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DETERMINATION OF PLUTONIUM IN SPENT NUCLEAR FUEL USING HIGH RESOLUTION X-RAY

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Abstract

Characterization of Pu is an essential aspect of safeguards operations at nuclear fuel reprocessing facilities. A novel analysis technique called hiRX (high resolution X-ray) has been developed for the direct measurement of Pu in spent fuel dissolver solutions. hiRX is based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF), which provides enhanced sensitivity and specificity compared with conventional XRF techniques. A breadboard setup of the hiRX instrument was calibrated using spiked synthetic spent fuel (SSF) standards prepared as dried residues. Samples of actual spent fuel were utilized to evaluate the performance of the hiRX. The direct detection of just 39 ng of Pu is demonstrated. Initial quantitative results, with error 4-27% and precision of 2% RSD, were obtained for spent fuel samples. The limit of detection for Pu (100 s) within an excitation spot of 200 µm diameter was 375 pg. This study demonstrates the potential for the hiRX technique to be utilized for the rapid, accurate, and precise determination of Pu. The results highlight the analytical capability of hiRX for other applications requiring sensitive and selective nondestructive analyses.

1.0 Introduction

1.1 Determination of Pu in nuclear spent fuel

Measurement of Pu in spent nuclear fuel is important for monitoring reprocessing activities and for material control and accountancy. The use of nondestructive assay (NDA) to quantify Pu in spent fuel should provide regulators the capability to conduct independent verification of Pu mass at sites with nuclear materials (i.e., detect diversion) and increase efficiency in reprocessing plant operations. At present, Pu assay of fuel assemblies is routinely conducted with neutron counting and gamma spectroscopy. These are indirect methods which permit calculation of expected mass of Pu and other fissionable materials, wherein experimental signatures are compared with operator declared values for burn up [1]. Knowledge of the operating history of the rector is required along with the use of modeling, and results are thus subject to some level of uncertainty. X-ray fluorescence is one of the 13 NDA techniques for elemental Pu determination that have been recently evaluated by the safeguards community [2]. Specifically, self induced (passive) XRF, in which U and Pu characteristic K X-rays are generated due to gamma flux in the sample, has been used to determine the U/Pu elemental ratio and an estimate of Pu mass [3-5]. Long counting times (> 1 h) are one potential limitation of this approach [6].

For the assessment of Pu content in spent fuel dissolver solutions, more accurate and sensitive methods including controlled potential coulometry and mass spectrometry may be utilized [7,8]. Due to their extensive sample preparation requirements and complexity, these approaches may not be well suited to routine analyses. Conversely, hybrid K-Edge (HKED) is a routine method which combines K-edge densitometry with XRF for determination of U and Pu in spent nuclear fuel samples. While sample preparation is limited, volumes in excess of 2 mL are required and typical counting times are 1000 s [9, 10]. Transmission-corrected K-XRF utilizing two radioactive isotopes has been demonstrated for U and Pu determination up to 300 g/L through container walls, but has not been widely adopted as an NDA approach despite on-line applicability [11]. The detection of characteristic L X-rays using conventional energy dispersive (ED)XRF has also been proposed as an approach to determine actinides in spent fuel solutions [12,13]. Berdikov et al. demonstrated sensitive detection of U and Pu based on direct measurement of 3.5 mL of solution in 1982, but the authors are not aware of any more recent publications describing the use of X-ray tube excitation-based XRF for monitoring Pu in reprocessing solutions [14].

1.2 High resolution X-ray (hiRX)

High resolution X-ray (hiRX) is a novel technique based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF), in which doubly curved crystal (DCC) optics are utilized for both excitation and detection. Coupled with an X-ray source, the point-focusing excitation optic creates a monochromatic, high flux source to excite characteristic X-ray fluorescence from the sample, while the collection optic passes X-rays of a specific energy and focuses them onto the detector. The use of two DCCs makes hiRX highly sensitive and selective, as background due to scatter and peaks outside the specified collection energy are removed from detection. MWDXRF technology is currently used in commercial instrumentation for the determination of S, Cl, Si, and P in petroleum products, and a limit of detection (LOD) of 0.36 mg/kg has been reported for S in a fuel matrix (4 mL, 300 s) [15]. The hiRX instrument is designed specifically for detection of actinide elements in spent nuclear fuel. A schematic of the single channel hiRX configuration for Pu detection is shown in Figure 1.

