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ULTRA HIGH ENERGY X-RAY FLUORESCENCE: A NEW PARADIGM FOR ACTINIDE CHARACTERIZATION OF SPENT FUEL

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ABSTRACT

Ultra high energy X-ray fluorescence (UHEXRF) has been demonstrated as a feasible means for characterizing actinide content in spent nuclear fuel. Depleted uranium (dU) samples have been characterized using the 1-ID-C beam line of the Advanced Photon Source (APS) at Argonne National Laboratory. The dU samples included both pressed pellets of UO_2 and dried spots of an aqueous uranium solution. The excitation energy was 117 keV which is above the absorption edge for the U Kα line of 115.591 keV. The XRF emission of the U Kα1 line at 98.428 keV was detected using a liquid nitrogen cooled high purity Ge detector. The samples were measured with and without a 1.3 millimeter Zircaloy shield in front of the samples which is twice the thickness of the normal fuel pin cladding. Although there was a decrease in U Kα XRF signal, sufficient intensity was obtained with as little as 5 live second dwell time resulting in several hundred counts for the smallest samples. The pressed pellets covered a concentration range from 40% to 90% dUO_2 and the dried spots were 10, 5 and 1 micrograms respectively. Elemental maps showed the heterogeneity of the dried spot specimens. This also illustrates the potential of UHEXRF for through the container sub-microgram sensitivity. The significance of this achievement demonstrates the feasibility of direct actinide composition measurement through the nuclear fuel cladding. Such measurements would reduce the uncertainty obtained with passive measurements such as gamma spectroscopy and neutron counting. Although this work was done with a synchrotron, it is conceivable that this measurement could be accomplished in the laboratory using a high power x-ray tube source and appropriate x-ray optics to provide quasi-monochromatic x-rays for excitation. The demonstration of uranium detection through container walls nondestructively, offers new opportunities for applying this technology for on-line through pipe characterization, field analyses of samples and increased reliability for safeguards measurements.

INTRODUCTION

Ultra high energy X-ray Fluorescence (UHEXRF) refers to the energy range above 80 keV for XRF spectrometry. This region has Kα and Kβ characteristic lines for elements with $Z>85$. A unique aspect of this energy range is first of all the simplicity of the spectral lines present. Only the Kα and Kβ lines appear in this energy regime. Therefore there is little chance for spectroscopic overlap and line interferences present. These ultra high energies have the added advantage of a long pathlength in many common materials. This offers the capability of obtaining XRF signals through container walls with sufficient intensity for quantification. Large pathlengths also offer reduced matrix effects and mineralogical effects as well. The deep penetration of the ultra high energies can reduce sampling error by averaging the signal over a larger sample volume. Thus there are a number of advantages for ultra high energy XRF implementation especially within the context of actinide quantification in nuclear spent fuel.

Within nuclear safeguards, the objective is to detect diversion of material in a timely manner. Current methods of analyses include gamma and neutron spectrometries, isotope dilution mass spectrometry, hybrid K-edge as well as inductively coupled plasma mass spectrometry. While the neutron and gamma methods indirectly measure plutonium, the mass spectrometry methods measure Pu directly, however they are time consuming and the hybrid K-edge method has limited sensitivity. Developing a direct, sensitive approach for Pu determination in spent nuclear fuel would offer a new method for safeguarding Pu in the nuclear fuel cycle and enhance the overall security of the plant processes.

This work demonstrates the potential feasibility of using UHEXRF to determine uranium and plutonium in spent nuclear fuel through container walls. This approach offers unique capabilities for both qualitative and quantitative elemental determinations for the nuclear fuel process. In this work we show detection of uranium through Zircaloy shielding twice the normal thickness used in nuclear fuel cladding.

EXPERIMENTAL

The Advanced Photon Source beam line 1-ID-C was used as the source for the excitation in this work. This line was chosen since it is one of the few beam lines that can attain the ultra high energies needed to excite the actinide elements, claiming an energy range of 50-150 keV. The monochromator was set at 117 keV which is above the K absorption edge of uranium at 115.591 keV. The $\Delta E/E$ of the monochromator is $\sim 1.4 \times 10^{-4}$. Incident flux measurements gave 7×10^9 photons per second. More details on the design and performance of the beam line used in this experiment are readily available [1].

