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WIPP Pu Data: SSRL Beam Lin 11-2; March 2016

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REPORT

WIPP PU DATA; SSRL BEAM LINE 11-2; MARCH 2016

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WIPP Experiments – Don Reed

Sample Prep – Don Reed

Experimenters – Alison Pugmire and Dan Olive

Data Analysis – Sharon Bone and Stosh Kozimor

SAMPLE DESCRIPTION

Six solid samples were measured at BL 11-2 in March 2106. As best we are aware, the samples were prepared in an 8 slot Conradson Holder and (as confirmed with Dan Olive on the 6th of July, 2017) analyzed at the Pu L$_3$-edge at ~70 K under vacuum in a N$_{2(Liq)}$ cryostat. Samples were generated as described in the 3rd annual workshop proceedings held in Balaruc-les-Bains (March 2011) [1]. Briefly, this involved adding a solution containing PuO_2^{2+} (0.1 mM) to a brine solution (either "GWB", which is a high Mg^{2+} brine; or "ERDA-6", which is a high Na^+ brine). Two additional variables were varied, namely the carbonate concentration and the pH of the brine solution. After two weeks of equilibration, Fe(0) (in the form of powder) or Fe^{III} (as crystalline Fe_2O_3 oxide) was added to the brine solutions. The experiments[4] that are the subject of this report were initiated on 3/8/2005 and sampled on 3/13/2016. Total equilibration time when sampled for XANES analysis was 132 months (11.0 years). Below is a list of the samples and the associated experiment measured. These data were compared with a Pu^{III}F$_3$ standard, that was prepared by the precipitation of ~ 99%+ Pu(III) with HF leading to a slightly hydrated PuF$_3$ solid.

Table 1: A description of the samples analyzed.

| Sample ID (SSRL)	#WIPP Experiment Designation	Brine type	Carbonate?	*pC$_{meas}$	Iron Form
Pu-1	Pu-FEP-E8-1	ERDA-6	No CO_3^{2-}	10.1	Fe^0 Powder
Pu-2	Pu-FEP-E8-2 (replicate of Pu-FEP-E8-2)	ERDA-6	No CO_3^{2-}	10.2	Fe^0 Powder
Pu-3	Pu-FEP-GWB7-1	GWB	No CO_3^{2-}	7.8	Fe^0 Powder
Pu-4	Pu-FEP-GWB7-2 (replicate of PuFEP-GWB7-1)	GWB	No CO_3^{2-}	7.6	Fe^0 Powder
Pu-5	Pu-FEP-2	ERDA-6	With CO_3^{2-}	8.8	Fe^0 Powder
Pu-6	Pu-Fe3-OX-1	ERDA-6	With CO_3^{2-}	8.1	Fe^{III} oxide
*pH measured, uncorrected for ionic strength (usually an increase of about 1 pH unit #See reference 4					

SUMMARY OF XANES ANALYSES RESULTS

First and foremost, there was a critical experimental mistake associated with the energy calibration. As a result, the X-ray absorption spectroscopy (XAS) experiments evaluated herein should be regarded as an informative preliminary study, but none of the data can be published as-is in peer reviewed literature (see, however additional discussion in Addendum). The experimental error is associated with the energy step size over the K-edge for the *in-situ* Zr foil. Typically, monochromator movements over the Zr K-edge (calibration foil) are equivalent to those used for the Pu L_3-edge (~0.35 eV). However, the experimental step size over the calibration foil was 10 eV for these data. Hence, it was not possible to fully account for the monochromator drift during the measurement. Monochromator instability (~1 eV is possible) can be similar in magnitude to energy shifts at the Pu L_3-edge, which can be ~2 eV with changes in oxidation state.

