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# **Application of Visible-Near Infrared Reflectance Spectroscopy to Uranium Ore Concentrates for Nuclear Forensic Analysis and Attribution**

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## **Abstract**

Uranium ore concentrates (UOC) are produced at mining facilities from the various types of uranium bearing ores using several different processes that can include different reagents, separation procedures, and drying conditions. The final UOC products can consist of different uranium species which are important to identify in order to trace interdicted samples back to their origin. Color has been used as a simple indicator; however, visual determination is subjective and no chemical information is provided. In this work, we report the application of near-infrared (NIR) spectroscopy as a non-contact, non-destructive method to rapidly interrogate UOC materials for species and/or process information. Diffuse reflectance spectra from 350-2500 nm were measured from a number UOC samples that were also characterized by x-ray diffraction. Combination and overtone bands were used to identify the N-H and O-H containing species, such as ammonium uranates or ammonium uranyl carbonate, while other uranium oxide species (e.g.  $\text{UO}_3$  and  $\text{U}_3\text{O}_8$ ) exhibit absorption bands arising from crystal field effects and electronic transitions. Principal component analysis was used to classify the different UOC materials.

## **Keywords**

Near infrared spectroscopy, nuclear forensic analysis, Uranium ore concentrate, Yellowcake, Ammonium Uranates, uranium speciation.

## **Introduction**

Production of enriched uranium is of international interest as it can be used for nuclear power reactors or nuclear weapons or improvised nuclear devices. Illicit trafficking of uranium and other nuclear materials present a considerable threat, and attributing interdicted materials relies on applying a number of analytical techniques to provide information about the samples.<sup>1-4</sup> Rapid identification of signature species in the samples is desirable to identify potential sources in a timely manner and enhance countermeasures to control further trafficking attempts. The area of nuclear forensic analysis has emerged as a key discipline to provide measurements and interpretations regarding the age, composition, provenance, industrial history, and implications of nuclear materials.<sup>5</sup> Considerable effort has focused on trace element and isotopic analyses, using techniques such as inductively coupled plasma-mass spectrometry (ICP-MS), stable isotope analysis, and, more recently, laser induced breakdown spectroscopy (LIBS). All have demonstrated an ability to link material to a potential geological source.<sup>6-8</sup> Less effort has been put forth in developing techniques to determine the chemical process history of nuclear materials which is also valuable information for nuclear forensics. Thus, material signatures can provide insights to chemical process history, which may be assessed to establish potential manufacturing origin in favorable cases.

Uranium production starts with the mining and processing of suitable ores to produce uranium ore concentrates (UOCs), which are also referred to by the historical name of Yellowcake. Processing of an ore entails a number of steps that begins with comminution

(crushing and grinding the ore to produce small particles for efficient leaching). Following either an acidic or basic leach, a series of separation, concentration and purification steps are applied to preconcentrate uranium in solution. The uranium is then precipitated by one of several reagents, including ammonium hydroxide, magnesium oxide, hydrogen peroxide, or sodium hydroxide. Final drying of the precipitate at high temperature then drives off excess moisture.<sup>9</sup> The drying step may alter the final chemical form, depending on temperature and time, by evaporating volatile material species and oxidizing the uranium. Different UOC products may also have diverse colors, which could provide indication of compound speciation.<sup>10</sup>

The color of the UOC material is usually the first and easiest discriminator, and has been used for a number of years.<sup>10-11</sup> Merritt studied the relative weight loss of ammonium diuranate (ADU) as a function of temperature and noted the color changes associated with each step.<sup>11</sup> The sample started pale yellow, became darker yellow, then orange/red, and eventually changed to dark green and black at higher temperatures. The color transitions correlated to a loss of water and formation of an  $\text{NH}_4\text{UO}_3$  hydrate, which began decomposition to  $\text{UO}_3$  at  $400^\circ\text{C}$ , conversion to  $\text{U}_3\text{O}_8$  (bottle green) between  $600^\circ$  and  $800^\circ\text{C}$ , and a final slow conversion to  $\text{UO}_2$  (black) above  $900^\circ\text{C}$ . Although color can be a valuable presumptive method to evaluate UOCs, it is subjective and does not provide specific chemical information. In addition, different polymorphs of the same material can vary in color, as Hoekstra and Siegel reported for several forms of  $\text{UO}_3$  that displayed tan ( $\alpha$ ), orange ( $\beta$ ), and yellow ( $\gamma$ ).<sup>12</sup>

Infrared spectroscopy of UOC materials to characterize different classes of UOC materials has been reported by several different groups.<sup>13-20</sup> Eidson investigated synthesized mixtures of ADU and  $\text{U}_3\text{O}_8$  by transmission IR with the goal to determine speciation in urine samples.<sup>13</sup> Kim et al. used ATR IR of uranium oxides to determine the O/U ratio, which was varied by heating in air. X-ray diffraction was used to determine the ratios, and primary IR

bands at 638 and 715  $\text{cm}^{-1}$  were monitored.<sup>14</sup> Allen used transmission IR (CsI or KBr) press to study binary uranium oxides of  $\text{UO}_2$ ,  $\text{U}_4\text{O}_9$ ,  $\text{U}_3\text{O}_7$ , and  $\text{UO}_3$  in different crystal phases.<sup>15</sup>

Reaction mechanisms to produce ammonium uranates were studied with diffuse reflectance IR spectroscopy by Lin et al., while Rofail investigated ammonium uranyl carbonates by IR to provide band assignments for vibrational modes of  $\text{NH}_3$ ,  $\text{CO}_3$ , and U species.<sup>16,17</sup> Deane explored hydrated  $\text{UO}_x$  and ammonium diuranates.<sup>18</sup> Hausen provided a review of methods used to characterize and classify yellowcake samples by XRD, IR, and DTA, and summarized various protocols and processes.<sup>19</sup>