The samples were doubly contained in a custom designed sample holder to minimize any radioactive contamination of the experimental hutch. The samples consisted of pressed pellets of depleted uranium oxide (dUO_2) with stearic acid as a binder, dried spots of dU aqueous solutions, and dU metal. The samples and the masses of dU present are shown in Table 1. The experimental arrangement is shown in Figure 1 which is a picture of the sample holder on the

Figure 1. Picture of experimental setup showing the muti-stage assembly for positioning of the sample holder and the HPGe detector. The monochromatic synchrotron beam enters from the right, shown by the arrow inset.

multi-stage positioning assembly and the high purity germanium detector (HPGe).

Table 1. List of samples of depleted uranium analyzed using UHEXRF.

sample	**dUO_2**
Pellet 1	91%
Pellet 2	69%
Pellet 3	41%
Pellet 4	0%
Dried spot 1	1 μg
Dried spot 2	5 μg
Dried spot 3	10 μg

Both single point spectra and elemental mapping were done on the specimens using the beam line control software for positioning the samples.

RESULTS

The objective of this experimental work was to demonstrate the feasibility of obtaining XRF signals through container walls, specifically Zircaloy 4 cladding of nuclear fuel rods. This material has over 95% zirconium and around 1.5 wt% tin and typically around 600 micrometers thick. The Zircaloy used in these experiments was around 1.3 mm thick, twice the nominal nuclear fuel cladding thickness. Figure 2 shows several spectra of interest: a) the bare dUO_2 pellet (black), b) the pellet with the Zircaloy shielding (red) and c) the pellet with 4 mm aluminum 6061 alloy shielding (blue). The $K\alpha 1$, $K\alpha 2$, $K\beta 1$ and $K\beta 2$ peaks of uranium are clearly visible at 98.428, 94.648, 111.289 and 114.549 keV. We will focus on just the $K\alpha 1$ line at 98.428 keV. The $K\alpha 1$ line intensity changes with the different shielding: from over 200,000 counts with no shielding, to around 150,000 counts with the 4 mm aluminum and just under 50,000 counts for the 1.3 mm Zircaloy shielding. The Zircaloy reduces the unshielded uranium signal by 76%. While this is significant, the $K\alpha 1$ signal is visible and quite strong for the 40% dU pellet using a count time of only 100 live seconds for these spectra. There are interesting features at lower energies attributed to the zirconium $K\alpha$ and $K\beta$ lines (red peaks around 15.7 and 17.7 keV) while the U $L\alpha$ lines around 13.61 keV disappear due to absorption by the Zircaloy shielding. The aluminum $K\alpha$ line is also visible around 1.487 keV. The feature between 80 and 85 keV is the Compton scatter. This scatter is due to the interaction of the excitation beam with the sample.

Figure 3. shows the comparison of the measured spectrum with the Zircaloy shielding (black) and the model spectrum created using the equations for fluorescence intensity [2] and the equations for scattered intensity [3], both for bulk materials. Fluorescence cascade effects were included to provide the correct intensity for the U L lines. These calculations rely heavily on an

accurate set of atomic parameters, which were taken from Elam [4]. The agreement is quite good matching both the peak positions, relative intensities, and the Compton peak. To reproduce the energy dependence of the Compton scatter, a doubly-differential cross section was computed using the approximation of Brusa [5]. Further refinement will allow reliable and accurate predictions of the capabilities of UHEXRF for a wide variety of applications using both synchrotron and X-ray tube sources. This predictive capability permits assessment of the suitability for a particular application in advance of measurements or specimen preparation and aids in the design of protocols. Reliable modeling will also assess the feasibility of laboratory measurements using the technique and will be a valuable resource during the design of laboratory based instrumentation.

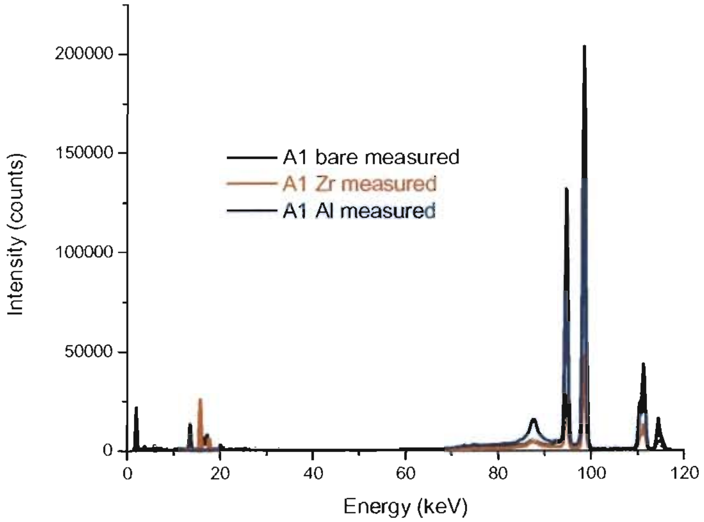

Figure 2. Spectra of dUO_2 sample with various shielding in place, (black) no shielding, (blue) 4 mm of 6061 aluminum alloy and (red) Zircaloy 4 shielding 1.3 mm thick.

