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Enhanced Uranium Ore Concentrate Analysis by Handheld Raman Sensor: FY15 Status Report

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INTRODUCTION and EXECUTIVE SUMMARY

High-purity uranium ore concentrates (UOC) represent a potential proliferation concern. A cost-effective, "point and shoot" in-field analysis capability to identify ore types, phases of materials present, and impurities, as well as estimate the overall purity would be prudent. Handheld, Raman-based sensor systems are capable of identifying chemical properties of liquid and solid materials. While handheld Raman systems have been extensively applied to many other applications, they have not been broadly studied for application to UOC, nor have they been optimized for this class of chemical compounds. PNNL was tasked in Fiscal Year 2015 by the Office of International Safeguards (NA-241) to explore the use of Raman for UOC analysis and characterization. Specifically, the following tasks were assigned:

1. Create an expanded library of Raman spectra of a UOC sample set, which should include samples from various sources across the globe and multiple Raman wavelengths including those commonly used in hand-held devices;
2. Create optimal chemometric analysis methods to classify UOC samples by their type and level of impurities;
3. Explore the various Raman wavelengths to identify the ideal instrument settings for UOC sample interrogation.

The eventual goals of the project are to share the spectral libraries and operational knowledge with the IAEA, as well as make recommendations regarding the usefulness of the approach for the intended analysis and an optimal Raman wavelength for the UOC analysis application. If the results of the study were promising but lack an ideal commercial option, PNNL would then attempt engage in a collaboration with a vendor of handheld Raman instruments to aid in making an ideal version commercially available to the IAEA. The following report is an update on the project status.

Task Summaries:

1. **Expanded library**: Eight available in-house samples were measured in FY15. The anticipated full data set is expected to be ~100 samples but was limited in FY15 due to constraints on the available sample set.
2. **Algorithm optimization**: We performed initial algorithm optimization on the small data set in FY15. Full data analysis optimization will be performed once a full (expanded) data set is acquired. Initial results indicated promise in the approach.
3. **Laser wavelength optimization**: This task was initiated using the limited PNNL sample set.

The following sections of this report contain detailed summary of each of these tasks.

UOC Samples

A set of UOC samples was originally identified at PNNL to be used to accomplish the above tasks. However, it quickly became apparent that the restrictions surrounding the use of the samples would make the analysis and distribution of the results somewhat limited. As such, the NNSA sponsors directed PNNL to pursue obtaining a new set of UOC samples in conjunction with parallel efforts by NNSA. Attempts to obtain samples from several international commercial UOC producers or consumers by both PNNL and NNSA were initially not successful. Eventually, in early summer 2015, PNNL and NNSA were able to identify a domestic source of UOC samples from around the world. Negotiations are ongoing but it is anticipated that a sample set with over 100 samples will arrive in early FY16.

Analysis of UOC Compounds via Raman Spectroscopy

Raman spectroscopy continues to prove itself a useful analytical technique for chemical analysis of myriad compounds, having evolved from a cumbersome laboratory technique for molecular spectroscopy to a convenient method for rapid chemical analysis. Multiple handheld units are now commercially available for such analyses, most with instant chemical identification. However, in order to be useful for such analyses it is important that the analytes of interest have spectra that are sufficiently different from one another and from the background materials. In the case of Raman spectroscopy, it also is important that the analytes (as well as any impurities) neither fluoresce nor chemically degrade under the wavelength of laser light used for the Raman analysis. (McCreery 2002; Long 1977)

In theory (and somewhat in practice) it has been shown that handheld, Raman, laser-based sensor systems are capable of identifying liquid and solid materials relevant to the fuel cycle. These sensors are based on the optical process of Raman light scattering whose signal originates between the interaction of the laser photon with the chemical vibrational modes inherent in all molecular substances: gas, liquid or solid. Several of the key fuel cycle species e.g., $Na_2U_2O_7$, U_3O_8, UO_2F_2, UO_3, and UO_2 (including in separate phases and from different sources), consist of a unique arrangement of atoms; consequently, the energies/frequencies of the vibrational modes for any given species are unique. A primary PNNL task is to construct a Raman library for identification of such UOC compounds and their derivatives. The library could then be tested for identification of unknown UOC materials, and possibly their composition. This report details preliminary efforts towards that end.