More recently, Varga et al. investigated various UOCs from different locations and different processes that resulted in different products.<sup>20</sup> The samples were interrogated by transmission FTIR in a KBr press and were classified into several general categories, including AU, UOH, NaDU,  $\text{UO}_4 \cdot x\text{H}_2\text{O}$ , ammonium uranyl carbonate (AUC), and  $\alpha\text{-U}_3\text{O}_8$ . Based on libraries of spectra of known materials, UOC samples were classified using SIMCA, and quality predictions were presented in a Cooman's plot. However, although IR spectroscopy can provide valuable chemical information, it is a destructive technique in that the original sample is no longer available for subsequent analyses in its initial state.

Near-infrared (NIR) spectroscopy provides rapid, non-contact and nondestructive chemical speciation analysis provided characteristic absorption bands exist in this region. The only reported analysis of uranium compounds by NIR diffuse reflectance spectroscopy in the literature is by the Frost et al., who measured spectra of a number of uranium ores/minerals.<sup>21-22</sup> Heinrich et al. used photoacoustic spectroscopy to study the absorption of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  up to 1500 nm, but did not observe any absorption features in the NIR.<sup>23</sup> More recently, our group demonstrated application of NIR spectroscopy to determine process signatures of uranium oxides.<sup>24-26</sup> Reference NIR spectra were empirically determined on uranium compounds

synthesized in the laboratory via standard chemical procedures and followed by separation and precipitation as UOC with ammonia, hydrogen peroxide, sodium hydroxide, ammonium carbonate, and magnesia. The spectra were sufficiently unique for each compound, and absorption-band assignments could be made for O-H and N-H combination and overtone bands. Comparisons of laboratory-characterized reference species with real-world samples were favorable and suggested that the use of NIR spectroscopy for accurate classification of unknown samples may be achieved using multivariate methods such as principal component analysis.

In the present work, NIR spectra for collected UOC process samples, identified and specified with X-ray diffraction, are presented as characteristic absorption profiles for different questioned materials. Since several industrial processes do not completely eliminate all OH and NH groups, overtone and combination bands were readily identified. In cases where the product was a uranium oxide, unique electronic or crystal field transitions were also observed. Using principle component analysis, UOC samples were readily classified by the dominant major phase and the various differences between samples.

## **Experimental**

A visible/NIR spectrometer (LabSpec Pro, Analytical Spectral Devices, Inc.) was used for this work and it was equipped with three separate detectors that spanned consecutive spectral regions: 350 – 1000 nm, 1000 – 1800 nm, and 1800 – 2500 nm. The light source was a 20W tungsten halogen lamp with an operating color temperature of 3000° C that covered the NIR range. Although the system was capable of battery operation, all measurements were performed using house power. A bifurcated fiber-optic bundle was used to transmit light to the sample surface, collect the reflected light, and return it to the spectrometer. The fiber was held fixed and the sample to fiber distance was adjusted using a lab jack under a sample rotator. Reflectance data were acquired from a standoff distance of approximately 6 cm, and a lens coupled the light

to the sample. Standoff distance and spot size were maintained approximately constant for all of the samples. A white reflectance standard (Spectralon, Inc) was used as reference to calculate absorbance values, reported as  $\log(1/R)$ . Each analysis consisted of an average of 10 scans over the complete range of the spectrometer, 350 – 2500 nm. Samples were analyzed as received without sample preparation, and in their original containers (generally 20 mL glass or polyethylene vials). The vials were centered on the rotating stage during analysis in order to minimize heterogeneity effects. If unable to rotate a specimen (e.g. due to size constraints) different surface locations on a given sample were interrogated to provide five analyses of each sample.

A variety of UOC powder samples from various worldwide locations and processes were analyzed. Chemical phase information was obtained through XRD pattern matching using the EVA software package by Bruker and the 2009 database from the International Centre for Diffraction Data ®. Major identified phases were used to classify the material for the calibration data set for chemometric analysis.

Data reduction and analysis were performed using the Unscrambler X (ver. 10.1, CAMO Software AS). A standard normal variate (SNV) transformation, common pretreatment for reflectance data, was applied prior to the principal component analysis. This procedure removes interferences due to scatter and particle size effects and centers the data on zero.<sup>27</sup>

## **Results and Discussion**

As shown in Figure 1, UOC materials can range in color from bright yellow to black, and presumptive chemical information is routinely inferred about a sample based on its appearance.<sup>10-12</sup> The chemical species associated with these samples were determined by XRD and represent major phases only (many minor phases are below the XRD detection limit).

Although these samples were representative of UOCs and their major chemical species, the exact

color of a specimen can be variable. However, UOC materials often consist of several different phases, which can complicate XRD patterns and make spectral interpretation and assignment challenging. Since visual color assessments are subjective and prone to error or misinterpretation, absorption spectra over the Vis/NIR range were employed to provide objective chemical information (see Figure 2). Standoff nondestructive analysis data acquisition from the as-received samples is important to maintain the sample integrity for subsequent trace elemental analysis. The spectra were separated into three primary sections (Vis+, NIR1, and NIR2) for presentation corresponding to the 3 detectors in the instrument. The region between the dashed lines in the Vis+ range delineates the visible spectrum from 400-700 nm, where color is determined. Although spectral data in the visible region provide limited information and more objective sample discrimination than visual assessment, absorption features in the NIR can be better correlated to chemical information in the sample.

