

Feasibility of Uranium Detection Through Container Walls Using Ultrahigh-Energy X-ray Fluorescence

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Introduction

The quantitative analysis of uranium in spent nuclear fuel is at best a challenging task, even for the specialized laboratories designed to handle such materials. The reason this measurement is important is the need to account for all nuclear materials under the control of international safeguards agreements. Although there are existing methods employed for this measurement, efforts to improve the accuracy of nuclear material accountability are of continuing interest. A new approach for making such measurements involves ultrahigh-energy X-ray fluorescence (UHEXRF). UHEXRF is defined in this application as XRF above 80 keV. Although there have been previous efforts exploring the use of high-energy XRF, almost all these have dealt with XRF below 80 keV [1]. The appeal of using UHEXRF for quantitative analysis of uranium in spent nuclear fuel is primarily focused on the very penetrating X rays of the fluorescent radiation [2]. In the case of uranium, the $K\alpha$ line is at 98.428 keV with an absorption edge energy of 115.591 keV. At these energies, both the exciting and fluorescent radiations can penetrate significant shielding. In this particular case, the Zircaloy (zirconium metal alloy) cladding of nuclear fuel rods provides a significant barrier to most spectroscopic elemental analysis methods. For excitation energies just above the uranium K edge, the calculated penetration depth is on the order of several hundred micrometers into a UO_2 nuclear fuel pellet after penetrating a 600 μm thick Zircaloy cladding wall. The ability to penetrate the cladding wall and the pellet offers an opportunity to measure the uranium nondestructively through the container walls with typical XRF accuracy and precision. The ability to measure the U content directly through the container wall offers a simple analytical protocol because (a) there would be no sample preparation, (b) the analyte is measured directly, and (c) the matrix and mineralogical effects are reduced. In addition, at this high energy, there are few if any line overlaps, which simplifies the spectrometry measurements. By using a restricted or focused X-ray beam for excitation, spatially resolved elemental distributions within the fuel rod can be obtained, whether it is fresh nuclear fuel or spent nuclear fuel. This article presents the feasibility of employing UHEXRF for qualitative and quantitative elemental analysis of uranium in nuclear fuel surrogates and demonstrates nondestructive, through-container-wall analyses.

Materials and Methods

Calibration. The samples used in this study were created in the laboratory using depleted uranium solutions from

a stock 10,000 $\mu\text{g/mL}$ commercial standard (High Purity Standards, Charleston, SC). The calibration samples were prepared by depositing known concentrations with a pipet, typically 1 μL , onto a Kapton film substrate. Two types of samples were prepared: one was an acidified aqueous-based matrix with known uranium concentrations, whereas in the second set the uranium solution was spiked into a synthetic spent fuel (SSF) matrix. The SSF matrix is a mixture of nearly 50 elements typically found in spent nuclear fuel, each with a mass of 100 ng. The deposited uranium ranged from 10,000 ng to 1 ng in the dried spot residue of the 1 μL drop. These samples were used to generate a calibration plot for the uranium intensity versus the known U mass. In each case the deposit was mapped by sequentially moving the probe beam over an area larger than the visible deposit. This approach was used to ensure the entire deposit was measured. The samples were doubly sealed in Kapton film to ensure no possible leaks of radioactive material.

Simulated fuel rod. A mock fuel rod sample was fabricated within an 8 mm diameter Zircaloy alloy tube, 25 mm long, with a wall thickness of 600 μm . Mock fuel pellets were made by mixing UO_2 and ThO_2 in known masses to generate several different UO_2 compositions within the mock fuel pellets. In this instance the uranium is a surrogate for plutonium, whereas the thorium is a surrogate for the typical uranium fuel matrix. The pellets were mixed with stearic acid as a binder and pressed into 8 mm diameter pellets, 2 mm thick. The pellets were loaded into the Zircaloy tube and sealed with silicone glue, then encapsulated with Kapton film.