A second and related task given to PNNL was to evaluate optimal laser excitation wavelength for the UOC Raman analysis. One difficulty associated with the Raman measurements of UOCs is identifying a suitable laser wavelength to avoid the generation of interfering fluorescence signals; this is especially true for the yellow-orange diuranate compounds, all of which absorb strongly at wavelengths shorter than 600 nm. Other UOC compounds have strong absorptions at red or near-infrared (IR or NIR) wavelengths that result in heating signals that can mask the Raman signatures, or even lead to sample photolysis. As a result, lasers emitting at longer wavelengths are likely better suited to suppress UOC fluorescence or decomposition. Several red or near-IR lasers (in wavelength range from 660-1064 nm) are logical candidates. While such lasers can effectively suppress fluorescence, they may not be optimized for UOC measurements, and other wavelengths may provide higher measurement efficiency; several longer wavelengths handheld systems are just now coming to market. (Zachhuber, 2011) PNNL will use its many wavelength systems (632-, 670-, 785-, and 1064-nm, etc.) to identify an optimal laser excitation wavelength for analysis of UOCs and uranium materials. The recommendation and selection of optimized laser wavelength will take into account the need to be able to be used within a hand-held system. Current handheld Raman systems, such as the Thermo Scientific® FirstDefender RM^{TM}, use the 785 nm laser excitation source. We have also recently shown (Kunkel 2011; Johnson 2012) that, amongst the Raman data that use different near-IR laser wavelengths for excitation, it is in fact possible to port an entire database of spectra (i.e. a spectral library of a wide range of substances) recorded at one wavelength (e.g. 1064 nm) and employ them for analysis at another wavelength (e.g. 785 nm).

With these considerations borne in mind, we began by using a high-fidelity laboratory Fourier-transform (FT)-Raman spectrometer with two optical channels. It has both a 785 nm and 1064 nm wavelength laser for analysis; this can be used to 1) identify a useful λ for UOC analysis and ultimately to construct a UOC compounds Raman library. This can 2) be used to develop improved identification algorithms.

EXPERIMENTAL AND CALIBRATION

Samples and Sample Mounts

For the first year, the project has been partially limited by the inability to acquire multiple UOC samples from multiple sources; efforts to acquire additional UOC specimens continue. Currently, however, PNNL does have in its possession a set of UOCs that are part of an ongoing alternate NNSA project for use with other spectroscopic methods. While limited in number, these samples provided a good set with which to start and a way to anticipate the instrument response to different types of materials, and consequently spectra. The UOC samples are from various locations and facilities, as are other materials that PNNL had at hand (U_3O_8, UO_3). An example is seen below in Figure 1. In most cases the chemical identity of the materials was known from analytical methods – primarily x-ray diffraction (XRD). Also, because the samples had previously been used for UV-visible spectroscopy, they were already mounted behind quartz windows (Figure 1) which is conveniently transparent to the visible and NIR light used in Raman spectroscopy.

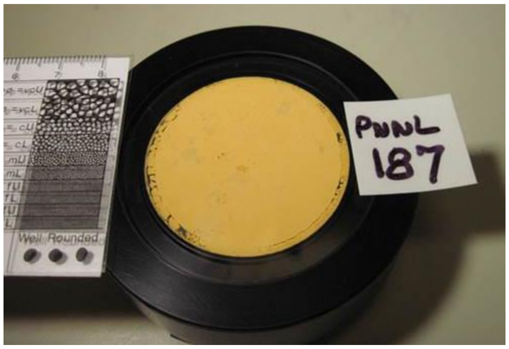

Figure 1. Photograph of UOC sample (largely metastudtite), PNNL U sample #187. The sample is in a holder that can be used for Raman analysis and is illuminated by a common halogen lamp.