hiRX offers a new approach for the rapid and accurate determination of Pu. Low sample volumes (<10 µL) and simple sample preparation reduce safety risks and costs associated with handling and disposing of radioactive materials. This low sample volume may also permit more frequent sampling of a spent nuclear fuel reprocessing stream, allowing more complete characterization of the dissolver tank composition. The use of MWDXRF permits direct, nondestructive measurement of Pu at sub-ppm levels, much lower than other XRF approaches. The development of the hiRX prototype and its preliminary applications to detection of Pu, U, and Cm in various surrogate matrices as has been described previously [16-20]. This is the first work in which hiRX is utilized to detect Pu in an actual spent fuel matrix. Dried residues of Pu-spiked synthetic spent fuel (SSF) are used to calibrate the hiRX for determination of Pu in the spent nuclear fuel residues. The low Pu content of the successfully measured samples relative to the 1 g/L levels expected in reprocessing streams highlights the sensitivity of the hiRX technique.

2.0 Experimental

2.1 Instrumentation

The hiRX breadboard setup is shown in Figure 2. A 50W Rh anode X-Beam (XOS, East Greenbush, NY) X-ray source is coupled with the excitation DCC optic which transmits the Rh Kα line at 20.2 keV. The optic is Si<200> crystal in Johann geometry with 1.2º by 51.2º solid angle and source to optic distance of 181.5 mm. The reflection efficiency is estimated at 5%, flux is 4×10^8 photons/s, and focal spot size is 190 by 250 µm. The 360º collection DCC optic passes the Pu Lα line at 14.279 keV, with a bandwidth of approximately 200 eV. This optic is Si<400> crystal in log spiral geometry with 0.22 steradian solid angle and sample to optic distance of 144 mm. The reflection efficiency is 2% and focal spot size on the detector is 1000 by 1350 µm. The Vortex-90EX silicon drift detector (Hitachi High-Technologies Science America Inc., Northridge, CA) has 50 mm^2 active area, 300 µm thick Si layer, and energy resolution of approximately 130 eV at the Mn Kα line (5.9 keV).

The components of the hiRX breadboard system including the source with DCC, sample mount, DCC collection optic, and detector are mounted on translation stages (Newport URS100BCC and 443 Series, Newport Corporation, Irvine, CA) which permit precise alignment and provide the mapping capability of the instrument. Stages are controlled with a Newport XPS 8 channel motion controller and the X-Beam is controlled with an XOS PCS500 power control system; both are connected to a PC via Ethernet interface. Detector data collection is done using in-house developed acquisition software based on LabView (National Instruments, Austin, TX).

All hiRX measurements were completed with 50 kV, 1 mA operating conditions with 200 µm step size and 10 second dwell per point. Pu elemental maps were obtained for each of the samples and standards. For the standards, the mapped area was 3x3 mm, while the larger size of the sample deposits necessitated maps as large as 6x6 mm. Data was processed using a custom MATLAB (Version 7.1, The MathWorks, Inc., Natick, MA) script. An integrated intensity for the Pu region of interest (ROI) was generated for each of the maps and a filter was utilized to remove noise, i.e., pixels with <1.5 counts were recorded as 0.

The commercial micro-EDXRF instrument (Eagle III, EDAX Inc., Mahwah, NJ) utilized in this study has an Rh anode, operating at 40 kV, 1 mA maximum. It has a 50 µm spot size at the Cu Kα energy of 8.04 keV, provided by a focusing polycapillary optic. Measurements were conducted at 40 kV and 600 µA.

2.2 Sample preparation

Calibration standards were prepared by spiking various amounts of an aqueous Pu/HNO_3 solution into a SSF matrix. SSF consists of low levels (100 ng/µL) of more than 40 elements present in real spent fuel. Table 1 lists these elements along with the Pu concentration of the six standards. The SSF matrix was prepared by combining several standard solutions (VHG Labs, Manchester, NH) and allowing them to evaporate, then reconstituting in 100 µL of 0.8 M HNO_3. One µL of each standard solution was pipetted onto Kapton film on a 32 mm double open ended sample cup (Chemplex Industries, Palm City, FL) and allowed to dry. A 1.5 µL drop of polystyrene dissolved in toluene was placed on top of the deposit to fix it in place, and once dry, this was covered with 8 µm thick Kapton film (SPEX Sample Prep, Metuchen, NJ).