In spite of these issues, our preliminary assessment of the data suggests that the plutonium oxidation states for samples Pu-1 though Pu-5 are similar. It seems that reduction from PuO_2^{2+} to Pu^{III} occurred (**Figure 1** and **Table 2**). For example, the edge energies (defined to be the point at which the second derivative crosses the y-axis) for Pu-1 to Pu-5 were only 0.0 to 0.6 eV lower in energy than the $Pu^{III}F_3$ standard (see **Table 2**). It is important to note that reproducibility between replicate samples (Pu-1 and Pu-2 or Pu-3 and Pu-4) was poor, with changes in the inflection point of 0.1 to 0.5 eV (see **Table 2**). This discrepancy is likely a result of the calibration issue discussed above. Regardless, the data suggest that the Pu^{III} oxidation state was dominant over the pH range of 8 to 10, in the presence and absence of carbonate, and in the presence of either brine type (ERDA-6 or GWP), so long as Fe^0 powder was present. However, we encourage the reader to evaluate this interpretation with caution unless a more robust series of +3 Pu containing standards can be evaluated.

There was one outlier in the series: the sample that was equilibrated with iron(III) oxide, namely Pu-6. For Pu-6, reduction to Pu^{III} did not occur. The inflection point energy was 3.0 eV higher than the $Pu^{III}F_3$ standard (see **Table 2**). Additionally, there was a post-edge shoulder near 18,080 eV, which is characteristic of a multiple scattering feature associated with PuO_2^{x+} plutonyl feature. Although tempting to interpret this spectrum as containing only plutonyl (PuO_2^+ or PuO_2^{2+}), we cannot (without a substantially more detailed analysis and possibly additional experimentation) rule out the possibility that some Pu^{IV} was also present.

To alleviate issues associated with the monochromator drift, we could (over the next 4 to 8 weeks) calibrate the data to the I_0 glitch associated with the Si(220) PHI = 0 crystal. The energy position for this glitch is constant, and would enable us to put the March 2016 data on the same energy scale as used in our May 2017 measurements, when we analyzed a series of Pu^{III}, Pu^{IV}, and PuO_2^{2-} standards. These standards have a good calibration to a Zr foil. This is the best opportunity to accurately determine the inflection point energies for Pu-1 – Pu-5 samples in this study and may establish these data as publishable. However, to obtain publishable results, the data may need to be re-measured. If there is interest in reproducing these spectra, the following should be considered:

- Effort should be placed on identifying relevant Pu^{III}, Pu^{IV}, and PuO_2^{x-} standards. These standards need to be run during the same experimental campaign as Pu-1 to Pu-6.
- The Si(220) PHI = 90 crystal set should be used.
- The dead time for the 100-element Ge detector needs to be characterized.
- A proper *in-situ* Zr K-edge calibration needs to be collected for each spectrum.
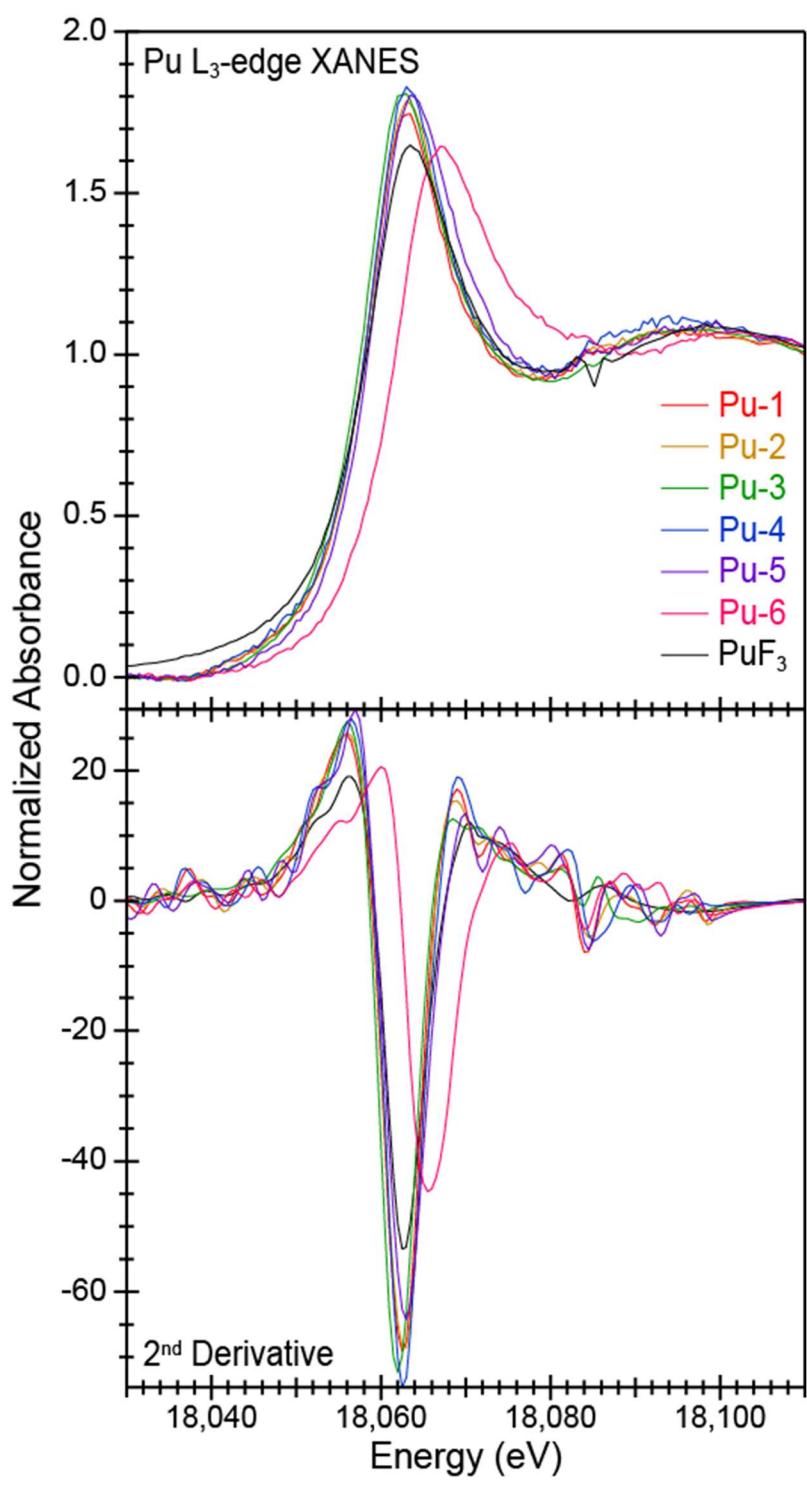
Figure 1. The background subtracted and normalized Pu L_3-edge XANES spectra (top) and second derivative (bottom) obtained for Pu-1 to Pu-6 and PuF_3.

