QUANTITATIVE WDS ANALYSIS TO DETERMINE PLUTONIUM HOMOGENEITY IN CANDU MIXED-OXIDE FUEL

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ABSTRACT

As part of AECL's mixed-oxide (MOX) fuel development program, a quantitative X-ray wavelength dispersive spectrometric (WDS) analysis was conducted to determine plutonium homogeneity in as-fabricated MOX fuel, using a shielded analytical scanning electron microscope. This paper describes the technique and some results of the analysis.

The as-fabricated fuel exhibited a duplex microstructure: a matrix with randomly distributed plutonium-rich particles. The particle size ranged from 10 to 30 µm. To conduct the WDS analysis, PuO_2 and UO_2 standards were used; plutonium M_β and uranium M_α lines were monitored. Point analysis with a 2-µm interval was conducted diametrally across the particles to obtain uranium and plutonium distribution profiles. The profiles all exhibited a similar shape; a compositional transition band was observed around each particle, indicating the occurrence of plutonium and uranium interdiffusion. Uncertainty and consistency of the determinations were examined, and the results are satisfactory.

1. INTRODUCTION

$(U,Pu)O_2$-type mixed-oxide (MOX) fuel, manufactured by mechanical blending, has a duplex microstructure: a uranium-rich matrix mixed with dispersed plutonium-rich particles. Compared to natural UO_2, the fuel exhibits some unique irradiation features, which are directly associated with the compositional and microstructural inhomogeneity. For example, local burnup, temperature, pore density and fission-product (e.g., Xe and Cs) concentrations are higher in the particles than in the matrix [1-4]. This can have a significant effect on fuel irradiation performance. For optimum fuel performance, the extent of plutonium homogeneity in the as-fabricated fuel should be as high as possible. To assist in achieving this goal, a method to quantitatively determine plutonium homogeneity in the fuel is required. Ideally, the same method should also be applied during post-irradiation examination of MOX fuel to determine any redistribution of plutonium.

As part of the CANDU® MOX fuel development program, a method using alpha

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autoradiography combined with image analysis is being applied to determine plutonium homogeneity in the fuel. This method provides a quick and practical means of quantitatively determining the extent of plutonium homogeneity of MOX fuel in a production environment. To properly benchmark and qualify the method, a quantitative X-ray dispersive spectrometric (WDS) analysis was also conducted. The analysis used a WDS spectrometer attached to the shielded JEOL-840 scanning electron microscope (SEM) at the Chalk River Laboratories (CRL).

This paper describes the technique and results of the WDS analysis; uncertainty and consistency of the determinations are also discussed.

2. SAMPLE PREPARATION

Two samples were cross-sectioned from a MOX fuel pellet fabricated by the Recycle Fuel and Fabrication Lab (RFFL) in CRL. The pellet consists of 99.65 wt % UO_2, 0.30 wt % PuO_2 and 0.05 wt % Dy_2O_3; density of the pellet is 10.63 g/cm^3. One sample was mechanically polished and the other was polished and etched. The etchant was a mixture of H_2SO_4 and H_2O_2 (1:9 in volume). The samples were carbon coated to improve electrical conductivity before examination in the SEM.

3. RESULTS

3.1 Microstructure

In the etched condition, the particles were observed to be surrounded by an annular light band (Figure 1a). The band was ~8 to 10 µm in width; fine grains (~1 µm) were observed within the band. The particles are distributed randomly in the matrix, their size ranging from 10 to 30 µm. Pores and cracks were observed inside the particles and along the interphase boundaries. Some porous regions (Figure 1a) were observed in the matrix which had a grain size of 5 to 10 µm.

Because of the significant difference in composition, good contrast between the particle and matrix was obtained using the back-scattered electron image (BSI) mode. The particles appeared lighter than the matrix (Figure 1b) because they contain more plutonium, which has a higher atomic number (94) than does uranium (92) .

Initially, the band was not readily observable in the polished sample, making it difficult to identify the particles. However, after careful examination, the particles were discernible in both the secondary electron image (SEI) and BSI modes (Figures 1c and 1d). This made it practical to use the polished sample for composition analysis and avoid any measurement error that might be induced by etching.

3.2 The WDS Quantitative Analysis

The major M-family of X-ray lines produced by elements plutonium and uranium have higher intensity and less overlap than other lines do [3,4], and therefore, were selected for the analysis. The lines fall in a wavelength range of 3.8 to 4.0 Å, which is covered by the spectrometer's PET diffraction crystal (1 Å = 0.1 nm.).

