



Identifying anthropogenic uranium compounds using soft X-ray near-edge absorption spectroscopy

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ABSTRACT

Uranium ores mined for industrial use are typically acid-leached to produce yellowcake and then converted into uranium halides for enrichment and purification. These anthropogenic chemical forms of uranium are distinct from their mineral counterparts. The purpose of this study is to use soft X-ray absorption spectroscopy to characterize several common anthropogenic uranium compounds important to the nuclear fuel cycle. Chemical analyses of these compounds are important for process and environmental monitoring. X-ray absorption techniques have several advantages in this regard, including element-specificity, chemical sensitivity, and high spectral resolution. Oxygen K-edge spectra were collected for uranyl nitrate, uranyl fluoride, and uranyl chloride, and fluorine K-edge spectra were collected for uranyl fluoride and uranium tetrafluoride. Interpretation of the data is aided by comparisons to calculated spectra. The effect of hydration state on the sample, a potential complication in interpreting oxygen K-edge spectra, is discussed. These compounds have unique spectral signatures that can be used to identify unknown samples.

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1. Introduction

By mass, uranium oxides such as pitchblende and uraninite ($\text{UO}_2 + x$) make up the bulk of uranium on Earth, along with a plethora of secondary minerals containing the uranyl ion (UO_2^{2+}) [1,2]. In contrast, uranium halides are not found in nature, but are essential to many uranium purification and enrichment methods. Gaseous diffusion and centrifuge enrichment processes require the conversion of UO_2 to uranium hexafluoride (UF_6), the most volatile known uranium compound. Enriched UF_6 is converted back to uranium oxides—typically UO_2 —for use in power-generating nuclear reactors. Uranium tetrafluoride (UF_4) is an intermediate in these conversion and deconversion processes, although it also sees practical uses—for example, as the source material for the production of metallic uranium by the Ames process [3], as the primary fuel of molten salt reactors [4], or as long-term storage for depleted uranium [5]. Uranyl fluoride (UO_2F_2), produced by the hydrolysis of UF_6 , is another intermediate in the deconversion of UF_6 to UO_2 . Solid UO_2F_2 will precipitate out whenever UF_6 is allowed to come into contact with moisture [6–8]—for example, when UF_6 gas lines are not sufficiently dry or if a storage cylinder has been structurally compromised.

Methods that can non-destructively detect and characterize these compounds would be highly desirable to monitor process chemistry

and to chemically identify any environmental contamination. While a variety of spectroscopic probes exist for detecting uranium, including fluorescence spectroscopy [9,10] and Raman spectroscopy [11,12], X-ray absorption techniques are advantageous in that they are element-specific and highly sensitive to physical and chemical structure. Soft X-rays—X-rays with an energy below 1 keV—are particularly useful because absorption edges in this regime show minimal lifetime broadening (0.1–0.3 eV) [13–15], and as a result sharper absorption peaks and greater chemical information can be obtained. The non-destructive nature of X-ray techniques means that subsequent analyses can be performed to obtain further information about the sample (e.g., laser ablation ICP-MS to determine isotopic composition). Furthermore, it is important to develop techniques that can yield spatially resolved information. The ability to extend spectral signatures down to the nanoscale, while not in the scope of the current research, is important because environmental (i.e., samples collected after an accidental release) and IAEA verification samples can be inhomogeneous, with the chemistry of interest at the nanoscale. In the case of X-ray absorption spectroscopy, the incident beam can be focused to a spot size of 10–100 nm, allowing one to map the chemical state of a sample on a fine spatial scale (i.e., on the spatial scale that directly probes the interfaces where the chemical conversion process reactions occur). Scanning transmission X-ray microscopy (STXM) beamlines with a soft X-ray source can produce a focused beam diameter on the order of 20 nm and can penetrate particles hundreds of nanometers thick, thereby sampling a crucial size range not adequately covered by complementary

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spectromicroscopic techniques such as electron energy loss spectroscopy (which can produce images with atomic spatial resolution, but is limited by sample thickness) or micro-Raman (which is not limited by sample thickness, but produces images with lower spatial resolution). Although laboratory-based NEXAFS techniques are becoming increasingly common and practical [16–19], access to a synchrotron beamline and the need for an X-ray source that is high-flux and broadly tunable between 500 and 800 eV (see below) ultimately drove us to pursue synchrotron sources specifically.

Most soft X-ray beamlines can probe the uranium N_{4,5}-edges (736.2 eV and 778.3 eV) directly. The presence of these peaks can serve as a specific marker for uranium in a sample. However, these edges do not contain much chemical information aside from slight shifts in peak positions due to oxidation state, because these peaks result from transitions between nonbonding d and f orbitals [20]. On the other hand, the K-edge absorption spectra of light ligand atoms such as oxygen (543.1 eV) or fluorine (696.7 eV) can exhibit high chemical sensitivity. There is precedent in the literature for using ligand K-edge absorption spectroscopy to obtain information on uranium compounds, e.g., to study π -bonding in uranyl compounds [14,21] and to study the structures of uranium oxides [22]. Previous work from our group used oxygen near-edge X-ray absorption fine structure (NEXAFS) to classify various uranyl minerals according to their counterion type and to identify uranium oxide samples [23]. These results were extended to classify submicron-diameter schoepite particles at a STXM beamline (ALS beamline 5.3.2.2), to the exclusion of nearby oxygen-containing contaminants.

More generally, for compound identification, it would be desirable to collect X-ray absorption data covering the entire spectral range from the oxygen K-edge at 543.1 eV to the uranium N_{4,5}-edges at 736.2 eV and 778.3 eV. This data set would also encompass the fluorine K-edge at 696.7 eV. The U N_{4,5}-edges would be used to confirm the specific presence of uranium, compared to other actinides such as plutonium. The oxygen K-edge would be used to classify the uranium mineral according to type, and the fluorine K-edge can be used to distinguish important anthropogenic uranium compounds from other fluorine-containing compounds.