Table 2. The inflection point (eV) obtained by Pu L_3-edge XANES spectroscopy measurements from PuF_3 and Pu-1 to Pu-6. The difference in the energies- "ΔE (PuF_3 - Pu Sample)"- between the inflection point of the reference Pu(III) compound, PuF_3, and the samples are also provided.

| Sample	Inflection point (eV)	ΔE (PuF_3 - Pu Sample) (eV)
PuF_3	18059.2	0.0
Pu-1	18058.9	0.3
Pu-2	18059.0	0.2
Pu-3	18058.6	0.6
Pu-4	18059.1	0.1
Pu-5	18059.2	0.0
Pu-6	18062.2	-3.0

RESULTS AND DISCUSSION

CALIBRATION. A Zr foil was measured during each sample scan with the intent of providing *in situ* calibration. However, the energy spacing over the edge was 10 eV, an order of magnitude larger than the typical 0.35 eV step size appropriate for energy calibrations. As such, there were only two points over the defining Zr pre-edge, which was not resolved. Although the monochromator seems stable over the course of the experimental campaign, we have not yet been able to account for monochromator drift during the experiments. Because of the lack of data at the Zr K-edge, calibrating using this standard is imprecise. Hence, the spectra were calibrated by comparing the position of the PuF_3 edge (defined as the point at which the second derivative was equal to zero) to the edge energy of a PuF_3 standard measured previously [2]. This analysis indicated that the PuF_3 spectrum from March 2016 was shifted by – 6.49 eV relative to the older standard, thus + 6.49 eV was added to all spectra collected in March 2016.