A number of elemental maps were collected for both pellets and dried spot residues. The dried spots showed interesting features particularly when comparing the maximum intensities with different shielding and with different excitation spot sizes. As might be expected the maximum intensity decreases with decreasing excitation spot size. We observe a reduction from around 9000 counts for 1 mm excitation beam to around 1000 counts for a 25 micrometer beam. Similar signal reductions are observed for shielding as well. Figure 4 shows the map of the 1 microgram dried spot deposit obtained with the smallest excitation spot size and highest spatial resolution of around 18 micrometers.

Clearly the dried spot residue is not a uniform deposit. In addition, we can infer that the sensitivity, even with the 1.3 mm Zircaloy shielding, is well below 1 microgram. Elemental maps with larger excitation spot sizes produced circular images with little structure. Only the excitation spot sizes less than 50 micrometers generated maps showing structure of the deposit. Since the 1 microgram of dU is spread over the entire area, we can surmise that the detection limit is most likely in the nanogram regime. Further measurements will confirm the detection limit.

The ultimate goal of this work is to quantify the Pu content within containers. We obtained elemental maps of all the dried spots, added the intensities of all the pixels and plotted the measured intensity with the known mass of dU in the deposit. We obtained a linear correlation with a correlation coefficient of 0.999. This was expected. The more difficult quantitation will be through the Zircaloy shielding. The results of the second set of measurements with the Zircaloy shielding are shown in Figure 5. The correlation coefficient is a respectable 0.902. The scatter of the points is most likely indicative of the variations in the Zircaloy shielding thickness.

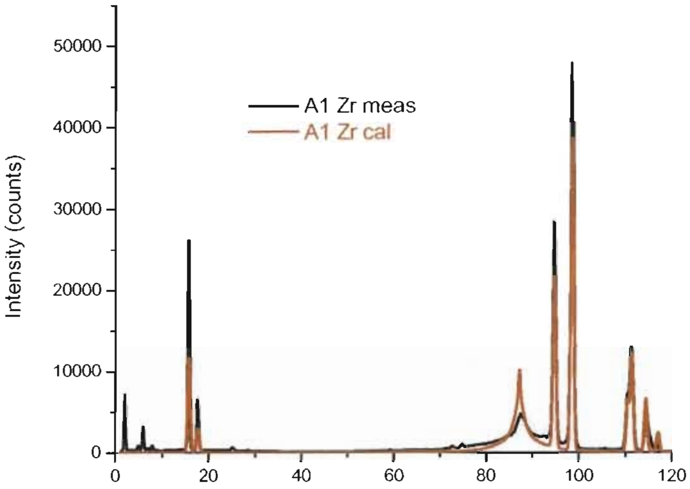

Figure 3. Comparison of measured dUO_2 spectrum (black) with calculated model spectrum (red) with 1.3 mm Zircaloy shielding.

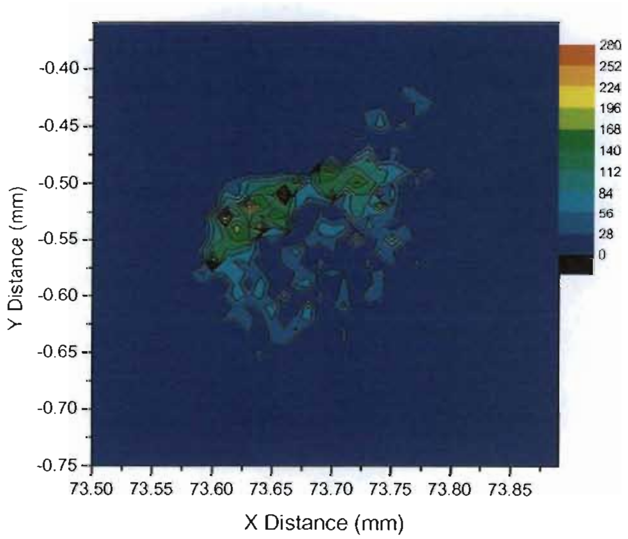

Figure 4. Elemental map of 1 microgram deposit of depleted uranium solution through the Zircaloy shielding. Excitation beam was about 18 micrometers, dried spot deposit is around 200 x 150 micrometers.