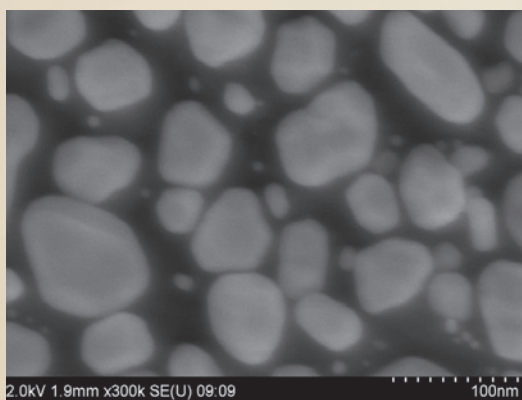
Excitation of U X rays. The measurements were done on the 6-ID-D beam line of the Advanced Photon Source at Argonne National Laboratory. This beam line can produce monochromatic excitation from 50 keV to 150 keV with a $\Delta E/E = 1.4 \times 10^{-4}$ and a photon flux of 1×10^{11} photons per second at 130 keV. In this work an excitation energy of ~ 117 keV was used to effectively excite uranium above the K absorption edge of 115.591 keV. The experimental setup is shown in Figure 1. The samples were mounted on multiple axis stages to accurately position the sample for single point spectra, line scans, and elemental maps.

The beam size was controlled by programmable slits. Elemental maps were acquired by stepping the beam over a selected area and recording a full spectrum at each point. The dried spot deposits were collected using a 500 μm beam spot size with a 500 μm step size in both x and y directions with a 5-second dwell time. The mock fuel rod was mapped using a 100 μm beam spot and 100 μm steps in x and y with a 3 second

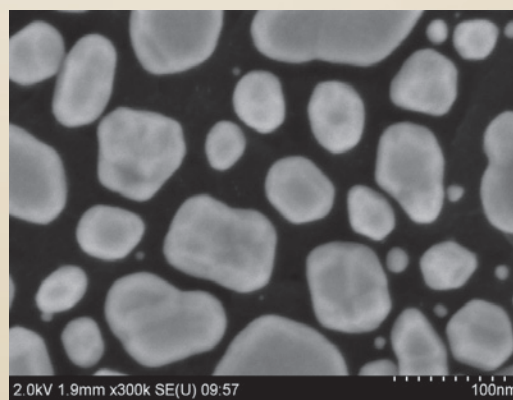
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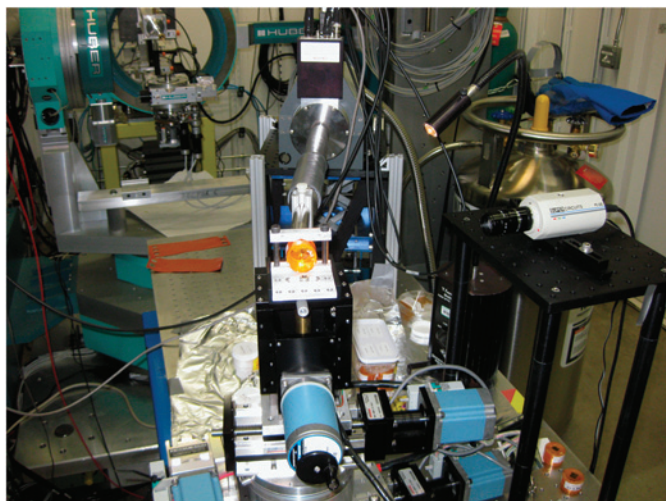


Figure 1: End-on view of the UHEXRF experimental setup at APS 6-ID-D beam line, which shows the sample mounted on multiple translation stages for positioning of the sample, a camera to observe sample location, detector, and in the upper-left background the entrance of the synchrotron beam.

dwel time. The programmable slits allow selectable spot sizes down to 25 μm .