Please proceed with caution in using these data to evaluate the plutonium oxidation state for Pu-1 – Pu 6. The method of calibration was imprecise because (1) it could not account for monochromator drift during the course of the run and (2) it relies on the use of Pu(III) reference materials (which was synthesized as a PuF_3 hydrated precipitate from 99+% impurity) instead of a standard metal foil. In addition to the difficulty involved in comparing spectra within this data set, the imprecise calibration makes it so that data within this report cannot be compared with data collected on other dates or at other beamlines. It may be possible to align the March 2016 spectra with other Pu data sets collected at beamline 11-2 on the Si(220) PHI = 0 crystal set using the large glitch that occurs at the Pu edge for that crystal set. Doing so would help us to assess the amount of monochromator drift that occurred throughout the run and would also allow us to put

the March 2016 spectra on the same energy scale as spectra for Pu(III) and (IV) references materials that were collected in May 2017 under similar operating conditions.

SAMPLES PU-1 TO PU-6 PU L_3-EDGE XAS. The background subtracted and normalized Pu L_3-edge XANES spectra from Pu-1 to Pu-6 were compared with the $Pu^{III}F_3$ standard in **Figure 1**. The quality of the data was fair: As evident by comparing multiple spectra obtained during data acquisition, there were no signs of radiation damage during the experiment for any of the samples (an example of this is provided for Pu-1 in **Figure 2**). However, there was a step feature in the pre-edge region, which is an artifact that may arise from poor normalization to I_0 because the data were not corrected for detector dead time. Also, the Si(220) PHI = 0 crystal set exhibits a glitch in this region, which could contribute to poor I_0 normalization. This step feature was removed during the background subtraction procedure, but precluded a robust pre-edge line to be fit to the data, which will interfere with linear combination fitting of the XANES region for quantification of the oxidation state.
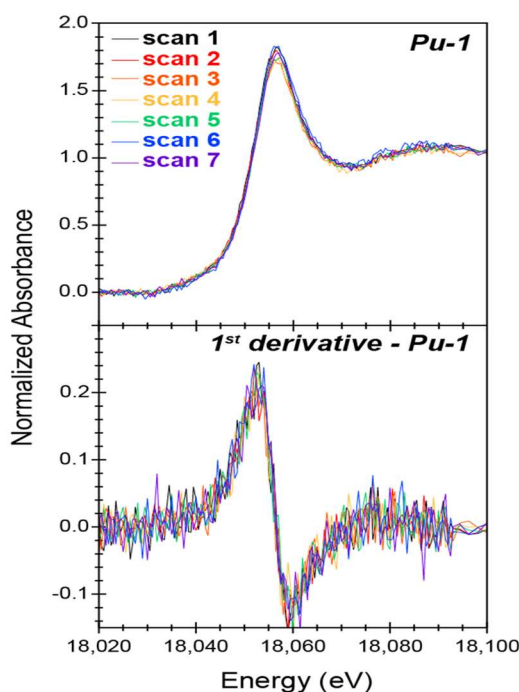
Figure 2 Comparison of Individual Scans that were averaged to yield the spectrum of PU-1

The XANES spectra were dominated by large edge features superimposed on step-like absorption threshold. From the perspective of a free ion, the edge features in these spectra originated from electric-dipole allowed transitions from Pu $2p$-orbitals to unoccupied states that contain Pu $6d$-character, e.g. for a Pu^{III} ion there would be $2p^6 \ldots 5f^5 6d^0 \to 2p^5 \ldots 5f^5 6d^1$ transitions. The edge-positions were defined by the absorption peaks whose inflection points were determined by the point at which the second derivative of the data equaled zero (**Table 2**). Inflection point energies for Pu-1 and Pu-5 were between 0 and 0.6 eV