Additional measurements will be done to identify the source of the error and work towards reducing the error. The modeling calculations indicate that each millimeter of Zircaloy attenuates the U Kα1 line intensity by about a factor of two.

CONCLUSION

The UHEXRF of uranium has been demonstrated for both pressed pellets and dried spot residues. The primary goal of detecting uranium through Zircaloy shielding has been achieved with twice the nominal thickness of nuclear fuel cladding. The sensitivity is most likely in the nanogram regime. The elemental mapping of the 1 microgram deposit shows both the sensitivity of this approach as well as the potential for future applications. Although the uranium concentration in nuclear fuel is the major component (>95%) the sensitivity exhibited in these experiments should be applicable to other actinides such as plutonium and curium. Thus the nanogram sensitivity for Pu will provide both a direct measure as well as a more accurate Pu assay of spent nuclear fuel, through the cladding walls. This feasibility demonstration lays the foundation for development of a laboratory based instrument. Such an instrument will enable a myriad of measurements not currently achievable with conventional instrumentation. Quantification through container walls will provide the nuclear safeguards community with a new tool for insuring the accountability of plutonium throughout the nuclear fuel process. Ultimately this technology could be deployed for in-line measurements in reprocessing plants, as well as person-portable instrumentation. Such instrumentation would provide new capabilities for the nuclear safeguards community.

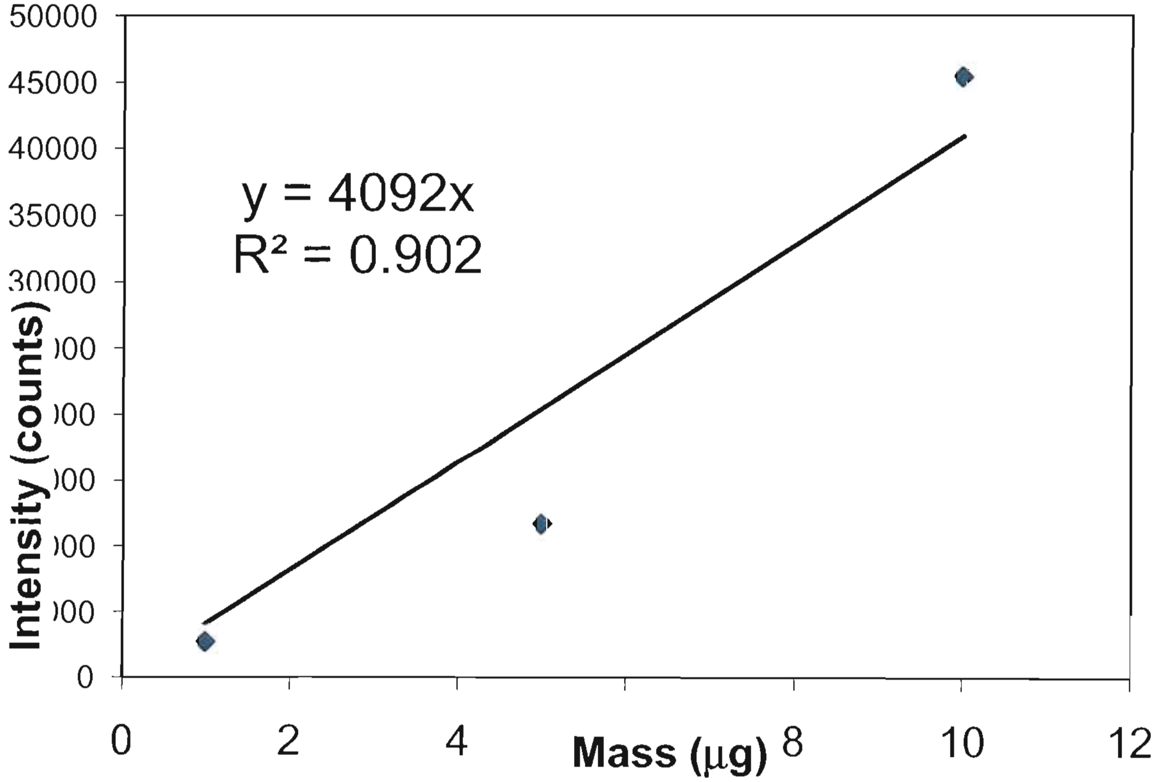

Figure 5. Linear correlation plot of deposit mass with measured Kα1 uranium XRF signal through 1.3 mm of Zircaloy shielding.

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