The most common methods of uranium ore processing use ammonium hydroxide as a precipitating reagent and produce ammonium uranate (AU, or commonly referred to as ammonium diuranate, ADU) products, which have the general formula  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ ,  $\text{UO}_3 \cdot x\text{H}_2\text{O} \cdot y\text{NH}_3$ , or  $\text{UO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O} \cdot y\text{NH}_3$ .<sup>16,19,20,28</sup> Spectra of several AU samples are given in Figure 3, with NIR1 and NIR2 ranges presented separately due to the shift in the detector response. The numbers labeling each spectrum are unique identifiers that correspond to specimens in our database. Absorbance following SNV preprocessing normalizes the absorbance scale without changing the shape of the spectrum.<sup>27</sup> The first OH overtone band appears at 1460 nm and the NH overtone similarly at approximately 1570 nm, with corresponding combination bands appearing at 1956 and 2143 nm, respectively. Although precise molecular speciation cannot be determined from the NIR spectra, preliminary indications suggest that the ratios of 1460 to 1570 nm peaks could be used to approximate stoichiometry.

This premise is under development and will require measurements of additional AU samples that have been carefully defined by XRD analyses.

The production of UOCs precipitated with ammonium carbonate are less common and produce AUC with the formula  $\text{UO}_2\text{CO}_3 \cdot 2(\text{NH}_4)_2\text{CO}_3$ . Although this compound does not possess associated OH bonds, Varga reported overlapping OH and NH bands in the IR spectrum proposed to result from  $\text{H}_2\text{O}$  in the structure.<sup>20</sup> Thus, similar OH and NH overtone and combination bands might be expected in the NIR, similar to those observed in the AU samples (Figure 3). However, the AUC NIR spectra (Figure 4) were considerably different, and no OH contribution observed. No preliminary drying of these samples was performed in our laboratory, and dry storage history minimized any adsorbed moisture, perhaps explaining the disagreement over the presence of  $\text{H}_2\text{O}$ . As expected, these spectra did present a strong absorption band at 1590, correlating to the NH overtone, a small band at 1296 correlating to the second NH overtone, and two overlapping combination bands at 2047 and 2159 nm.

Production of uranium peroxide hydrates results from precipitation with hydrogen peroxide.<sup>9,20</sup> These products are not common and upon further heating will transform to  $\text{UO}_3$ . Figure 5 shows the spectra from several  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$  samples (or  $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ , also represented as  $\text{UO}_3(\text{H}_2\text{O}_2) \cdot \text{H}_2\text{O}$ ). The peaks at 1459 and 1952 nm are due to the OH overtone and combination bands, respectively. Of note is the increasing background at longer wavelengths after the peak at 1459 nm. Although, this phenomenon appeared to some extent in the AU and AUC samples, it was more pronounced in these  $\text{UO}_4$  samples.

Precipitations with magnesia,  $\text{MgO}$ , at near-neutral pH or drying ammonium uranates produces uranyl hydroxides,  $\text{UO}_2(\text{OH})_2$ , or  $\text{UO}_3 \cdot x\text{H}_2\text{O}$  or  $\text{UO}_3$  hydrates.<sup>12,18,20</sup> With these the materials, NIR spectra are dominated by OH overtone and combination bands (Figure 6).

Sample 1 displayed the presence of an absorption band at approximately 1490 nm, which also

appeared as a shoulder in sample 7. This absorbance arose from to the  $\text{UO}_3$  and may be attributed to crystal field effects.<sup>32</sup> The band at 1711 nm could not be assigned and was perhaps a result of processing residues. Experimental protocols using higher drying temperatures will eliminate water or OH to result in  $\text{UO}_3$  as the final product. The specimens in Figure 7 were determined to be predominantly  $\text{UO}_3$  by XRD and displayed no OH overtone or combination bands. The band observed at 1490 nm was also seen in the  $\text{UO}_3$  hydroxide /hydrate samples. The additional absorption that appears as a shoulder at 1557 nm may also be attributed to  $\text{UO}_3$ . However, the XRD results indicated the presence of additional minor species, such as  $\text{U}_3\text{O}_8$ .

Upon drying the UOC materials at higher temperatures, the more volatile components are driven off and the complexes are converted to oxides.<sup>11</sup> Heinrich et al. reported NIR spectra of uranium oxide specimens,  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ , based on photoacoustic measurements from 200- 1500 nm for which were relatively featureless.<sup>23</sup> In Figure 8, however, our analyses of the  $\text{U}_3\text{O}_8$  materials clearly show strong absorption bands at ~1510 and ~1560 nm. These cannot be due to OH or NH bonds since the spectra in the NIR2 region are featureless with no combination bands present. Uranium in  $\text{U}_3\text{O}_8$  exists as a mixture of +4 and +6 oxidation states, which may contribute to the strong crystal field absorptions observed.<sup>31,32</sup> The weaker absorption band at 1340 nm may also be due to crystal field effects.

Finally, UOC materials that are extensively heated have all volatile components removed and all uranium reduced to the +4 state as  $\text{UO}_2$ . Gajek et al. reported on the crystal field effects in  $\text{UO}_2$  measured at extremely low temperature (4.2K).<sup>31</sup> Several strong bands were reported in the 1000 – 1100 and 1500 – 1730 nm ranges, with weaker bands observed in 1150 – 1325 nm. The NIR spectra from our  $\text{UO}_2$  samples were relatively featureless, with valleys measured around 1127 and 1350 nm (Figure 9). Disagreement with Gajek may be due to poor band resolution, which would be significantly poorer at room temperature than at 4.2K.