Spectroscopic Analysis

The spectra were measured using a Fourier-transform (FT) Raman spectrometer that can use either a 1064 nm- or a 785 nm-excitation laser. The Bruker MultiRam 27 dual wavelength instrument was used in both configurations. The MultiRam is a dedicated Fourier transform instrument that has a flex-pivot mechanical bearing interferometer, with a relatively fast optic (f/2.9) as compared other FT-systems. The

MultiRam was used with an internal aperture setting of 3.5 mm. For both excitation wavelengths the interferometer beamsplitter is silicon coated onto quartz, and the Raman detector for the 785 channel is a TE-cooled silicon avalanche pin-diode detector used in optical power mode. The laser is a GaAs 785 nm diode laser. The RFS 27 also uses a proprietary notch filter to remove the Rayleigh line before the interferometer. The 785 nm system is equipped with a proprietary anti-Stokes bandpass filter that passes light on only the low-frequency side of the laser line. The 1064 nm channel uses an air-cooled Nd:YAG laser to produce the 1064 nm monochromatic light, and also uses a proprietary notch filter to remove the laser line before entering the interferometer. The Raman scattered light is detected by a liquid nitrogen-cooled Ge detector; the Dewar holding liquid N_2 is seen as the tall reservoir in Figure 2.

Figure 2. Photograph of RFS 27 dual-wavelength Raman spectrometer. The instrument has two independent optical channels for the Raman 785 or 10644-nm excitation lasers.

The instrument has a dedicated sample compartment, with either 90- or 180-degree backscatter spectral light collection; for the present work the 180° configuration was used for an optimal signal. For the uranium solids, due to the radioactive nature of the materials, approximately 3 to 5 grams of the material were put into containers that have the sample behind quartz glass; an example is shown in Figure 1. All data were recorded at 2.0 cm^{-1} spectroscopic resolution. The excitation laser power was varied as needed, but seldom exceeded 500 mW. Data were collected using forward-backward double-sided interferograms and typically between 300 and 2000 interferograms were averaged, depending on signal quality. Further details of the spectrometer and collection parameters can be found in the paper by Johnson et al. (2012) or Kunkel et al. (2011). Spectra were recorded from $\Delta\nu = 0$ to 3,600 cm^{-1} but in some cases are only plotted to 2,000 cm^{-1} for clarity. In all cases the spectrometer was carefully calibrated on both the λ-axis using known methods (Kunkel 2011) as well as on the intensity axis. (Williams 2007; Choquette 2007).

Post-data Spectral Processing

Due to broad interferograms, the raw interferogram data were phase-corrected using the power method to convert from interferogram space to spectral space. For many of the 785 nm spectra, a broad fluoresce effect was observed as described below. For these spectra, the featureless fluorescence was simply subtracted from the spectra in order to facilitate better analysis using the Raman lines.

RAMAN SPECTRAL RESULTS

Using the set of UOC compounds that PNNL hadavailable for this study, several Raman spectra were recorded. Most (but not all) samples were run at both the 785 and 1064 nm wavelengths to begin wavelength optimization for the study at hand. Broadband Raman spectra for four of the samples (PNNL #184, 185, 186 and 187) are seen below in Figure 3 for both the 785 nm and 1064 nm excitation wavelengths. We note that these four samples are all yellow-orange in color (see Figure 1), and all four were confirmed by XRD to be nearly pure metastudtite in each case. Portions of the 785 nm spectra to the left of the peaks show significant amounts of fluorescence for some species. For the 1064 nm spectra, there is some noticeable, but suppressed fluorescence.