3.2.1 Spectrometer Calibration

The spectrometer was calibrated using a metal-uranium standard provided by SPI Supplies. Three characteristic uranium X-ray lines (M_α, M_β and M_γ) were detected (Figure 2). The wavelength (λ) of the lines is determined by

$$\lambda = dL / Rn \tag{1}$$

where n is the order of diffraction; R is the radius of Roland Circle of the spectrometer (140 mm); d is the lattice spacing of the crystal PET (4.371 Å); and L is the measured distance of each X-ray line from the detector.

Standard wavelength, relative intensity, energy and PET detection distance of these lines are listed in Table 1 [5]. Because the M_α line is strong, it was used to initialize the spectrometer.

It should be noted that the M_β line appeared stronger than the M_α line in the spectrum (Figure 2), which seems not to be consistent with the reported intensity ratio ($M_\beta : M_\alpha = 60 : 100$) listed in Table 1. The reason for this is the usage of an argon-filled proportional counter in the spectrometer [6]. Argon has an absorption edge located at L = 124.9 mm (Figure 2) and significantly reduces the intensity of the spectrum on the right side of the edge, causing the M_α line to appear weaker than would otherwise be expected.

3.2.2 Determination of Plutonium Homogeneity

As seen in Figure 2, other lines do not interfere with the uranium M_α line , and the extent of the interference between the plutonium M_β (dotted line) and the uranium M_γ lines is less than the interference between the plutonium M_α (dotted line) and the uranium M_β lines. Therefore, the intensity of the plutonium M_β and uranium M_α lines was monitored to determine the plutonium and uranium concentration in the sample. An accelerating voltage of 25 kV and a beam current of 50 nA were applied.

Twenty-five spots were analyzed along a line crossing the diameter of the particle shown in Figure 1c; the particle size was ~20 µm. The interval between two neighbouring spots was 2 µm, and every spot was analyzed once.

The uranium and plutonium concentrations (c_i) of each local spot can be calculated by [6]

$$c_i = c_s (I_i/I_s)(ZAF)_i \tag{2}$$

where I_i and I_s are X-ray intensities of the sample and the standards respectively; c_s is the known concentration of the element in the standard. In equation (2), Z is a factor associated with difference in the mean atomic number between sample and standard; A is related to internal absorption of the X-ray generated in the sample; F is a correction factor for X-rays generated in the sample by other X-rays. Sintered PuO_2 and UO_2 pellets prepared by the RFFL were used as the standards; it is assumed that the density of the standards is similar to the density of the pellet and that the standards are stoichiometric. The calculated ZAF factors for both uranium and plutonium are very close to 1, which simplifies the calculation and reduces measurement uncertainty.

The measured uranium and plutonium concentration profiles are shown in Figure 3. They are bell-shaped and symmetrical with respect to the particle centre. The average concentrations of uranium in the matrix and plutonium in the central region of the particle are 87.6 wt % and 87.1 wt % respectively. The stoichiometric weight percentages of Pu in PuO_2 and U in UO_2 are 88.4 and 88.2 respectively, indicating that the matrix is essentially UO_2 and the particle PuO_2. There is a compositional transition band about 10 µm wide around each particle, indicating that interdiffusion of uranium and plutonium has occurred in this region. As seen in Figures 1a and 1b, this region is easily etched, making it identifiable as a light annular band in the etched sample.

Figures 4a and 4b are uranium and plutonium X-ray maps of the particle and matrix respectively, confirming that plutonium is concentrated in the particle and uranium is uniformly distributed in the matrix.

Determination of plutonium and uranium distributions of particles ranging in size from 15 to 30 µm exhibited similar concentration profiles.

4. DISCUSSION

4.1 Measurement Uncertainty

In alpha autoradiography, the plutonium-rich particles appear dark and the matrix light. The transition band around the particles also has a certain contrast with respect to the matrix, depending on the local composition. The task of an image analyzer is to convert the contrast into gray-levels. If a relationship between the gray-level and composition can be established, plutonium and uranium distributions can be determined directly by image analysis, making it practical and economical for a MOX pellet-fabrication facility. In the previous section, plutonium and uranium distribution profiles across a particle were determined. The highest plutonium and uranium concentration measurements can be correlated with the darkest and lightest gray-levels identified by the image analyzer to establish a calibration procedure.