lower in energy than the $Pu^{III}F_3$ standard. Note also that the inflection point for spectra from replicate samples (*i.e.* Pu-1 and Pu-2 or Pu-3 and Pu-4) were not equivalent, likely a result of the imprecise calibration. Overall, these data suggest that the Pu oxidation state was similar in compounds Pu-1 to Pu-5. Given the good agreement of these inflection point energies and overall absorption peak shape with PuF_3, it is tempting to assign the plutonium oxidation states in Pu-1 to Pu-5 to be Pu^{III}. However, without a better series of Pu^{III} and Pu^{IV} standards, we refrain from doing so. We remind the reader of the energy shifts that can result from changes in coordination environment, causing the inflection point energies for Pu in the same oxidation state to range up to 3 eV. Furthermore, in certain chemical environments, ~1 eV edge shifts have been observed between Pu^{IV} and Pu^{III}. **Figure 3** demonstrates the wide range of inflection point energies observed for the different Pu oxidation states and highlights how Pu^{III} inflection point energies can overlap with Pu^{IV} [3].
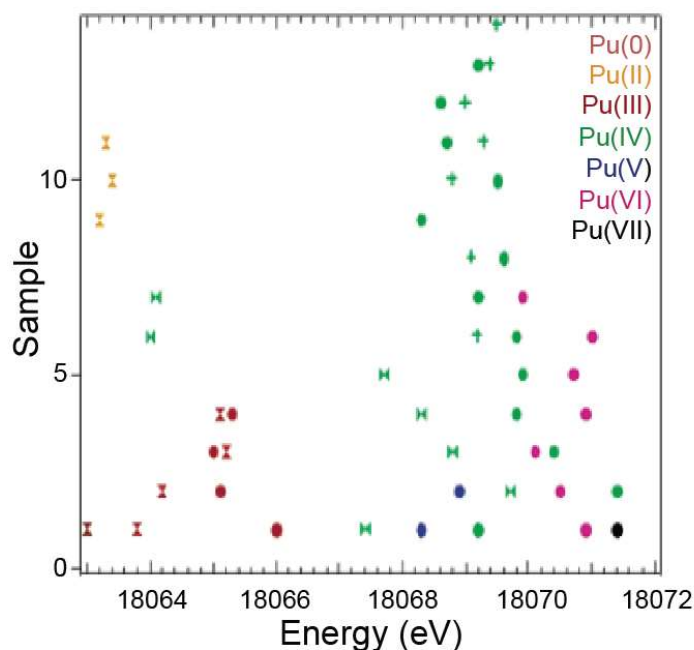

Figure 3. A plot showing variation in inflection point energies for a wide range of plutonium samples in varied coordination environments and oxidation states.

In the Pu-1 to Pu-6 series, there was one clear outlier, specifically Pu-6. This was the only sample that was equilibrated with an Fe(III) oxide; the others were equilibrated with Fe^0 powder. This Pu-6 sample showed that reduction to Pu(III) did not occur. The inflection point energy was 3.0 eV higher than the $Pu^{III}F_3$ standard. Furthermore, the spectrum of Pu-6 exhibited a shoulder on the high-energy side of the white line, which is not seen for $Pu^{III}F_3$ and not in general, for most Pu(III/IV) solid phases.

In terms of the extended X-ray absorption fine structure (EXAFS) spectra, the quality was poor for all samples (see **Figure 4**). The spectra are useable to approximately k = 7 Å^{-1}. After this, the ratio of the signal

to noise is at least 50 %. Hence, we do not recommend fitting this data. Only 3 – 5 scans were collected; 3 to 4 times the number of scans should be collected.
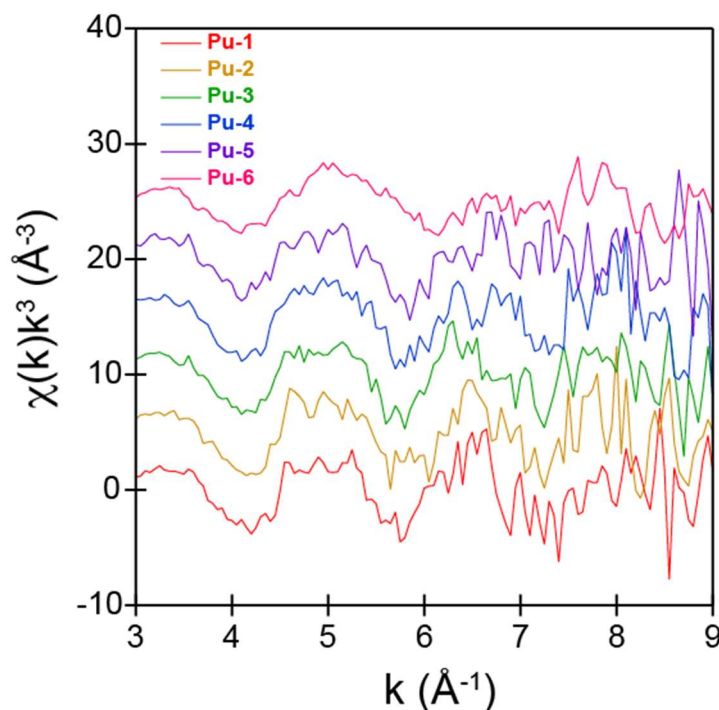
Figure 4. The low temperature solid-state Pu L$_3$-edge EXAFS function $k^3\chi(k)$ from Pu-1 to Pu-6.

