On the analysis of Pu distribution in MIMAS MOX by EPMA.

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Abstract :

Advanced modelling of MOX fuel behaviour calls for a more detailed characterisation of
the Pu dispersion in the matrix. Electron Microprobe Analysis (EPMA) is a technique that
can be used to determine elemental distributions with a spatial resolution of 1 μm.
Quantitative EPMA investigations are generally performed on individual points or along a
straight line (linescan). Using two-dimensional scanning (maps), a large number of points is
measured (typically 10^6 for an area of 1x1 mm^2), but the analysis is at best semi-
quantitative.
In this presentation, we will show how quantification using X-ray maps can be improved.
Our approach is based on the acquisition of digital maps, directly calibrated on peak
intensities. An advantage of the 2D method compared to linescan acquisitions, is that a 2D
representation is more demonstrative and has much better statistics.

1. Introduction :

The production of MOX fuel through powder metallurgical ways is based on the blending of
UO_2 and PuO_2. The followed procedure (e.g. a one or two step blending process) depends on
the specific fabrication process involved. Therefore, the microstructure and more specifically
the final Pu dispersion varies accordingly. The method presented in this paper was developed
in the course of a series of analyses on MOX fuel fabricated via the MIMAS process.
The MIMAS (MIcronized MASter blend) process was developed in the mid-eighties at
BelgoNucleaire, to produce soluble fuel, which can be reprocessed and meet the specific
conditions of LWR fuel specifications [1]. Basically, MIMAS MOX pellets are made of a
solid solution of UO_2 and PuO_2, soluble in nitric acid, and homogeneously dispersed in a UO_2
matrix. This is obtained through two blending steps : the primary or master blend (typically
25-30 % enrichment) obtained by ballmilling and a secondary or final blend (5-10%
enrichment).
For each new blend, the resulting Pu distribution and the enrichment has to be validated.
Alpha-autoradiography is used to obtain a qualitative cross-pellet view of the PuO_2
distribution in the UO_2 matrix. Wet chemical analysis complements this information by
providing the global enrichment of a pellet.
A technique that permits visualisation and quantification with high spatial resolution is
Electron Microprobe Analysis (EPMA).
Basically, EPMA is a non-destructive method for qualitative and quantitative analysis of
chemical elements based on the measurements of the wavelengths and intensities of their
characteristic x-ray spectra excited by an electron beam having a diameter of the order of one

micron. EPMA permits the determination of composition and spatial variation of the composition on a microscopic scale.

2. Instrumentation

The EPMA instrument is equipped with an electron gun and 4 wavelength dispersive spectrometers, which allow for simultaneous measurement of the intensity of characteristic x-rays of 4 elements.

Quantification of an unknown composition is based on the measurement of standards. The analyte line intensity is measured from a sample and from a reference standard. This standard may be the pure element, or a compound with known composition. The measured intensities are corrected for dead time (detector dependent), background and line overlap. The relative intensity ratio of the analyte line intensities from sample and reference standard is calculated. Finally this relative intensity ratio is corrected for the atomic number (Z), absorption (A) and fluorescence (F) effect to give the analyte concentration. [2]

The most common measurement modes used in EPMA are the 1D- line scans or 2D maps. A linescan across a sample can be made by either moving the specimen with small increments (motor driven sample stage) or deflecting the electron beam in the X (or Y) direction by the scanning coils. Information on composition and elemental distribution over an area (width : several μm, height : up to 1 cm) can be gained in this way.

To obtain accurate results, a measuring time of the order of several seconds per point has to be applied. Given the fact that for a global view of the composition distribution in a sample, several linescans have to be defined, the linescan method would be too time-consuming to acquire local and global composition distribution.

Another mode of measurement is measuring x-ray maps (2D-analysis). In this case the specimen is moved with small increments in two directions (X and Y). Similar results can be obtained by deflecting the electron beam, but defocusing should be considered when measuring larger areas.

Opposite to the linescans, 2D scans only collect raw intensity data and the measuring time per point is very low (of the order of 20 ms per point). The loss of accuracy due to a low measuring time per point is compensated by increasing the number of points measured. In case of a 1024x1024 x-ray map and using an electron beamsize of 1 μm, the number of measured points is 10^6 and the analysed area is approximately 1mm^2.

