



Nuclear proliferomics: A new field of study to identify signatures of nuclear materials as demonstrated on alpha-UO₃

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ABSTRACT

The use of a limited set of signatures in nuclear forensics and nuclear safeguards may reduce the discriminating power for identifying unknown nuclear materials, or for verifying processing at existing facilities. Nuclear proliferomics is a proposed new field of study that advocates for the acquisition of large databases of nuclear material properties from a variety of analytical techniques. As demonstrated on a common uranium trioxide polymorph, α -UO₃, in this paper, nuclear proliferomics increases the ability to improve confidence in identifying the processing history of nuclear materials. Specifically, α -UO₃ was investigated from the calcination of unwashed uranyl peroxide at 350, 400, 450, 500, and 550 °C in air. Scanning electron microscopy (SEM) images were acquired of the surface morphology, and distinct qualitative differences are presented between unwashed and washed uranyl peroxide, as well as the calcination products from the unwashed uranyl peroxide at the investigated temperatures. Differential scanning calorimetry (DSC), UV–Vis spectrophotometry, powder X-ray diffraction (p-XRD), and thermogravimetric analysis-mass spectrometry (TGA-MS) were used to understand the source of these morphological differences as a function of calcination temperature. Additionally, the SEM images were manually segmented using Morphological Analysis for MAterials (MAMA) software to identify quantifiable differences in morphology for three different surface features present on the unwashed uranyl peroxide calcination products. No single quantifiable signature was sufficient to discern all calcination temperatures with a high degree of confidence; therefore, advanced statistical analysis was performed to allow the combination of a number of quantitative signatures, with their associated uncertainties, to allow for complete discernment by calcination history. Furthermore, machine learning was applied to the acquired SEM images to demonstrate automated discernment with at least 89% accuracy.

1. Introduction

The ability to rapidly detect and respond to a nuclear event is one of the greatest mechanisms for deterring the future use of nuclear weapons [1,2]. Nuclear forensics provides critical analysis of interdited nuclear materials and materials following detonation of a nuclear weapon to help identify signatures indicative of the materials processing history and origin [3]. On the other hand, nuclear safeguards aims to prevent the spread of nuclear weapon materials and technology through policy and treaty verification. To enable more effective safeguards and forensics, large databases of nuclear material properties are needed and Nuclear Proliferomics is the field to acquire that data. In nuclear forensics and nuclear safeguards, research is driven by the need to answer specific, hypothesis driven questions. In contrast, nuclear proliferomics research is conducted to acquire the

maximum amount of data possible. This is the same philosophy practiced in almost all fields of “omics” [4]. The investigation of these large and varied datasets can generate additional fields of research, or lead to the discovery of additional processing signatures.

At the core of almost all “omics” is mass spectrometry [4]. This technique is also critical to nuclear proliferomics for measuring isotope ratios of uranium and plutonium [5]. Nonetheless, recent advances in nuclear investigations have demonstrated the use of mass spectrometry for identifying many other key signatures including rare earth element signatures of uranium ores [6], and molecular solvent signatures of spent nuclear fuel reprocessing [7]. In addition to these mass spectrometric signatures, many other signatures can be realized from exploring the vast analytical techniques available to nuclear scientists including morphology [8], X-ray fluorescence [9], Vis/NIR reflectance spectroscopy [10], and thermal analysis [11,12]. It is a collection of all of these

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signatures which is needed for nuclear proliferomics.

Due to the size and complexity of data collected in all “omics” fields, machine learning has become a pivotal tool for processing and interpreting the data [13–15]. Nonetheless, the application of machine learning to any nuclear related research is very rare. Porter et al. has worked to develop segmentation software and interactive machine learning to interpret morphological features of nuclear materials [16,17]. In other studies, Jones et al. utilized machine learning to classify reactor type based on isotopic and elemental measurements [18], and to repurpose historical industrial quality control records from uranium ore concentrate (UOC) production to discriminate country of origin and deposit type [19]. In all of these cases, more data would greatly improve the application of machine learning. In fact, Luetzenkirchen and Mayer reported on the need of nuclear databases to aid in combatting trafficking of nuclear materials [20]. Nonetheless, extensive research in nuclear proliferomics is needed to develop these databases. As the nuclear threat continues to grow, the need for novel signatures is imperative to continue to deter nuclear material smuggling, and the use of nuclear weapons [21].

In this present study, a common uranium trioxide polymorph, α - UO_3 , was investigated from one of its many synthetic pathways. Cordfunke et al. previously discovered that unwashed uranyl peroxide results in α - UO_3 when calcined at 425 °C in air. This was in contrast to washed uranyl peroxide resulting in amorphous- UO_3 at the same temperature. The two routes resulting in drastically different morphological forms [22]. While this particular synthetic route is unlikely to be encountered in a legitimate commercial operation where the uranium oxide purity is paramount, it could result from hasty illicit production or insufficient washing during commercial processing. Furthermore, its complex chemical behavior presents an interesting case for demonstrating nuclear proliferomics. In this investigation, microstructural and morphological features of α - UO_3 were quantified using both manual particle segmentation and machine learning. Quantitative powder X-ray diffractometry (p-XRD), differential scanning calorimetry (DSC), UV–VIS spectrophotometry, and thermogravimetric analysis–mass spectrometry (TGA-MS) were used to understand why morphological features were changing based on the calcination conditions. To fully illustrate the power of nuclear proliferomics, statistical analysis was performed on a collection of the analytical data to reveal signatures not readily visible from a single analysis.