EXPERIMENTAL

Pu L$_{III}$-edge XAS data were obtained at beamline 11-2 at the Stanford Synchrotron Radiation Light Source (SSRL) , under dedicated operating conditions (3.0 GeV, 5%, 500 mA using continuous topoff injections) on end station 11-2. This beamline – which was equipped with a 26-pole and 2.0 tesla wiggler – utilized a liquid nitrogen-cooled double-crystal Si(220) monochromator and employed collimating and focusing mirrors. A single energy was selected from the white beam with a liquid-N$_2$-cooled double-crystal monochromator utilizing Si(220) (PHI = 0) crystals. It is unclear at this stage how harmonic rejection was achieved. As best we can tell, samples were loaded into a sample holder designed for safe handling of plutonium. The primary consisted of an aluminum plate with eight slots, Samples were loaded into the slots and the holder was sealed with Kapton windows. This sample plate was nested within a secondary container equipped with Kapton windows (2 mil) and sealed with indium wire. Upon arrival at SSRL, the sample holder was loaded into a N$_{2(liq)}$ cryostat (Kapton windows; 2 mil) and transported to the beamline. The system was put under vacuum (10^{-7} Torr) and cooled with N$_{2(liq)}$. The cryostat was attached to the beamline 11-2 XAFS rail (SSRL), which was equipped with three ionization chambers through which nitrogen gas was continually flowed. One chamber (10 cm) was positioned before the cryostat to monitor the incident radiation (I$_0$). The second chamber (30 cm) was positioned after the cryostat so that sample transmission (I$_1$) could be evaluated against I$_0$ and so that the absorption coefficient (μ) could be calculated as $\ln(I_0/I_1)$. The third chamber (I$_2$; 30 cm) was positioned downstream from I$_1$ so that the XANES of a calibration foil

could be measured against I_1. A potential of 1600 V was applied to the ionization chambers. Sample spectra were obtained in fluorescence mode using a 100-element solid state Ge detector and the spectrum of the $Pu^{III}F_3$ reference material was collected in transmission mode. For the fluorescence mode measurements, a Ti filter was placed in front of the detector to remove scatter from the sample; however, it is not stated whether Soller slits were also employed. A Zr foil was placed downstream of the sample, between I_1 and I_2. Although duplicate samples were interrogated in February, only spectra from March are discussed herein.

Initial data processing steps were performed in Sixpack and the individual scans were averaged. The quality of the detector channels was checked and individual scans were stacked for comparison to assess whether beam damage occurred. Typically, a detector dead time correction would be applied to the fluorescent data at this point, however, no file was available with which to do this correction. Between 2 and 7 scans were averaged per sample.

Background subtraction and normalization was performed in Athena, yielding spectra normalized to a single Pu atom. This procedure involved fitting a line to the pre-edge region, -40 to -30 eV (relative to the inflection point), which was subsequently subtracted from the experimental data to eliminate the background of the spectrum. The data were normalized by fitting a first-order polynomial to the post-edge region of the spectrum (65 – 150 eV, relative to the inflection point) and setting the edge jump at 18059.5 eV to an intensity of 1.0. The EXAFS spectra were extracted by fitting a spline to the spectra between k = 0 and k = 14 Å^{-1}.

REFERENCES

1. Reed, D.T., et al. *Redox-controlling processes for multivalent metals and actinides in the WIPP*. in *7th EC FP - Recosy CP*. 2011. Balaruc-les-Bains, France.

2. Kropf, A.J. and D.T. Reed, *X-ray absorption near-edge spectroscopy of plutonium solid species*, in *10th International Conference of X-ray Absorption Fine Structure*. 1998: Illinois Institute of Technology, Chicago, Illinois.