Spectrum acquisition and analysis. A high-purity germanium detector (Canberra model GL0110S) with a resolution of around 1 keV, equipped with digital signal processor and acquisition interface module electronics, was used to collect the emitted X-ray fluorescence. In-house APS (EPICS) software was used to control the data acquisition. The data was processed with user-developed Matlab scripts to calibrate each spectrum, fit the peaks, remove background, and generate net intensities used for creating elemental maps. Of particular concern was the overlap from the Compton scatter peak, which was centered ~ 87 keV. The wings of the Compton peak extended for 1–2 keV on either side of the centroid and thus must be removed before each spectrum is processed. **Figure 2** shows the measured spectrum and the background. This full spectrum illustrates the separation of the typical low-energy spectra normally used to characterize U L-series at 13.6 keV compared with the UHEXRF U $K\alpha_1$ line at ~ 98 keV used in this work. The Compton scatter peak along with the tails is visible at ~ 87 keV.

Results

Uranium detection. **Figure 3** shows an overlay of a bare uranium spectrum (solid line) with a spectrum acquired with 1.3 mm of Zircaloy shielding (dashed line) in front of the sample. The Zircaloy shielding decreases the uranium signal by almost 80%, and there is a significant increase in Compton scatter. However, the uranium peaks are still clearly visible, even with twice the nominal thickness of conventional nuclear fuel rod cladding. Thus the detection of uranium in typical nuclear fuel rods is quite feasible.

Calibration measurements. An example of one of the uranium maps of the dried residue deposits is shown in **Figure 4**. The total uranium mass in the deposit is around 99 ng. The elemental map indicates the residue is not uniform with several hot spots. However by summing the region of interest for the uranium peak over all the pixels in the elemental map, a

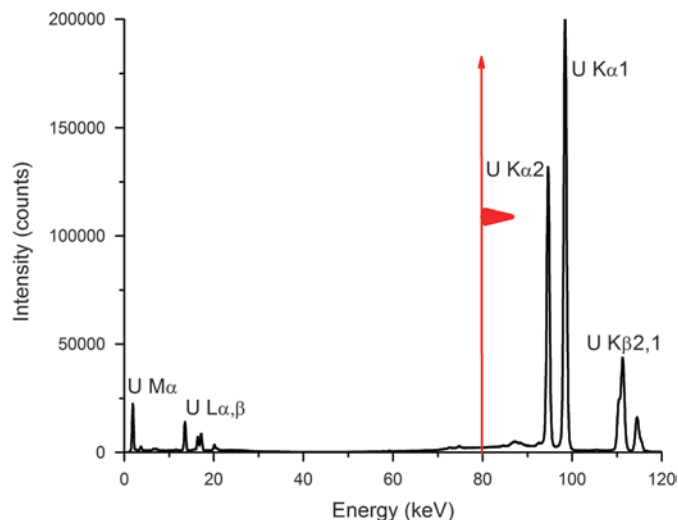


Figure 2: Full UHEXRF spectrum of an aqueous uranium dried spot residue showing both low- and high-energy U lines, which have been labeled. The red line designates the UHEXRF cutoff energy of 80 keV.