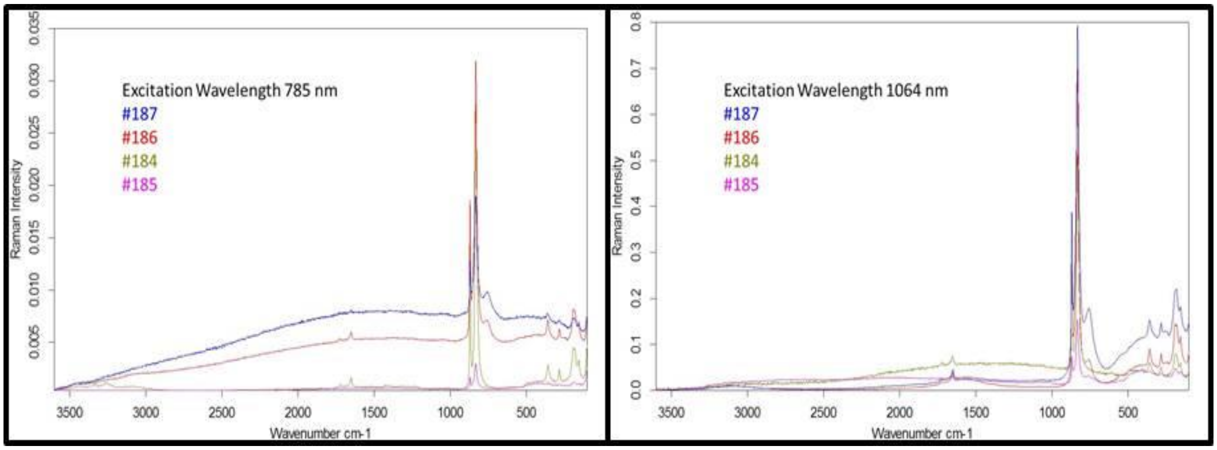

Figure 3. FT-Raman spectra of four UOC samples from PNNL holdings for uranium compounds. These species were all yellow-orange in color (see Figure 1) and were confirmed by XRD to be nearly pure metastudtite. The results at left show the 785 nm spectra which show significant amounts of fluorescence for some species. For the 1064 nm spectra, there is minimal fluorescence.

A more subtle aspect of comparing the 785 vs. 1064 spectra is that while the 785 nm excitation does generate Raman spectra atop the fluorescence, the fluorescent signal consumes much of the photonic and electronic dynamic range; the Raman signals represent a smaller overall fraction of the spectra. Spectral and electronic bandwidth is being sacrificed to incorporate both the Raman and fluorescence signals in a fixed dynamic range, resulting in lower signal-to-noise ratio for the Raman signal itself. Another subtlety associated with these spectra is that, in order to avoid sample degradation for the 785 nm data, the spectra were collected at a lower laser power. Typical power levels using the 1064 nm laser were in the 50 to 500 mW range, whereas typical power levels for the 785 measurements were 50 mW or less, even 30 mW for the dark U_3O_8 samples.

Raman spectra were collected from a total of eight UOC samples available for interrogation. Of these, none were 100% pure, but one (#154) was largely metaschoepite, also yellow-orange in color, three were mostly U_3O_8 (#183, 330 and 331), all of which were gray-black in color providing the greatest challenge to measure, and the last four (#184, 185, 186 and 187) were largely metastudtite. These samples are summarized in Table 1. It is well known in Raman spectroscopy that, if the sample absorbs light at the laser wavelength, there is a much greater probability of either fluorescence, heating or photodecomposition. For five of the samples (Sample 1 and 5 to 8), the yellow-orange color suggested that increasing the laser wavelength would reduce the interfering fluorescence, which turned out to be the case as there was somewhat less fluorescence at 1064 than 785 nm. For the three grey-black U_3O_8 samples, their color indicated that the samples absorb across the visible and likely into the near-IR ranges. Both the 1064 and the 785 nm lasers were expected to provide better spectra compared to visible lasers, e.g. 632 or 532 nm. This was indeed the case. By using long averaging times and very low laser powers, we were able to obtain reasonable-quality spectra, including those for the dark U_3O_8 samples of UOC. The 1064 nm data were slightly better than the 785 nm laser data, but both were successful at obtaining spectra.

Table 1. UOC samples containing Metaschoepite, U_3O_8, and Metastudtite.