2. Experimental methods

2.1. Materials and synthesis

The synthesis of studtite, $(\text{UO}_2)_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$, from an initial feedstock of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (International Bio-Analytical Industries, Inc., 99.9%) dissolved in a 1% HNO_3 solution to generate a 1.0 M uranyl nitrate solution was detailed previously [8,23]. A significant molar excess of H_2O_2 (30% v/v) was added rapidly to uranyl nitrate hexahydrate solution at room temperature. This resulted in a 5.9:1.0 M ratio of H_2O_2 to $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The initial pH of the solution was 1. The precipitation of studtite was allowed to occur for 30 min at room temperature. The resulting studtite in solution was not drained or washed of the residual nitrates, before being transferred into an oven at 80 °C for 24 h of drying. The resulting material was lightly ground in an aluminum oxide mortar and pestle, and p-XRD indicated that the material consisted of a mixture of uranyl nitrate trihydrate, metastudtite, and diuranyl dihydroxide bis(nitrate) tetrahydrate. Utilizing the calcination procedures detailed previously, the unwashed material was calcined at temperatures of 350, 400, 450, 500, and 550 °C [8,23]. The calcination products were stored at room temperature in a vacuum chamber at 20 kPa.

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

Powder XRD patterns of the starting material and the various

calcination products were acquired at room temperature on a Bruker D2 PHASER diffractometer with a 1-D LynxEye detector using $\text{Cu K}\alpha$ X-rays ($\lambda = 1.5418 \text{ \AA}$) operating at 30 kV and 10 mA. The instrument was calibrated with a CeO_2 NIST SRM 674b standard using structural data for CeO_2 refinement from Kümmerle et al. [24]. A divergence slit of 0.6 mm, an anti-scattering beam knife height of 1 mm, and a 3 mm receiving slit were used for the sample data acquisition. The quantitative analysis patterns were collected in the Bragg-Brentano geometry (Coupled $2\theta/\theta$) with a scan range of 10–90° 2θ , step size increments of 0.02° 2θ , and 2.5 s per step.

Two methods of performing quantitative analysis of the amorphous phase content were selected: the internal standard method with Rietveld refinement, and the degree of crystallinity (DOC) method as implemented in the X'Pert Highscore Plus v.2.2d software [25]. For quantitative analysis sample preparation, samples of ca. 200 mg were wet ground in a high-purity Zirconia mortar and pestle with 2 mL of n-pentane (99+%, extra pure, anhydrous, Acros Organics). Following grinding and room temperature drying, the powder samples were sieved to < 20 μm with an ASTM E11 certified No. 635 test sieve. For the internal standard method, the sieved samples were spiked with 20 wt% Cr_2O_3 (NIST SRM 674b), and well mixed in a 5 mL vial on a vortex mixer. Samples of ca. 50 mg were front-loaded on a P-type B-doped silicon crystal zero diffraction plate. The sample holder was rotated at 24 rpm during the scans to reduce the impact of preferred orientation and improve the counting statistics for the acquired patterns. For the quantification routine, a background was manually fit due to the difficulty in fitting the patterns with high amorphous content. The refined parameters for all phases were the scale factors, specimen displacement, lattice parameters, peak shape parameters, overall isotropic displacement parameters, and preferred orientation. The peak shapes were modeled using a pseudo-Voigt function. Starting models for the structural refinements for α - UO_3 (PDF#01-072-0246), α - U_3O_8 (PDF#01-073-6293), Cr_2O_3 (PDF#01-070-3766), α - $\text{UO}_2(\text{OH})_2$ (PDF#01-074-4842), $(\text{UO}_2)_4\text{O}(\text{OH})_6(\text{H}_2\text{O})_5$ (PDF#01-070-4765), $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_3$ (PDF#01-073-4459), $(\text{UO}_2)_2(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4$ (PDF#01-070-0176), $((\text{UO}_2)_2(\text{H}_2\text{O})_2)(\text{NO}_3)_2(\text{H}_2\text{O})$ (PDF#01-072-3827), and $(\text{UO}_2)(\text{NO}_3)_2(\text{H}_2\text{O})_2$ (PDF#01-072-2333) were acquired from the ICDD PDF-2 2008 database [26]. Additionally the starting structural model for $(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2$ was taken from Weck et al. [27].

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 3500 Sirius. Calibration of the temperature and detector sensitivity was performed at a heating rate of 10 °C/min using the onset temperature of melting and heat curve peak areas for Adamantane, Indium, Tin, Bismuth, and Cesium Chloride. The details of the sample preparation and acquisition parameters were presented previously [8].

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. The mass spectrometer was operated in the selected ion mode for the following ions: $m/z = 14$ (N^+), 16 (O^+), 17 (OH^+), 18 (H_2O^+), 30 (NO^+), 32 (O_2^+), 44 (N_2O^+), and 46 (NO_2^+). Sample preparation and data acquisition details were presented previously [8]. The TGA was calibrated for temperature using the melting point onset temperatures for indium (m.p. = 156.60 °C), zinc (m.p. = 419.53 °C), aluminum (m.p. = 660.32 °C), and silver (m.p. = 961.78 °C).

2.5. UV–Vis

In order to approximate the water-soluble nitrate concentration in

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