Spent fuel samples were obtained from Pacific Northwest National Laboratory. The bulk fuel sample contains 13 ng/µL total Pu. Three aliquots of the bulk fuel, 3, 6, and 9 µL, were dried and shipped to Los Alamos National Laboratory as residues. Each was reconstituted in 2 µL of 0.5M HNO_3. The samples were prepared on sample cups in the same manner as the standards, except that 2 µL of each was deposited. Thus, the dried deposits contain 39 (low), 78 (medium), and 117 (high) ng of Pu respectively. Figure 3 is an image of a sample deposit.

3.0 Results and discussion

The Pu elemental maps for three of the six calibration standards are shown in Figure 4. Collection time for each was approximately 45 minutes. The dried deposits were on the order of 1.5 mm in diameter, and high intensity "hot spot" regions are apparent, particularly towards the outer edge of some of the deposits. The presence of such "rings" is expected with dried deposits of this volume. The heterogeneous nature of the sample necessitates the use of the mapping approach applied here to capture all of the Pu signal present, that is, collection of single point spectra cannot be utilized to produce a calibration. A linear correlation coefficient of 0.993 was obtained for the relationship between integrated Pu signal intensity and Pu content in the standards. The LOD for Pu measured with this areal approach is 18 ng (per µL), based on the 50 ng Pu standard and a 10 second dwell time. When an individual spectrum (50 ng/µL standard, 100 s) is used to determine LOD, the result is 375 pg (per 200 µm). This is based on the calculated average Pu density of 0.016 pg/μm^2, which is equivalent to 500 pg per 200 µm excitation area. A 4x factor is applied to account for the difference in signal intensity between the hotspot measurement location and the rest of the sample area, resulting in an estimate of 2 ng material in the X-ray beam.

Figure 5 shows the Pu elemental maps from the spent nuclear fuel samples. These deposits were much larger than the standards, at approximately 3-4 mm in diameter, requiring total measurement times of 115 to 165 minutes. Table 2 shows the results obtained when the Pu calibration was used to determine the mass of Pu in the spent fuel deposits. Precision of 2% RSD for the medium sample was based on removal and replacement in the sample mount between measurements. This RSD therefore includes instrumental and operator uncertainty components. The agreement between the measured and expected values for the high and medium samples is quite good, especially when the numerous steps of sample preparation, including drying and reconstitution, are taken into consideration. The lower degree of agreement for the 39 ng sample may be attributed to a higher percentage of dead space in the mapped area, resulting in an increased level of noise, including that above the 1.5 count threshold. It should also be noted that the low sample contains Pu at only two times the LOD for the mapping approach. It is likely that the accuracy of the Pu determination would be enhanced with the production of more uniform, compact deposits.

The primary advantages of hiRX are selectivity and sensitivity provided by the use of DCCs. This is highlighted in Figure 6, which compares spectra collected from the hotspot of the high spent fuel sample using both the hiRX and conventional micro-EDXRF. A single peak (Pu Lα) is prominent in the hiRX spectrum while the EDXRF spectrum includes signals for many of the matrix elements. The most relevant of these is the U Lα peak at 13.61 keV. As is typical of spent fuel, U is present in this sample at a concentration ratio (U/Pu) of over 100/1. Presence of the large U peak directly next to the much lower intensity Pu peak at 14.28 keV can impact Pu quantitation with EDXRF, but this concern is eliminated with hiRX. Further, the hiRX spectrum has minimal (essentially zero) background, while the EDXRF spectrum has considerable background resulting from the bremsstrhalung excitation, as well as Compton and Rayleigh scatter peaks. While the count rate for the hiRX is considerably lower than for the Eagle III, the peak to background ratio is enhanced. For this sample, P/B for the hiRX is fifteen times that of the Eagle, which has P/B <1. The lack of other lines in the hiRX spectrum is especially notable since the sample has a background radiation level of $>10^6$ disintegrations per minute, with primary components of Cs, Eu, and Am. This demonstrates the capability of hiRX to exclude scatter and radiation background from spent nuclear fuel radioactive elements. With enhanced peak to background ratio and reduced complexity of spectral data, hiRX provides a more effective approach to Pu quantitation.