Classification by principal component analysis (PCA) is a generally useful method for categorizing materials. Figure 10 shows a PCA scores plot of the NIR1 spectral range and resultant grouping of different UOC species. In general, there was good segregation between different uranium chemical species, with the exceptions of  $\text{UO}_3/\text{U}_3\text{O}_8$  and  $\text{UO}_4/\text{AUC}$  groups. This result was consistent with the spectral similarities in this region, but visual evaluation and inclusion of the NIR2 region would provide better differentiation. Prediction of questioned materials may be achieved by projection of an assayed sample onto the scores plot, which would provide general classification that would be followed by visual spectral analysis.

## **Conclusions**

NIR spectroscopy has a long history as a valuable tool for process analytical chemistry, and the present work demonstrates similar utility in the field of nuclear forensics.<sup>33</sup> The rapid non-contact, nondestructive analysis of UOC materials provides technical scientific basis for attribution that is more valuable than more subjective evaluation of visual color. Thus, NIR spectroscopy is able to provide chemical speciation information without consuming or contaminating evidence, thereby enabling supplemental and uncompromised subsequent analyses. In addition, the speed of analysis, in conjunction with chemometric evaluation of the data, can provide valuable and expedient forensic information. Species identification and information about synthetic processes involved are helpful in attributing a potential source and provenance of UOC material.

This work presents the first reported use of NIR spectroscopy to identify chemical species of uranium, but further investigation is necessary to evaluate the capability of NIR to distinguish different polymorphs. Continued analyses of well-characterized and pure materials will provide spectral data necessary to evaluate different mixtures of uranium species.

Improvements in classification and analysis routines may also provide more specific knowledge about the potential source of questioned material via database comparisons.

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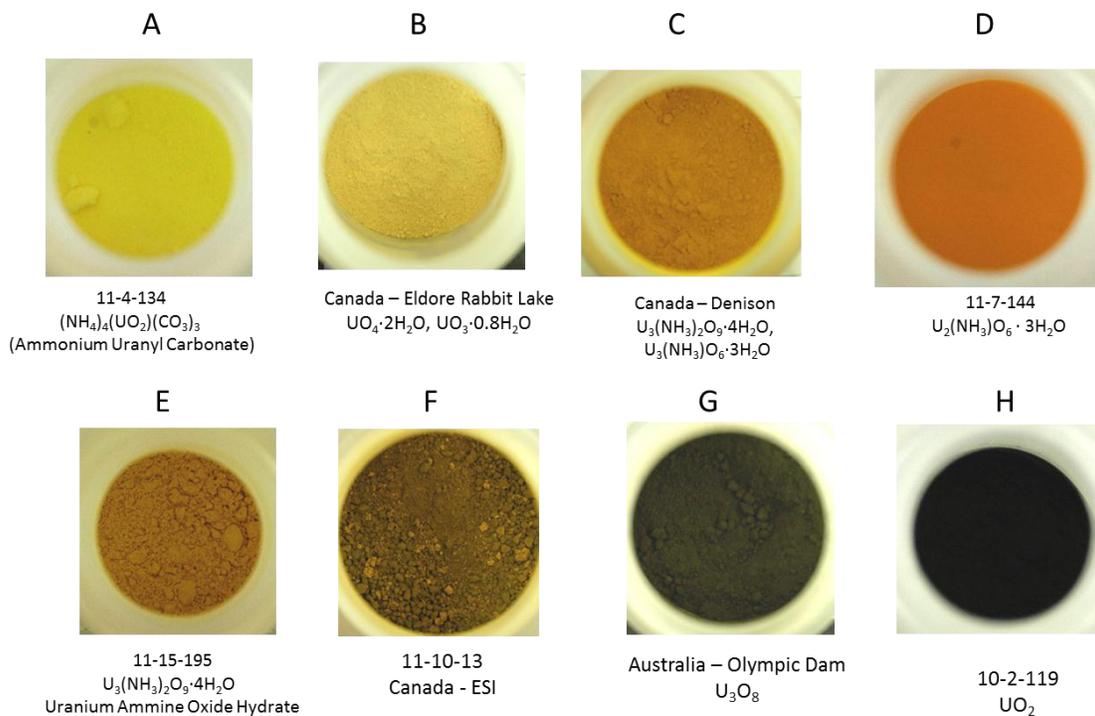


Figure 1. Color photos of several different species of UOCs.

