro-particle, at least 10 images were acquired across a wide area of the macro-particle surface at magnifications of 15,000–30,000x. Over the entire range of calcination temperatures, more than a thousand SEM images were acquired, providing a large population of images for statistical analysis.

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