The goal of this work is to identify soft X-ray spectroscopic signatures which can distinguish anthropogenic uranium compounds from a background that consists of natural uranium oxides, uranyl minerals, and various other metal oxides and fluorides. To that end, we will focus on two solid uranium fluorides commonly produced in the nuclear fuel cycle—namely, uranyl fluoride and uranium tetrafluoride. We will also analyze a sample of uranyl nitrate (UO₂(NO₃)₂), which, while not a halide, is a common intermediate in many uranium recovery processes. Finally, we will examine a sample of uranyl chloride (UO₂Cl₂). UO₂Cl₂ is not commonly used in the nuclear fuel cycle, although uranium compounds can be converted to uranyl chloride prior to electrolytic reduction during uranium purification [24] or as an intermediate in the production of UF₄ [25]. Its inclusion is primarily for comparison with UO₂F₂, which is a crucial fuel cycle intermediate and environmental contaminant. Because this work will partly focus on the spectroscopic signatures in the oxygen K-edge, the presence of extraneous water in the sample is a potential complication. Therefore, some effort will be spent to determine the extent of hydration under the vacuum conditions present in a typical soft X-ray beamline and what effect the presence of water would have on the oxygen K-edge. The compounds featured in this work are pure, bulk-quantity samples; however, in the future the spectra measured from these compounds may be applied to identify spectra obtained from particles analyzed by a spatially-resolved technique such as EELS or STXM. For example, the chemical composition of a uranium particle released during a nuclear accident [26] would provide data on how the released material weathered in the environment.

2. Experimental

All uranium samples—uranyl nitrate (UO₂(NO₃)₂), uranyl chloride (UO₂Cl₂), uranyl fluoride (UO₂F₂), and uranium tetrafluoride (UF₄)—were borrowed from a mineral repository stored at the Life Sciences Laboratory Complex at Pacific Northwest National Laboratory (PNNL). Sodium nitrate was obtained from Sigma-Aldrich (St. Louis, MO) and was included for comparison to uranium nitrate. For each sample, ~5 mg of powder was crushed onto a thin (0.25 mm), 10 mm diameter indium foil disk, which was secured to a 10 mm diameter, 0.5 mm thick copper disk with double-sided conductive carbon tape. Sample disks were stored in high vacuum prior to packaging for shipment to the Synchrotron Radiation Center (SRC) in Stoughton, WI.

X-ray absorption spectra were collected at the HERMON beamline at the SRC, a bending magnet beamline equipped with a spherical grating monochromator, using the X-ray absorption end-station [27]. Sample disks were mounted on the sample arm using double-sided conductive carbon tape. Samples were placed in an airlock and pumped down to at least 3×10^{-9} Torr prior to transfer to the sample chamber. Once loaded, the samples were exposed to an incident beam with a slit-defined beam size of 20 μ m. An X-ray probe of this size would encompass hundreds of particles, ensuring that the results would represent the bulk of the sample and not be dependent on the orientation of individual particles or grains. The oxygen K-edges were obtained for uranyl nitrate, uranyl chloride, uranyl fluoride, and sodium nitrate with the following scan parameters: 515 eV to 528 eV in 0.5 eV steps, 528 eV to 543 eV in 0.1 eV steps, 543 eV to 550 eV in 0.5 eV steps, and 550 eV to 580 eV in 1 eV steps. The fluorine K-edges were obtained for uranyl fluoride and uranium tetrafluoride with the following parameters: 670 eV to 682 eV in 1 eV steps, 682 eV to 702 eV in 0.1 eV steps, 702 eV to 710 eV in 0.5 eV steps, and 710 eV to 740 eV in 1 eV steps. For both edges, dwell times were 1 s per data point. At least three sweeps were performed for each edge of each sample, and possibly more depending on the signal-to-noise level. The sample position was moved several hundred microns between sweeps in order to minimize the effects of beam damage. Spectra from individual sweeps were examined prior to averaging to confirm sample homogeneity.

X-ray absorption was detected through total electron yield (TEY), the technique of choice when samples are much thicker than the X-ray absorption length [28]. The TEY signal is directly proportional to the sample X-ray absorption coefficient so long as the absorption length of the X-ray probe is much longer than the electron escape depth, and as long as the experimental geometry does not place the X-ray probe at grazing incidence [29–31]. For most of the materials presented in this work, the absorption length is roughly 200 nm right above the oxygen K-edge, whereas for most materials the mean free path for electrons in the soft X-ray regime is on the order of 10–100 Å [32]. The X-ray absorption end-station at the SRC also offered total fluorescence yield (TFY) measurement capabilities; however, this detection mode was not used because the sample thickness would have introduced self-absorption artifacts. The signal from an upstream gold mesh served as a monitor for the beam intensity, I_0 . Incident flux was on the order of 10^8 photons per second. For a typical experiment, the TEY count rate immediately below the edge was 9×10^6 counts per second, while the count rate was 1×10^7 counts per second far above the absorption edge, yielding an edge jump of ~1.1. The ratio of the TEY and I_0 signals plotted against X-ray energy yielded an absorption edge. I_0 -normalized data were averaged for each sample and loaded into SIXPACK [33] for background subtraction and spectrum normalization. Edge jumps were normalized to 1.0. The pre-edge region was modeled as a line, and the post-edge as a quadratic spline with five knots.

X-ray powder diffraction (XRD) measurements were carried out for each uranium sample to confirm their purity. Sample disks were sealed between two pieces of Kapton tape and sent to the Environmental

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