4.0 Conclusion

The direct detection of low levels of Pu in a spent fuel matrix has been demonstrated along with an initial quantitative analysis using hiRX. Detection limits in the low to sub-ppm range are more than sufficient for determination of Pu at the 1 g/L (1000 ppm) levels expected in spent nuclear fuel dissolver solutions, whose primary matrix component is U. The sensitivity of the hiRX technology offers a new capability to monitor Pu concentrations in reprocessing plant streams. Development of a bench top prototype and low volume liquid sampling system should permit near real time measurements for accurate and precise determination of Pu in spent fuel samples for safeguards applications. In addition, the application of hiRX for quantitative measurements is not limited to plutonium in spent nuclear fuel matrices. This work demonstrates the analytical capabilities of hiRX for a myriad of other applications where high accuracy, precision and rapid analysis is required.

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Table 1. Calibration standards matrix components for synthetic spent fuel (SSF)

Pu in standard (ng/µL)	Elements in SSF matrix (100 ng/µL)							
900	Mn	Ni	Cu	Zn	Ga	Ge	As	Se
687	Rb	Y	Zr	Mo	Ru	Rh	Pd	Ag
474	Cd	In	Sn	Sb	Te	Cs	Ba	La
262	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
50	Ho	Er	Tm	Yb	Lu	Hf	Ta	W
0	Re	Os	Ir	Pt	Au	Bi	U	

Table 2. Results for Pu determination on real spent fuel samples

Fuel sample	Pu (ng) expected	Pu (ng) measured	% Error	%RSD	N
high	117	126	8	-	1
medium	78	80	4	2	3
low	39	49	27	-	1