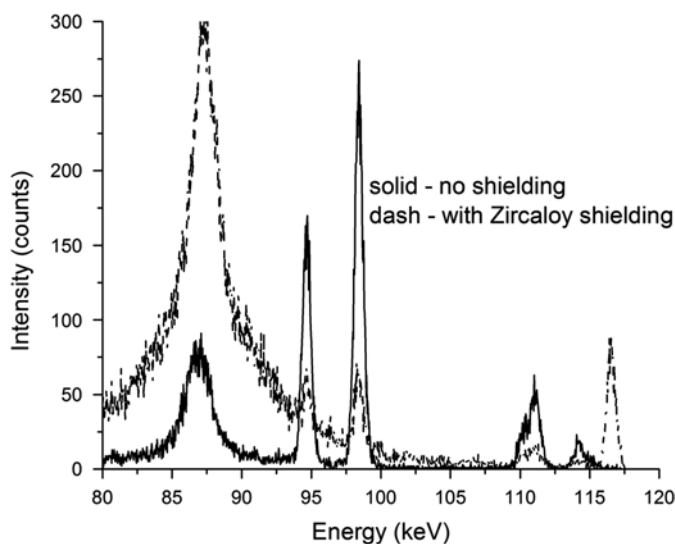


Figure 3: UHEXRF spectrum overlay of uranium for a bare sample (solid line) and a 1.3 mm thick Zircaloy shielded sample (dashed line). This thickness is twice the normal thickness of nuclear fuel rod cladding. The U signal decreases by almost 80% with the Zircaloy shielding, however the U signal is still detected.

summed intensity count rate was obtained for each calibration sample. Even though a relatively small volume deposit was used, only 1 μL , the deposit covers a rather large area of almost 3 mm in diameter.

The results of the calibration measurements on both the aqueous and SSF spiked dried residues are shown in **Figure 5**. This figure is a plot of the intensity (counts/sec) for each known mass of uranium in the deposit. Although the aqueous and SSF matrices are quite different, the correlation coefficient for the log-log plot is ~ 0.972 . This demonstrates the quantitative analysis capability of UHEXRF within the context of the matrix effects.

X-ray maps of the mock fuel rod. These results have demonstrated the qualitative and quantitative capabilities of UHEXRF. However, the ability to actually characterize a

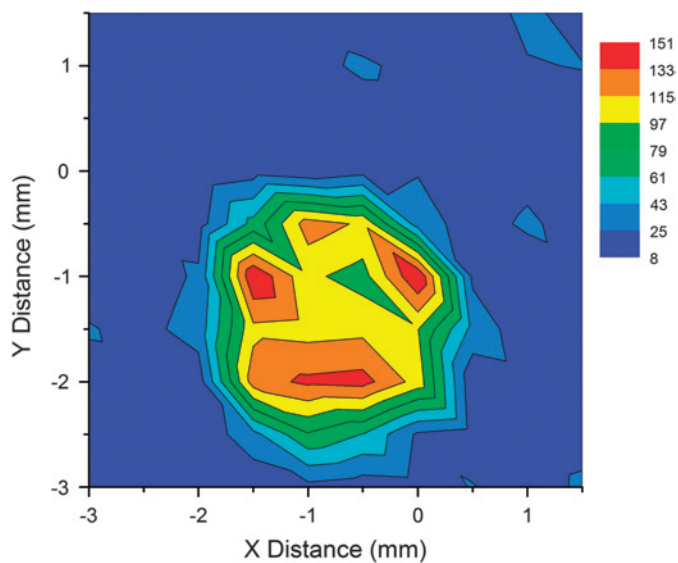


Figure 4: Uranium elemental intensity map of a dried spot deposit of a 1 μ L synthetic spent fuel matrix solution containing 99 ng U.

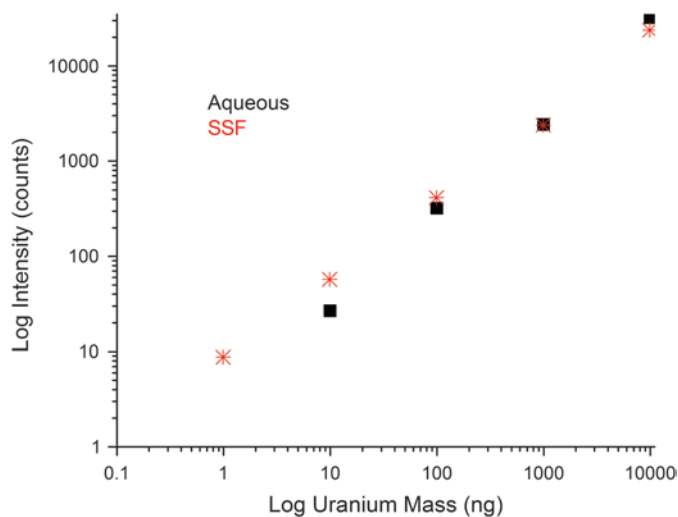


Figure 5: Calibration log-log plot of known uranium mass with measured integrated uranium intensity from elemental maps of dried spot deposits with different matrices, which includes aqueous and synthetic spent fuel. Correlation coefficient for both matrices is 0.974.