Sample ID	**PNNL ID**	**Primary Composition**
Sample 1	#154	metaschoepite
Sample 2	#183	U_3O_8
Sample 3	#330	U_3O_8
Sample 4	#331	U_3O_8
Sample 5	#184	metastudtite
Sample 6	#185	metastudtite
Sample 7	#186	metastudtite
Sample 8	#187	metastudtite

Results and Discussion – Statistical Analysis

Raman spectral files were collected into a matrix database within a MATLAB® environment (version 7.9, Mathworks® Inc., Natick, MA, USA). The resulting matrix is formatted in rows (one for each sample) and columns (Raman intensity values at different wavenumbers). Figure 4 shows spectra recorded using 1064 nm excitation, for the eight samples containing Metaschoepite (Sample 1), U_3O_8 (Samples 2 -4), and Metastudtite (Samples 5 – 8).

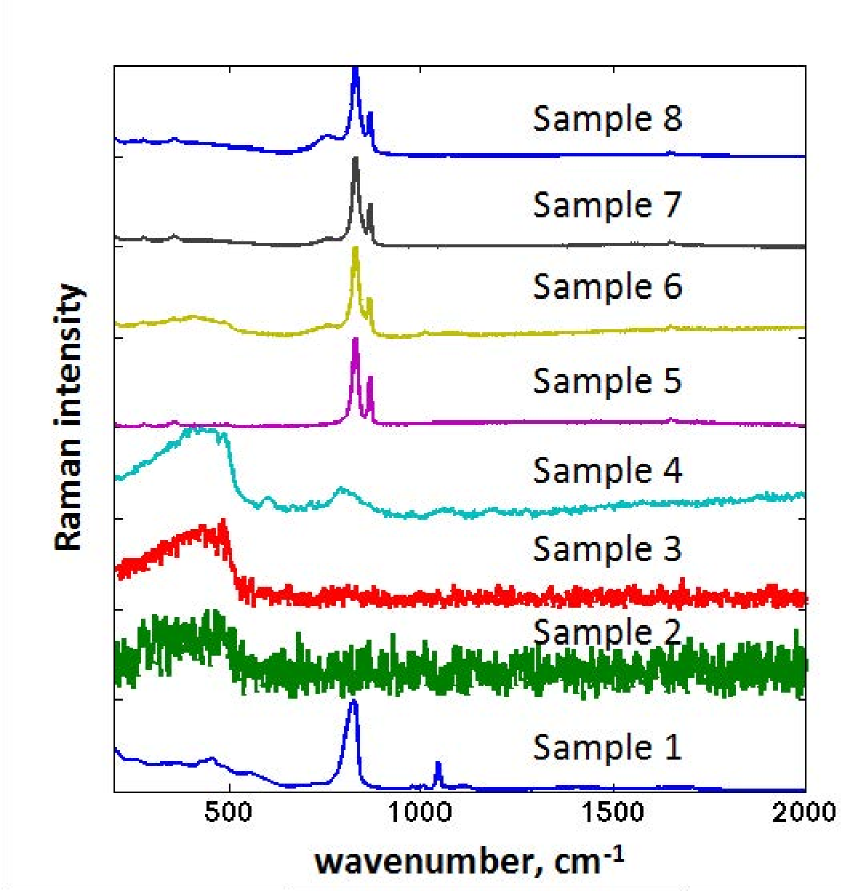

Figure 4. Raman spectra of UOC samples containing Metaschoepite (Sample 1), U_3O_8 (Samples 2 - 4), and Metastudtite (Samples 5 – 8).

The selection of one or more spectral ranges containing chemical information, as well as the elimination of spectral ranges that only contain noise, are widely used strategies to improve PCA models. (Beebe et al., 1998; Sharaf et al., 1986) The spectral region from 200 cm^{-1} to 2000 cm^{-1} was used to enhance the model sensitivity. Before chemometric analysis, two pretreatment steps were performed on the spectral data. The first derivatives of the spectra were computed by the Savitsky-Golay method (Savitsky and Golay, 1964), and was followed by mean centering of the sample data. (Sharaf et al., 1986) The purpose of performing a derivative of the spectral data is to reduce baseline offset effects. Mean centering subtracts the mean absorbance value from each sample with the result that the 'centroid' of the data set is at the origin; this technique strives to remove an overall bias from the data set.