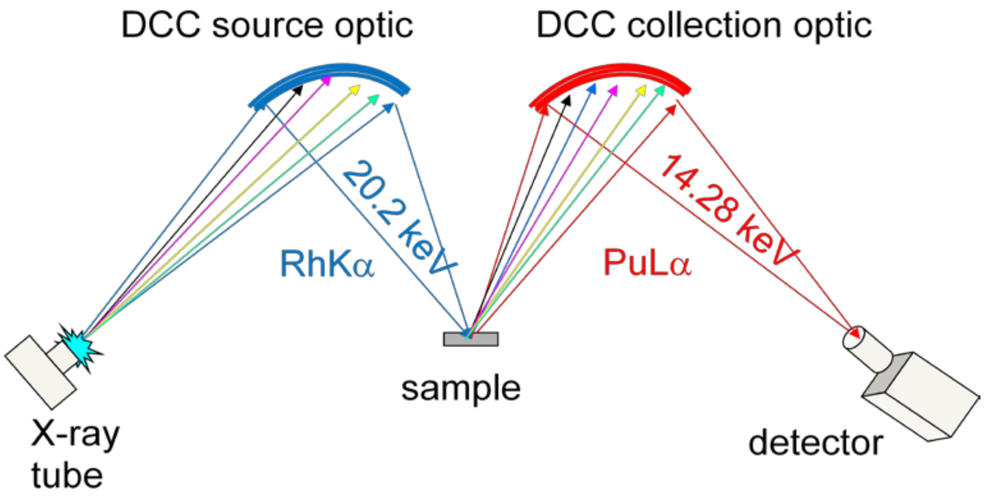

Figure 1. Schematic of hiRX prototype components

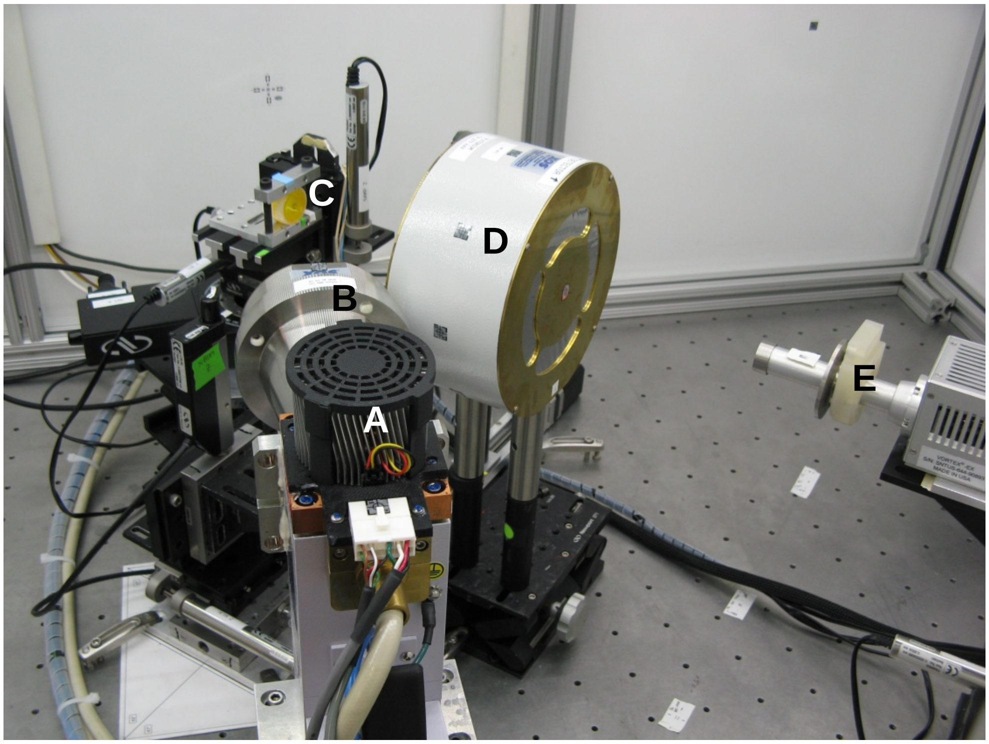

Figure 2. Image of hiRX breadboard set-up (A: X-Beam, B: Excitation DCC, C: Sample mounted on stage, D: Collection DCC, E: SDD)

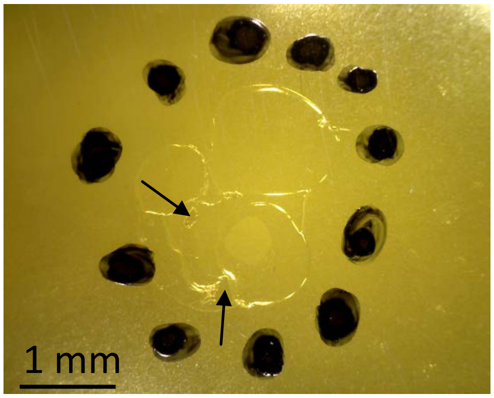

Figure 3. Image of the 2 µL high sample dried residue; black marks are permanent marker used to denote outer limits of deposit location, arrows indicate primary Pu locations

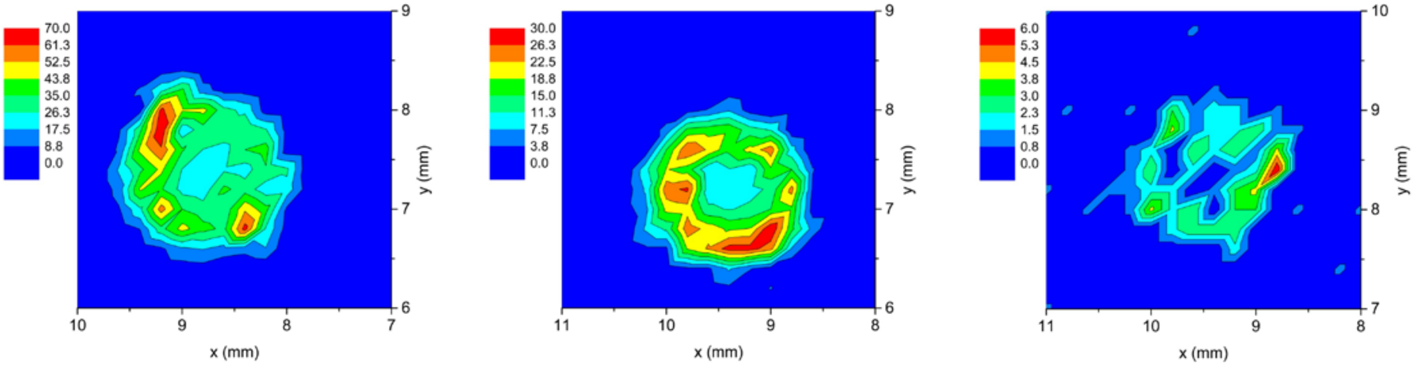

Figure 4. Pu elemental maps for 900, 474, and 50 ng standards in SSF matrix. Maximum counts per 10 s/point dwell time: 70, 30, 6 respectively.