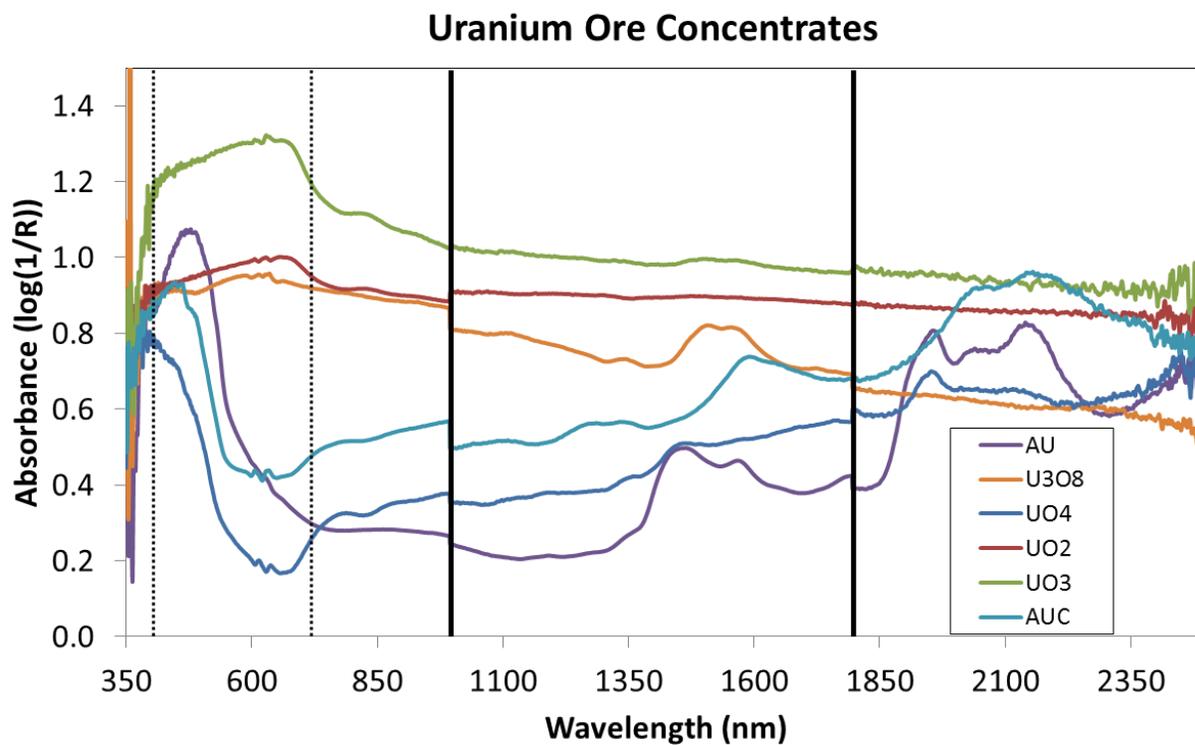


Figure 2. Full scan Vis/NIR spectra of various UOCs.

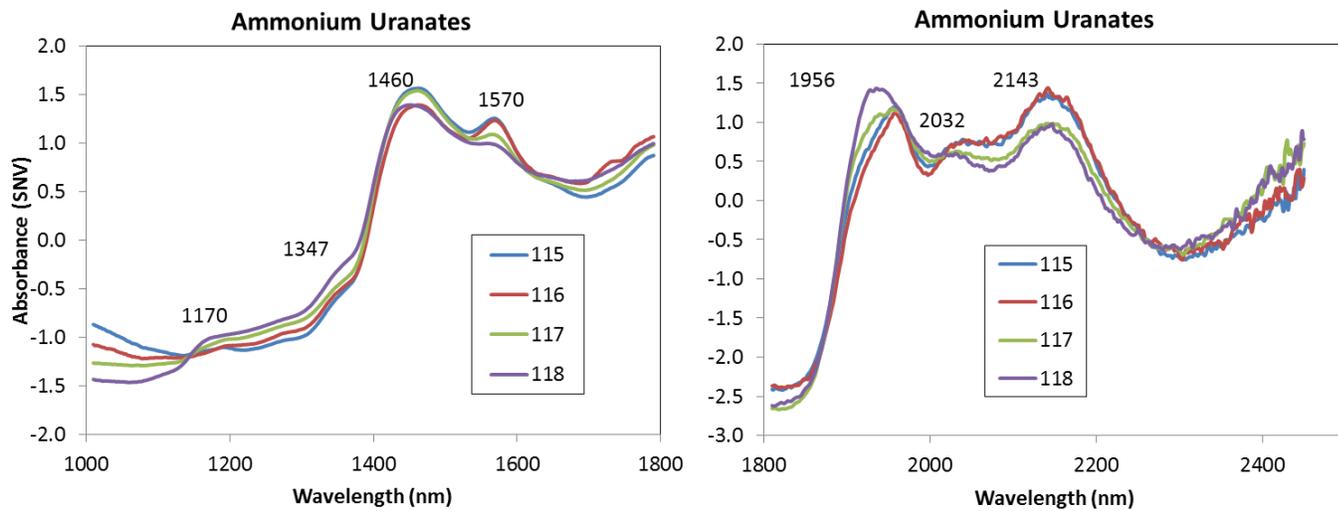


Figure 3. NIR spectra of ammonium uranates (AUs).