To ensure that the calibration can be qualified, uncertainty of the WDS measurements must be estimated. The uncertainty range determines the concentration interval corresponding to each step between two neighbouring gray-levels. Assuming the uncertainty range is ± W (wt %), the number of distinguishable gray-levels (N) can be determined by

$$N = 88\ (\text{wt }\%)\ /\ 2W\ (\text{wt }\%) \tag{3}$$

Because X-ray production is statistical in nature, a number of independent measurements should be taken and averaged to determine local composition. Statistically, the variation range ($W_{1-\alpha}$) of each determination at 1 - α degree of confidence level can be estimated by [6]

$$W_{1-\alpha} = \pm\,(t_{n-1}^{1-\alpha})\ S(\bar{x}) \tag{4}$$

where n is the number of measurements; $t_{n-1}^{1-\alpha}$ is the Student t value for a 1-α confidence level and for n - 1 degrees of freedom; $S(\bar{x})$ is the standard deviation of the measurement average, which is determined by

$$S(\bar{x}) = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)n}} \tag{5}$$

In Equation (5), x_i is the value of each individual measurement and $\bar{x}$ is the average of all the measurements respectively. The calculated values of $S(\bar{x})$ and $W_{1-\alpha}$ at a 90% level of confidence (α = 0.1) for the plutonium and uranium concentration measurements in the particle and the matrix are listed in Table 2. The table shows that the variation range (W_{90}) for uranium and plutonium determinations at a 90% level of confidence is ±0.8 and ±0.6 wt % respectively. Therefore, the number of distinguishable gray-levels for the uranium and plutonium determinations is 55 ($N_U = 88/(2 \times 0.8)$) and 73 ($N_{Pu} = 88/(2 \times 0.6)$) respectively.

4.2 Consistency of the Plutonium and Uranium Concentration Measurements

As seen in Equation (2), to determine plutonium and uranium local concentrations, the X-ray intensity of plutonium and uranium measured at each local point was directly compared with the intensity of the plutonium and uranium standards. In this way, the local uranium and plutonium concentrations are determined independently. On the other hand, the total uranium and plutonium weight percentage in MOX fuel should be in a range from 88.2 to 88.4 wt %, depending on the U/Pu ratio in the fuel. Therefore, it is possible to check the consistency of the two independent plutonium and uranium determinations by comparing the measured uranium and plutonium total concentration at each local point with the expected total of 88 wt %.

Figure 5 shows a comparison between the plutonium measurements and the normalized plutonium values, which are calculated by subtracting the uranium measurements from 88 wt %. Similarly, the figure also compares the measured and normalized uranium data. The figure shows that the measured and normalized values match well, especially inside the particle and in the matrix to the left of the particle. A small discrepancy between the measured and normalized data was observed in the transition region around the particle. Porosity in this region may account for it. Overall, the data indicate that the individual measurements are consistent and that accuracy is satisfactory.

5. SUMMARY

The as-fabricated MOX fuel exhibits a duplex microstructure with PuO_2 particles distributed randomly in the UO_2 matrix. The particles were revealed in the SEM using SEI and BSI modes and by X-ray mapping; their size ranged from 10 to 30 µm. To conduct quantitative WDS analysis, PuO_2 and UO_2 standards prepared by the RFFL were used, which simplified the calculation to determine plutonium and uranium local concentrations. The plutonium M_β and uranium M_α lines were monitored for analysis. Point analysis with a 2-µm interval was conducted diametrally across the particles to obtain the uranium and plutonium distribution profiles, which all exhibited a similar shape. A compositional transition band, ~10 µm in width, was observed between the particle and the matrix, indicating plutonium and uranium interdiffusion had occurred. Uncertainty (at a 90% confidence level) of the uranium concentration in the matrix (87.6 wt %) and plutonium in the particle centre (87.1 wt %) was estimated to be ±0.8 wt % and ±0.6 wt %, respectively. The individual measurements are consistent and accuracy is satisfactory. Further work is planned to compare uranium and plutonium concentrations in particles with corresponding alpha autoradiographic images to provide a bench mark for routine alpha autoradiographic analysis.