nuclear fuel rod is demonstrated by scanning the mock fuel rod prepared with 8 mock fuel pellets. A picture of the mock fuel rod is shown in Figure 6. The mock fuel rod is shown with the Kapton film used to encapsulate all samples containing radioactive materials to ensure no contamination of the experimental facilities is possible. The red line on the picture indicates one of the successive line scans that were done to create elemental maps of the thorium and uranium inside the Zircaloy tube. In this case the Zircaloy is a nominal 600 μ m thick, which is typical of nuclear fuel rods. Figure 7 shows an illustration of the mock fuel rod and the mock fuel pellets inside the Zircaloy tube. The numbers on the uranium doped pellets are the concentration of the uranium oxide mixed with the thorium oxide. The thorium (upper) and uranium (lower) elemental maps obtained through the Zircaloy cladding are shown below the cartoon. The elemental images provide

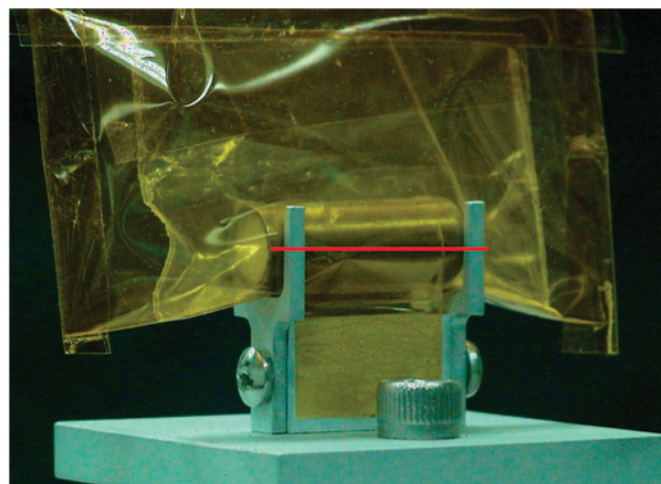


Figure 6: Picture of mock fuel rodlet covered in Kapton film, which contains 8 mock fuel pellets. The red line indicates one line scan of multiple line scans used to acquire elemental maps shown in Figure 7 for the 25mm long by 8mm diameter rodlet.