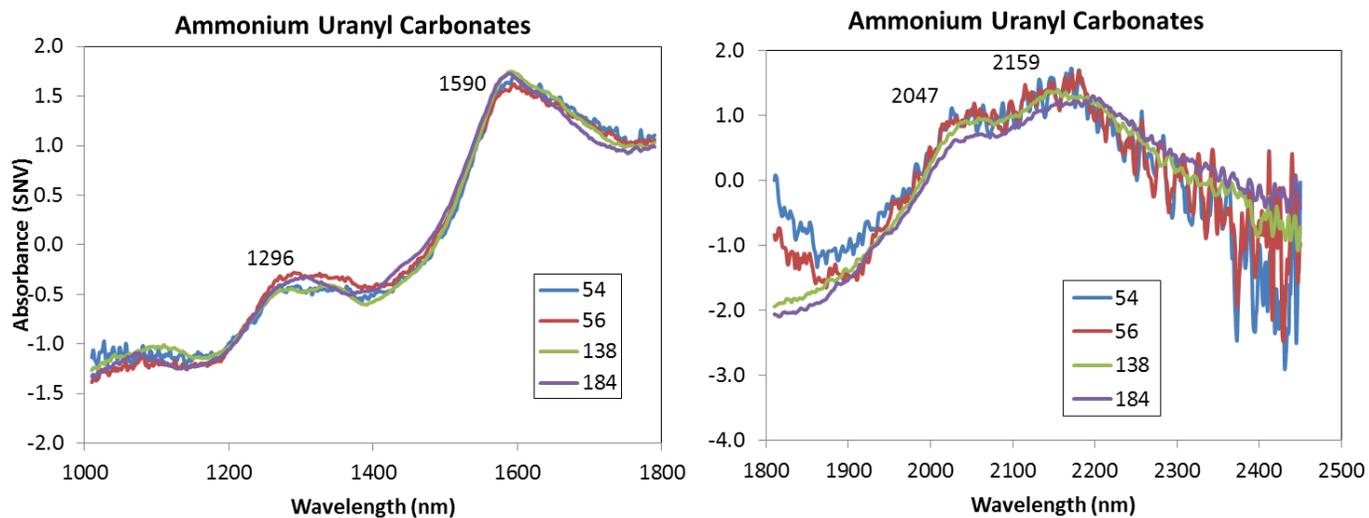


Figure 4. NIR spectra of ammonium uranyl carbonates (AUCs).

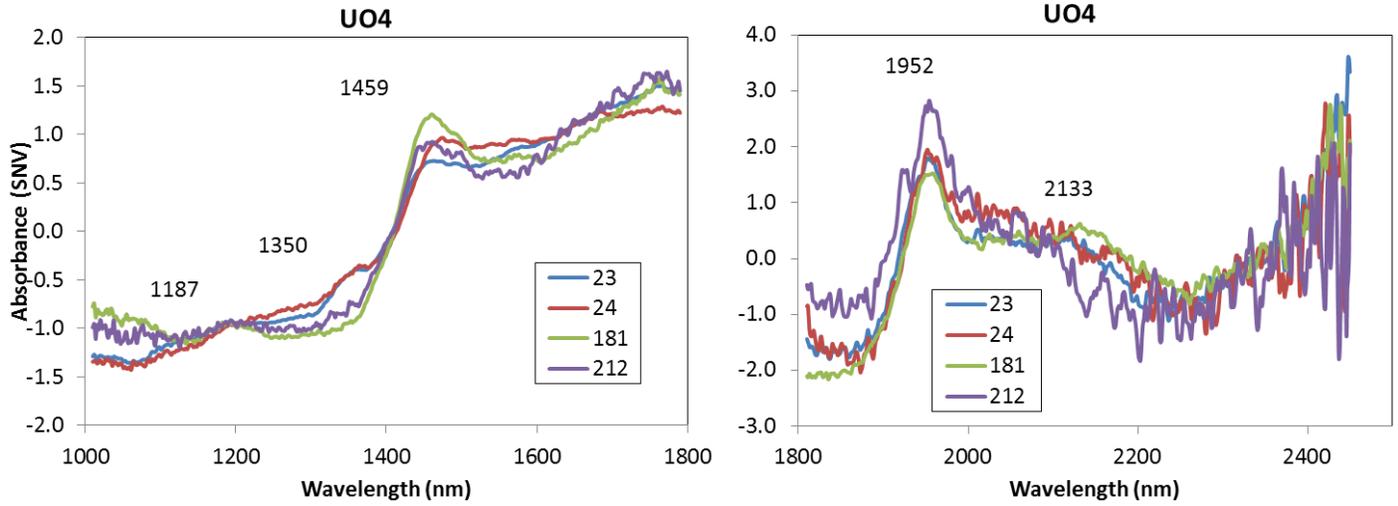


Figure 5. NIR spectra of  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$  samples.

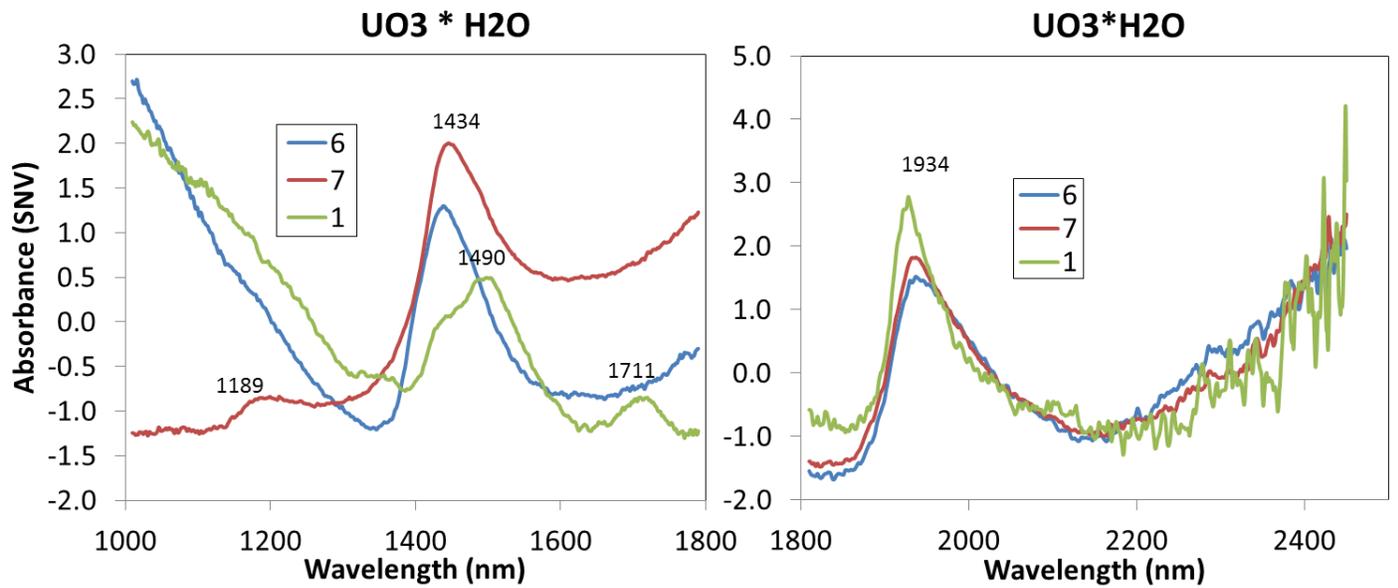


Figure 6. NIR spectra of  $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$  samples.