6. ACKNOWLEDGMENTS

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7. REFERENCES

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TABLE 1: PARAMETERS OF THREE URANIUM X-RAY LINES

Peak	Wavelength (Å)	Relative Intensity (%)	Energy (keV)	PET Detection Distance (mm)
M_α	3.91000	100	3.170	125.23
M_β	3.71600	60	3.336	119.02
M_γ	3.47900	5	3.563	111.43

TABLE 2: UNCERTAINTY ESTIMATION FOR THE MEASUREMENTS

Element	Number of measurements (n)	Average Concentration (wt %)	$S(\bar{x})$	t_{n-1}^{90}	W_{90} (wt %)
U	7	87.6	0.43	1.943	0.8
Pu	4	87.1	0.25	2.353	0.6

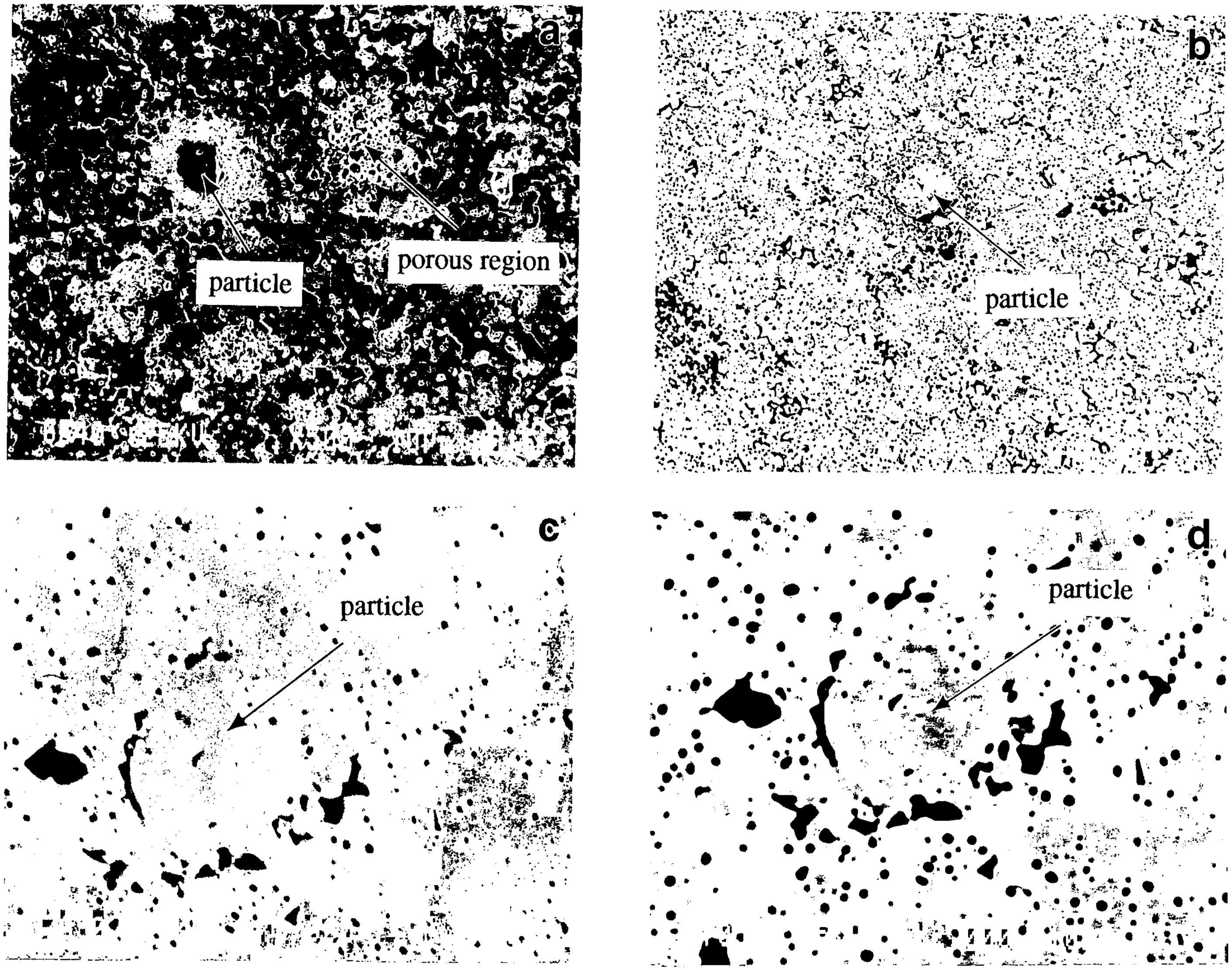

FIGURE 1: TYPICAL MICROSTRUCTURE OF THE MOX FUEL UNDER ETCHED (a: SEI, b: BSI) AND POLISHED (c: SEI, d: BSI) CONDITIONS.