3. Conradson, S.D., et al., *Higher order speciation effects on plutonium L-3 X-ray absorption near edge spectra.* Inorganic Chemistry, 2004. **43**(1): p. 116-131.

4. QA Traceability: WIPP Sientific Notebook ACP-04/1

    Experimental preparation and initiation - pages 9-26

    Experimental Matrix - p. 24

    Sampling for XANES analysis - pages 144-152

ADDENDUM

WIPP PU DATA; SSRL BEAM LINE 11-2; MARCH 2016

Synthesis – Don Reed

Sample Prep – Don Reed

Experimenters – Alison Pugmire and Dan Olive

Data Analysis – Sharon Bone and Stosh Kozimor

CALIBRATION BASED ON CRYSTAL GLITCH

The purpose of writing this addendum is to address major issues associated with the Pu L_3-edge data that Sharon Bone and Stosh Kozimor previously analyzed in '*REPORT PU DATA; SSRL BEAM LINE 11-2; MARCH 2016*." The data within that report suffered from a calibration error, which rendered the data unpublishable. However, we have overcome this technical challenge by calibrating to a glitch in the I0. Now, we believe that the data can be moved to publication. Overall, we found that samples Pu-1 to Pu-5 contained primarily plutonium in the +3 oxidation state. In contrast, the Pu-6 sample has not undergone reduction to Pu(III). However, given constraints associated with this data set it is impossible to determine if Pu existed primarily as Pu^{IV}, Pu^V, Pu^{VI}, or as some mixture of these oxidation states.

CALIBRATION BASED ON CRYSTAL GLITCH

The XANES spectra for PuF_3 and samples Pu-1 through Pu-6 were calibrated based on the position of a crystal glitch in I_0 that occurs for Si(220) (PHI = 0) crystal set. This glitch was observed during collection of Pu L_3-edge XAS during a subsequent run at beamline 11-2 in May, 2017. A Pu sample from this run ("Pu_L3_HNO3_1M_May17B") was calibrated to a Zr reference foil (17,998.0 eV) that was collected in line with the sample (between I_1 and I_2). The location of the glitch for the calibrated scan occurred at 18083.2 eV. The I_0 signals (as I_0/RTC; RTC is the real time clock) for PuF_3 and samples Pu-1 through Pu-6 were then shifted until the glitches were aligned with the spectrum collected in May 2017 (i.e. the minima of the glitch was centered at 18083.2 eV). We observed energy differences for the poorly calibrated analysis (Table 2 in original report) being 0.7 to 1.2 eV higher in energy than the more rigorous analysis described herein. The re-calibrated XANES spectra and their second derivatives are provided in **Figure 5**. These energy differences are a direct measure of monochromator stability on beam line 11-2, and highlight the need for rigorous calibrations when making delicate inflection point measurements. We remind the reader that differences in Pu oxidation state typically range from 1 to 2 eV, which is slightly outside of the stability of the monochromator.

The inflection points (**Table 3**) of the calibrated spectra were determined based on the position where the second derivative was equal to zero. The inflection point of PuF_3 was found to be within 0.3 eV of the value previously reported for PuF_3 [2] (see also **Table 2**), suggesting that this method of calibration was accurate. The inflection points of the spectra for samples Pu-1 through Pu-5 were between 0.7 and 1.0 eV *lower* in energy than the PuF_3 reference, indicating that the plutonium oxidation state in samples Pu-1 through Pu-5 was primarily +3.