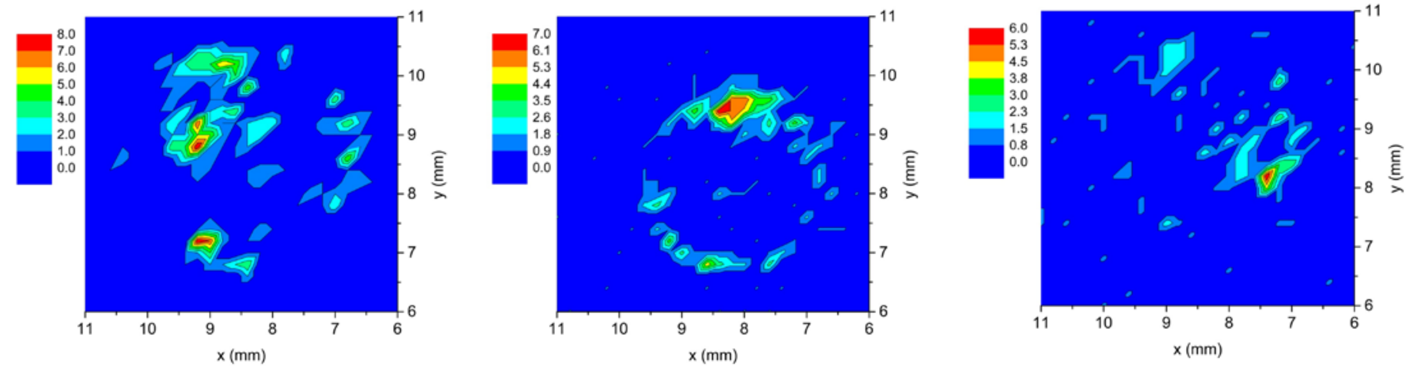

Figure 5. Pu elemental maps for high, medium, and low real spent fuel dried residue samples. Maximum counts per 10 s/point dwell time: 8, 7, 6 respectively.

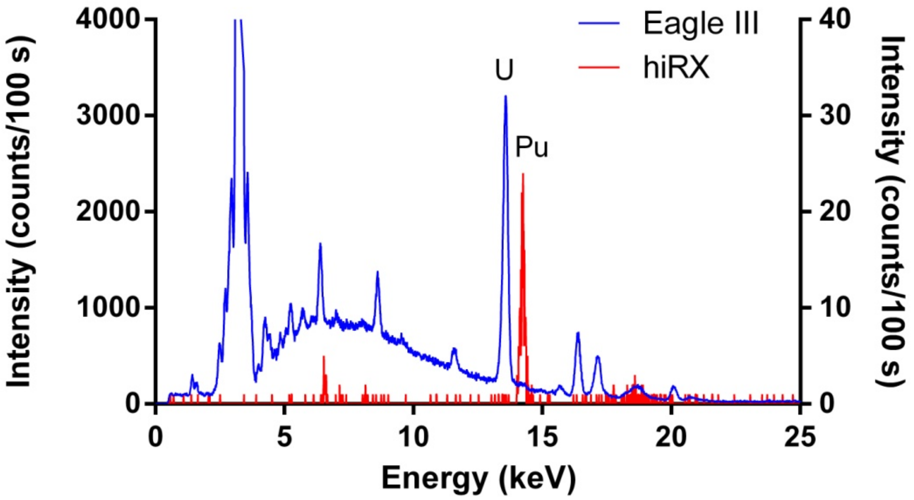

Figure 6. hiRX spectrum (right y-axis) overlaid with Eagle III spectrum (left y-axis) for high spent fuel sample (600 s). Pu peak in the Eagle III spectrum is just about lost in the background. Note the high uranium peak in the Eagle III spectrum next to the Pu peak in the hiRX spectrum.