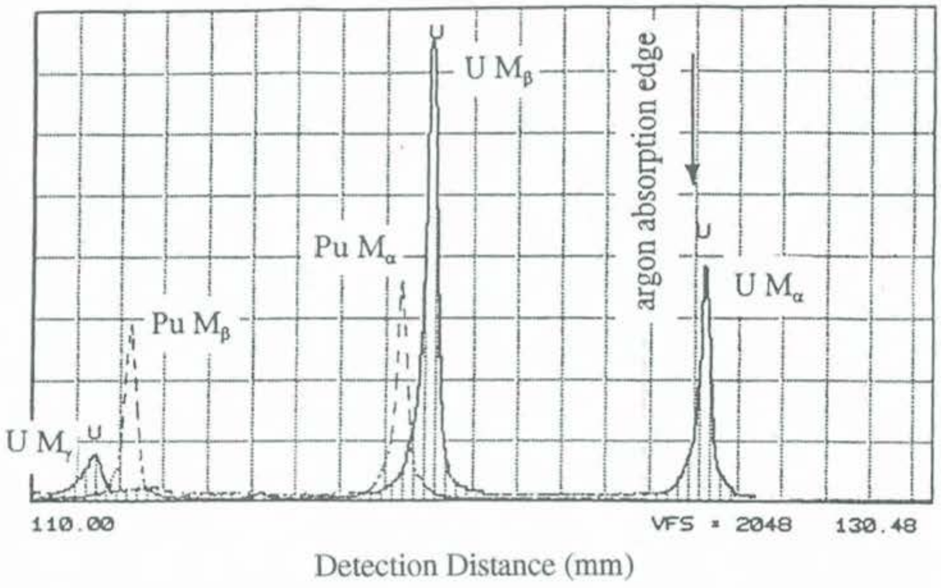

FIGURE 2: PLUTONIUM AND URANIUM X-RAY LINES.

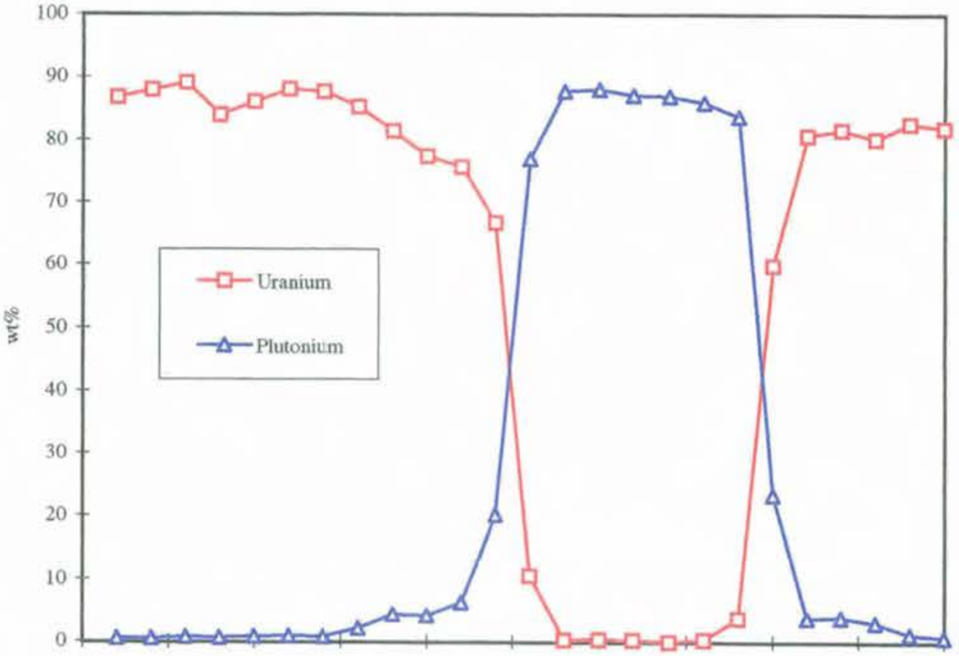

FIGURE 3: PLUTONIUM AND URANIUM DISTRIBUTIONS ACROSS A PARTICLE.