Principal component analysis (PCA) was performed on the spectroscopic data using commercial software (PLS Toolbox version 6.2.1, Eigenvector Research Inc., Wenatchee, WA, USA). PCA is a common tool in chemometric analysis for data compression and information extraction. PCA finds combinations of variables, or principal components, which summarize the systematic patterns of variation between samples. (Martens and Martens, 2001) The purpose of PCA is to express the main information in the variables of a data matrix, containing rows (samples) and columns (variables, i.e. Raman intensities), In this study, PCA was used to distinguish the systematic differences between groups of data and was found to be useful as a graphical display method in order to visualize the data in a lower dimension (2-D) structure.

For a demonstration of the PCA methodology, PNNL made initial steps using the eight UOC samples comprising three UOC compositional classes, summarized in Table 1. A principal component analysis (PCA) of the spectra shown in Figure 4 was performed to differentiate and pictorially show groupings of the various classes of UOC materials, and is shown in Figure 5. The PCA analysis clearly separated the three different sample types based on UOC composition. The PCA analysis also showed subtle but reproducible variations within the Metastudtite sample group (samples 5 – 8), showing the ability to differentiate between samples within the same mineral group; this group of mineral samples was derived from four different ore locations.

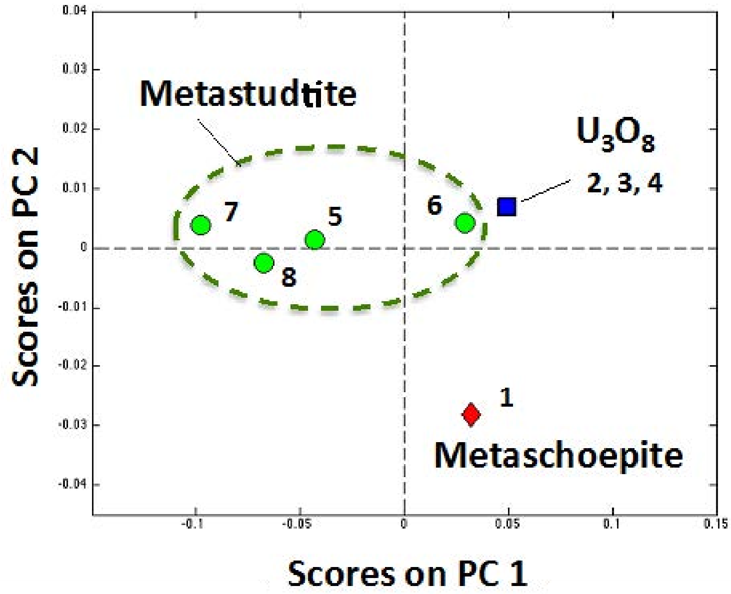

Figure 5. PCA analysis of Raman spectral data showing the group separations between the various types of UOC materials.

NEXT STEPS FOR FY16 AND FY17

FY16 plans include obtaining an expanded UOC sample set. As described above, PNNL and NNSA were able to identify a domestic source of UOC samples from around the world. Negotiations are ongoing but it is anticipated that a sample set with over 100 samples will arrive in early FY16. These will be available for testing during FY16. An excitation-wavelength study to determine the most effective excitation wavelength for Raman measurements (using compatible lasers available to the researchers) will be performed in F16. This will be based on measurements of a sample subset characteristic of the entire samples set becoming available in FY16. Collection of expanded library and preliminary examination of algorithm enhancements will be performed. The status of FY16 work will be conveyed in an Annual Report (FY16 Q4).

Early in FY17, algorithm enhancements will be completed, recommendations implementing for Raman UOC analysis will be compiled, and the final report will be written and reviewed for release.

A possible follow-on for this project is teaming with a commercial vendor such as ThermoScientific of FLIR for technology transfer of the enhanced methods and algorithms developed in this project.

Milestones:

FY16: Complete excitation-wavelength study. Collect comprehensive set of spectra from newly acquired set of samples for the expanded library. Complete algorithm enhancements.

FY17: Finalize analysis and recommendations. Compile a Final Report reviewed for release.–

Deliverables:

FY16: The status of FY16 work will be conveyed in an Annual Report (FY16 Q4)

FY17: Send Final Report to sponsor by end of the first quarter (FY17 Q1).

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