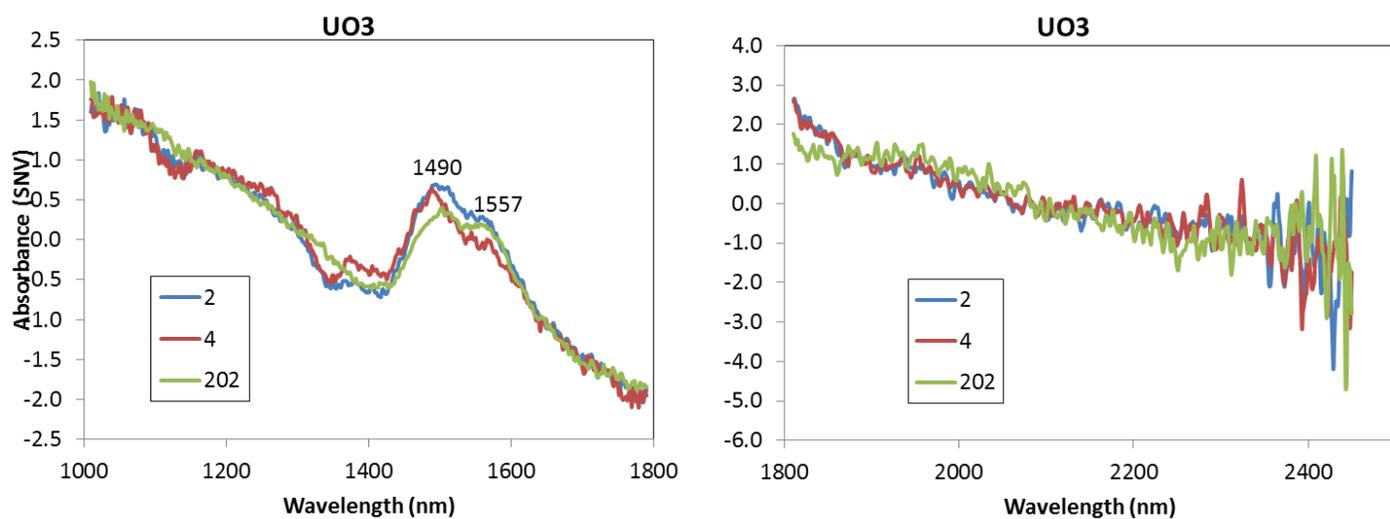


Figure 7. NIR spectra of  $UO_3$  samples.

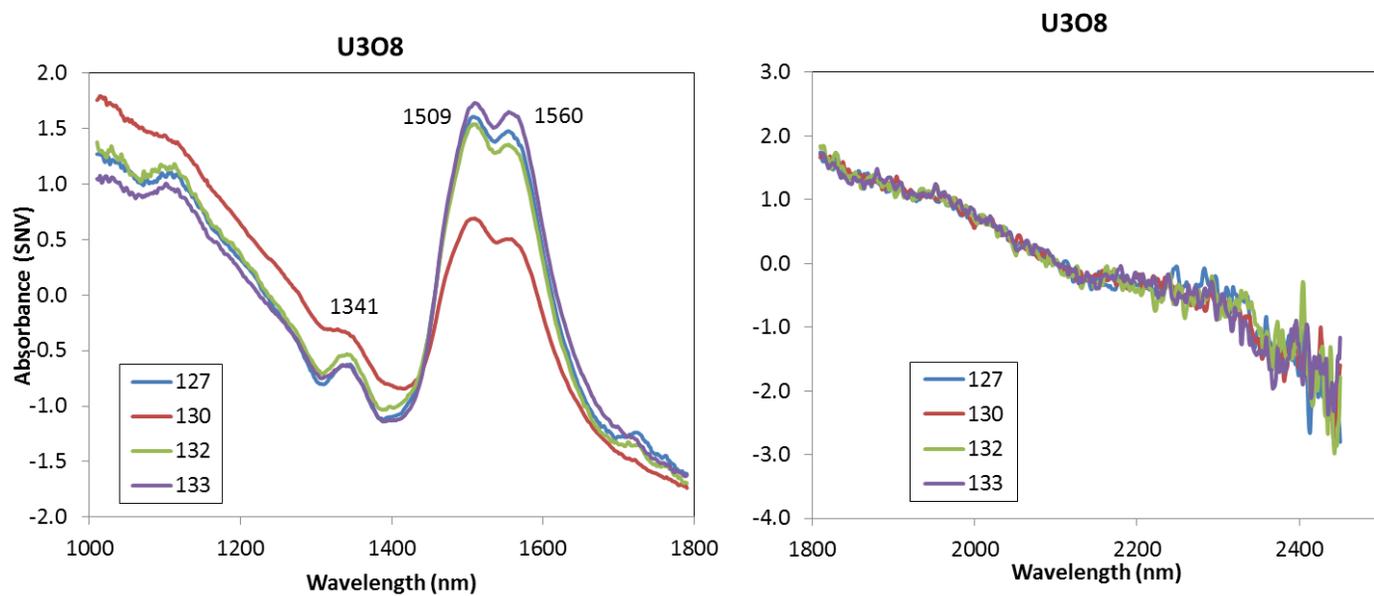


Figure 8. NIR spectra of  $U_3O_8$  samples.