The inflection point of Pu-6 was 2.2 eV *higher* in energy than the PuF_3 reference, indicating that it likely contained some Pu in higher oxidation states. However, given constraints associated with this data set, it is impossible to determine if the speciation in Pu-6 contains Pu^{IV}, Pu^{V}, Pu^{VI}, or some mixture of these oxidation states.
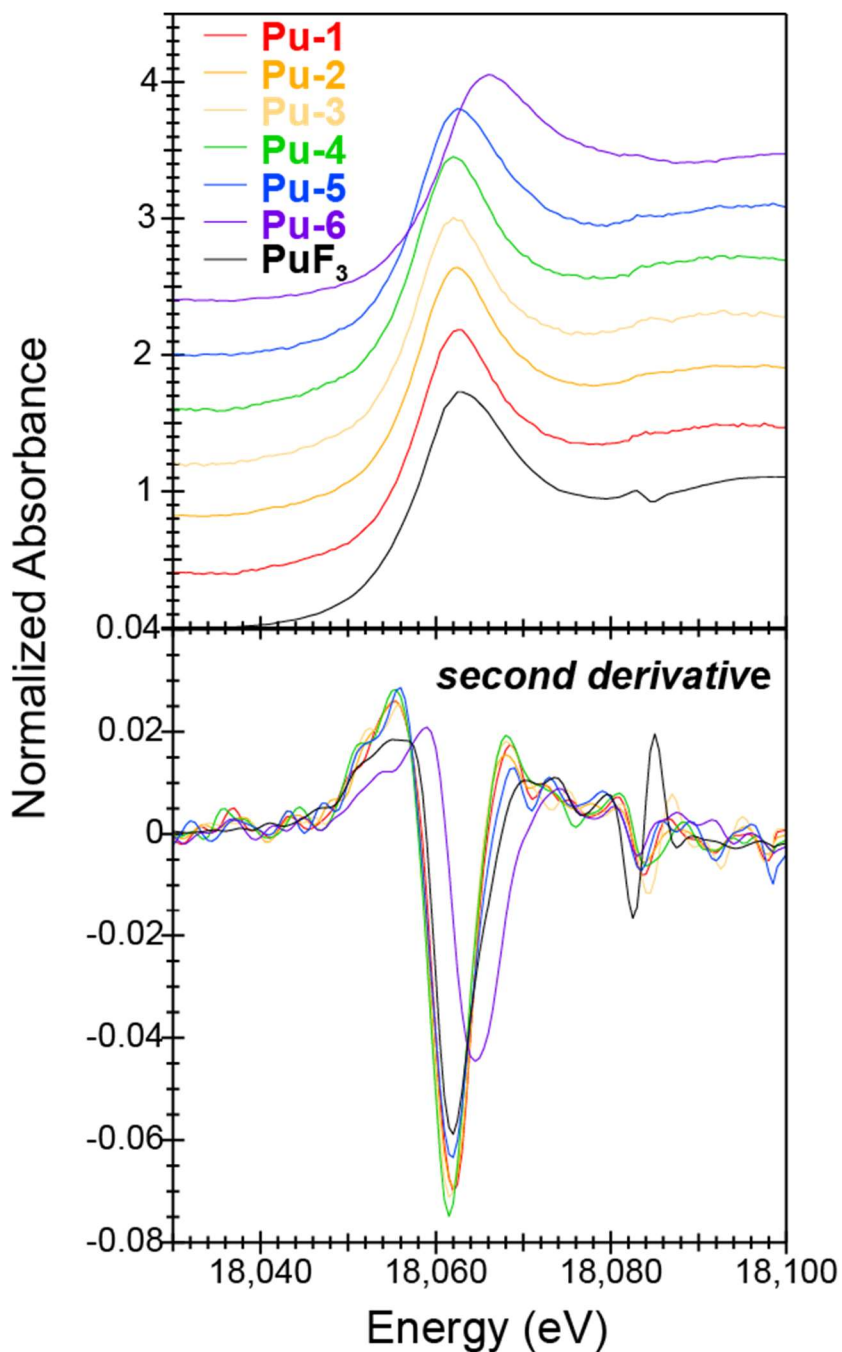
Figure 5. The background subtracted and normalized Pu L_3-edge XANES spectra (top) and second derivative (bottom) obtained for Pu-1 to Pu-6 and PuF_3.

Table 3. The inflection point (eV) obtained by Pu L_3-edge XANES spectroscopy measurements from PuF_3 and Pu-1 to Pu-6. The difference in the energies- "ΔE (PuF_3 - Pu Sample)"- between the inflection point of the reference Pu(III) compound, PuF_3, and the samples are also provided.

Sample	Inflection point (eV)	ΔE (PuF_3 - Pu Sample) (eV)
PuF_3	18058.9	0.0
Pu-1	18058.2	0.7
Pu-2	18058.2	0.7
Pu-3	18058.0	0.9
Pu-4	18057.9	1.0
Pu-5	18058.1	0.8
Pu-6	18061.1	-2.2