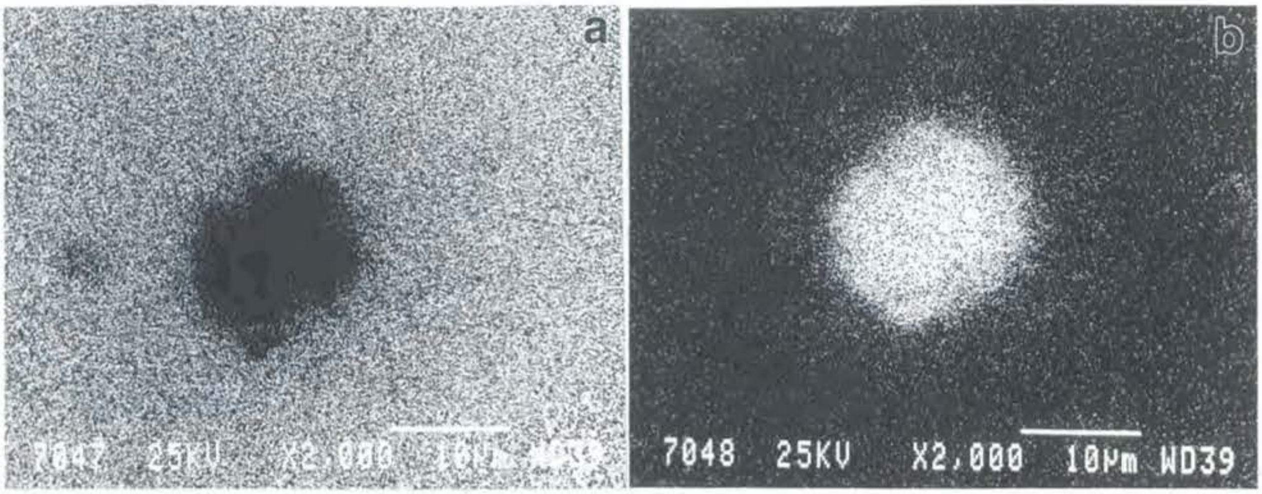

FIGURE 4: URANIUM (a) AND PLUTONIUM (b) X-RAY MAPS.

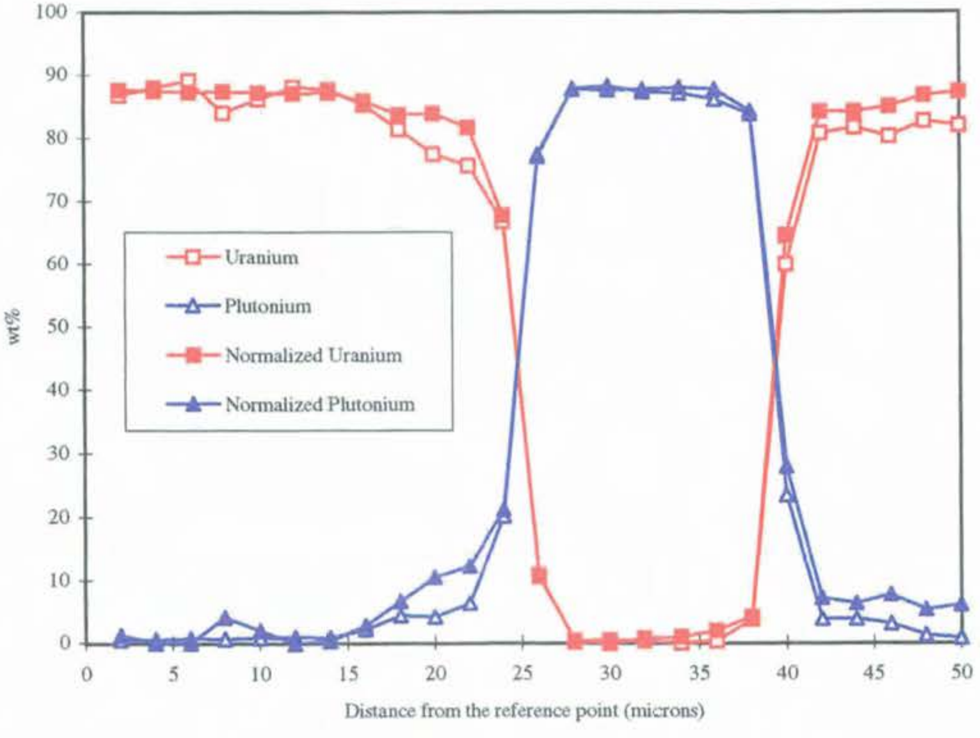

FIGURE 5: COMPARISON OF MEASURED AND NORMALIZED DATA.