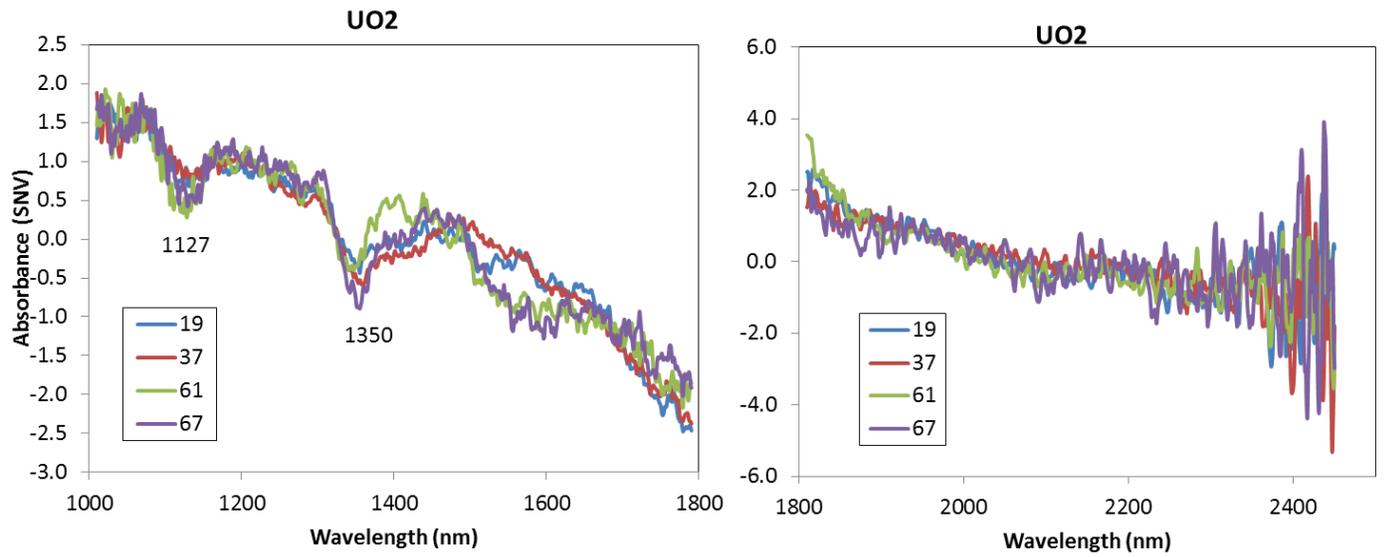


Figure 9. NIR spectra of UO<sub>2</sub>.

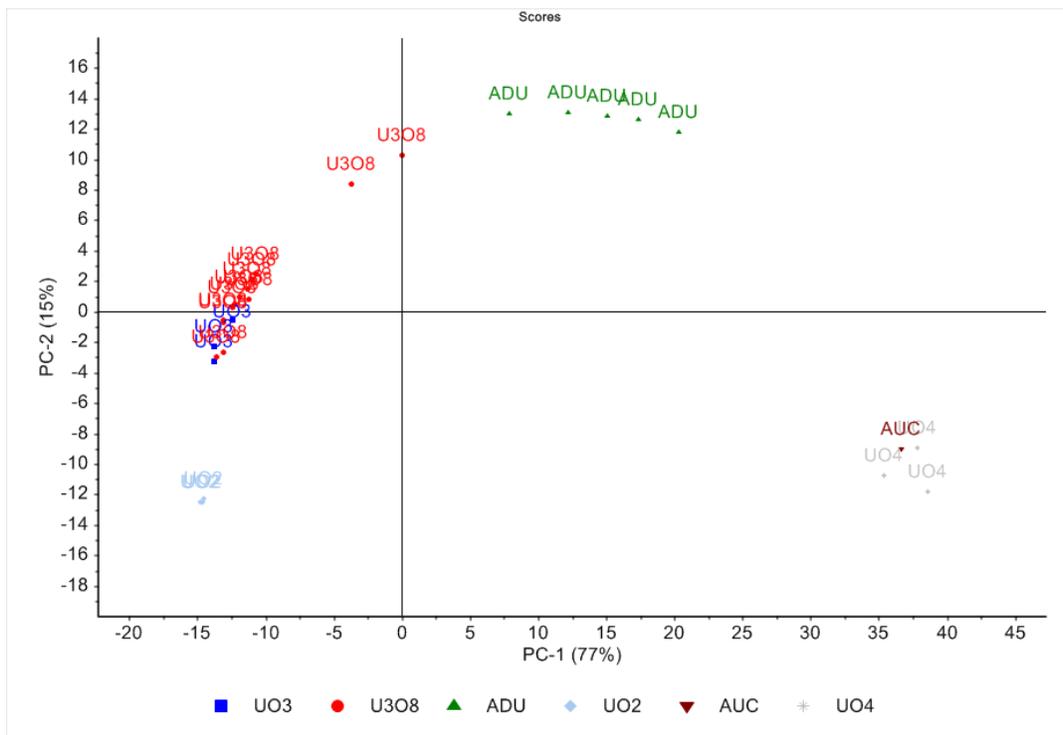


Figure 10. PCA scores plot from NIR1 spectral region after SNV preprocessing.