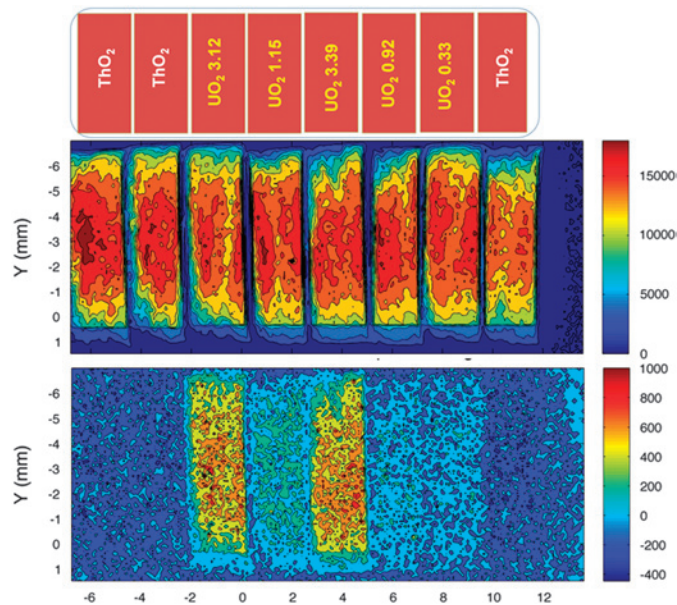


Figure 7: Cartoon of mock fuel pellets within mock fuel rod (top) with the values of the uranium oxide composition indicated in wt%. The elemental maps of the thorium matrix (middle) and uranium analyte (bottom) distribution acquired through the 600 μ m thick Zircaloy wall. The X-ray spot size was 100 μ m, and step size was 100 μ m.

several levels of information besides the spatial distribution of thorium and uranium. Fundamentally, the elemental maps indicate the heterogeneity of the matrix in these pellets. In real nuclear fuel the spatial distribution of the fuel element matrix should be uniform. The elemental maps show the shape of the pellets as well as spacing between the pellets. The elemental concentration of the uranium, which is the plutonium surrogate, demonstrates detection well below the nominal 1 wt% of Pu in real spent nuclear fuel.

Discussion

The results presented offer a new approach for elemental determination of spent nuclear fuel in a nondestructive manner

with no sample preparation. The calibration results indicate a detection limit of around 1 ng with Zircaloy shielding and sub-nanogram levels without the shielding. The advantage of this direct elemental analysis approach is that it avoids the typical radiometric techniques, which must use significant modeling of the measurement process to produce actual quantitative values. Such dependence on modeling corrections often leads to appreciable errors resulting in accuracy issues for values that require the utmost in accuracy. UHEXRF offers a potentially more accurate direct quantitative analysis of nuclear fuel. The results with the SSF matrix indicate that even with nearly 50 elements present, there are no apparent elemental interferences with the target elements of uranium or plutonium. The elemental maps of the mock fuel rod provide insights into the potential that UHEXRF offers for characterizing spent nuclear fuel. The significant aspect of this feasibility demonstration is that UHEXRF can be applied to quantification of plutonium in spent nuclear fuel. The Pu $K\alpha$ line is ~ 103 keV. The proximity of the Pu line to the U $K\alpha_1$ line means the quantification of Pu should be straightforward, providing a new analytical method for analyzing nuclear spent fuel for both the matrix component as well as the key element for safeguards concerns. The elemental maps of the mock fuel rod offer the following information on the nuclear fuel pellets, through Zircaloy cladding: nondestructive direct elemental measurements, uranium and thorium concentration distributions, nuclear fuel pellet homogeneity, pellet geometry, pellet orientation, and gaps between pellets. These are measurements that are not currently available for either fresh or spent nuclear fuel through the Zircaloy cladding. Although this demonstration used synchrotron radiation, it is feasible to construct a laboratory-based UHEXRF instrument with similar analytical capabilities. This statement is based on work conducted by X-ray Optical Systems [3]. They have demonstrated construction of a UHE doubly curved crystal (DCC) optic, which would provide quasi-monochromatic radiation for excitation using a high-energy X-ray tube (~ 250 keV). A second DCC collection optic could be used to create a monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) instrument with high sensitivity and selectivity similar to the low-energy MWDXRF instrument we have built [4]. Although this instrument would not have the photon flux of the synchrotron, it would be capable of

through-the-container-wall excitation and detection of the target analyte elements even with comparable signal loss through the Zircaloy cladding.

Conclusion

In this feasibility study ultrahigh-energy X-ray fluorescence (UHEXRF) nondestructively characterized both model fresh and model spent nuclear fuel through the Zircaloy cladding walls. This approach offers distinct advantages for quantitative elemental analysis of nuclear fuel rods, including sub-nanogram sensitivity, nondestructive through-container-wall measurement capability, and direct interrogation of both fresh and spent nuclear fuel. Although this demonstration used synchrotron radiation, it is feasible to construct a laboratory-based UHEXRF instrument with similar analytical capabilities.

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