However, considering that the accuracy of each individual point in an x-ray map is low, standard EPMA quantification procedures do no longer apply. The main reason is that shot noise becomes predominant at low concentration levels. Subtracting the background signal from the peak signal may then result in negative values, which can not be treated correctly by the X-ray correction methods.

In this paper, we will present a method to correlate the raw intensity data obtained by x-ray maps to a corresponding quantitative enrichment map of a MOX specimen.

3. Analysis of Pu distribution in MIMAS MOX

3.1. Fundamentals

In principle, the measured intensity of an element is not directly proportional to the concentration of that element, because the emitted x-ray line is affected by electron backscattering and the electron stopping power, X-ray absorption and secondary fluorescence

effects. In quantification procedures, the relative intensities (k-ratio = $I_{element}/I_{standard}$) are corrected for these matrix effects by applying ZAF corrections.

However, one can always optimise the instrumental settings such that the correction factors are small for one element or a group of elements. This is particularly true in case of MOX, where the determination of the local enrichment ($\frac{Pu}{U+Pu}$) is based on the analysis of two almost neighbouring elements (U, Z=92 and Pu, Z=94).

In case of $Pu_{M\beta}$ in a MOX matrix, one can calculate (fig.1.a.) that under the instrumental conditions of 15 kV, the matrix effects are small and that in the region of interest (in present case between 0% and 40 % enrichment) one can even take a linear correlation between measured Pu intensities and Pu concentration (fig.1.b.). A linear regression analysis on the calculated data in this domain gives a correlation coefficient R^2 of 0.998. The deviation from the linear approximation for values below 50% enrichment is smaller than 3%.
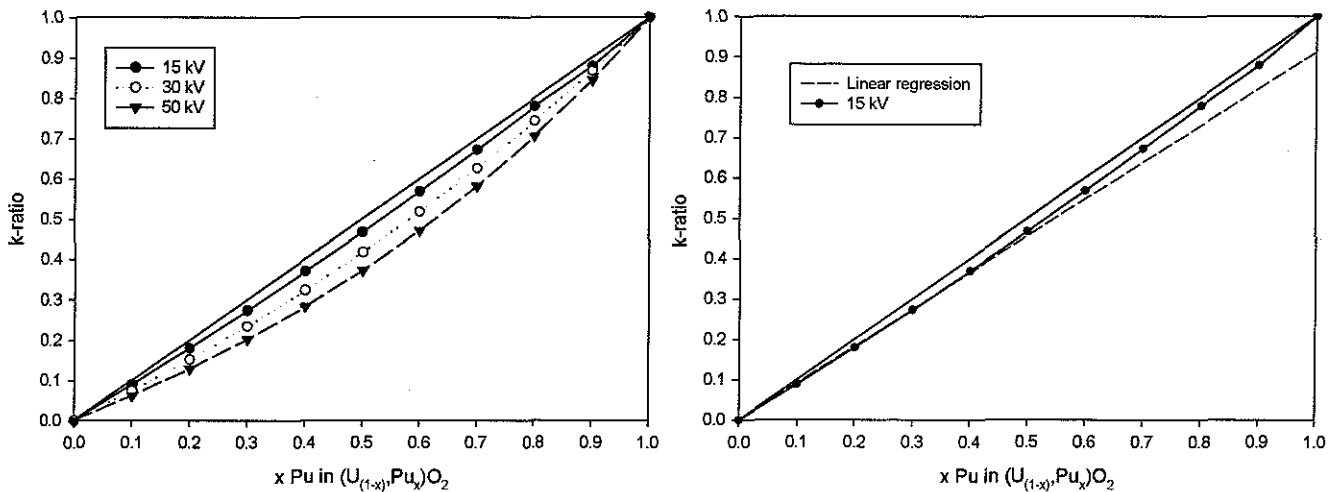

Fig.1. a. Theoretical calculated k-ratio versus Pu concentration at different instrumental settings
b. Linearisation between Pu concentration and Pu intensity

The existence of such a linear correlation can be verified with the results obtained from a linescan over a Pu grain in MOX (fig.2.).
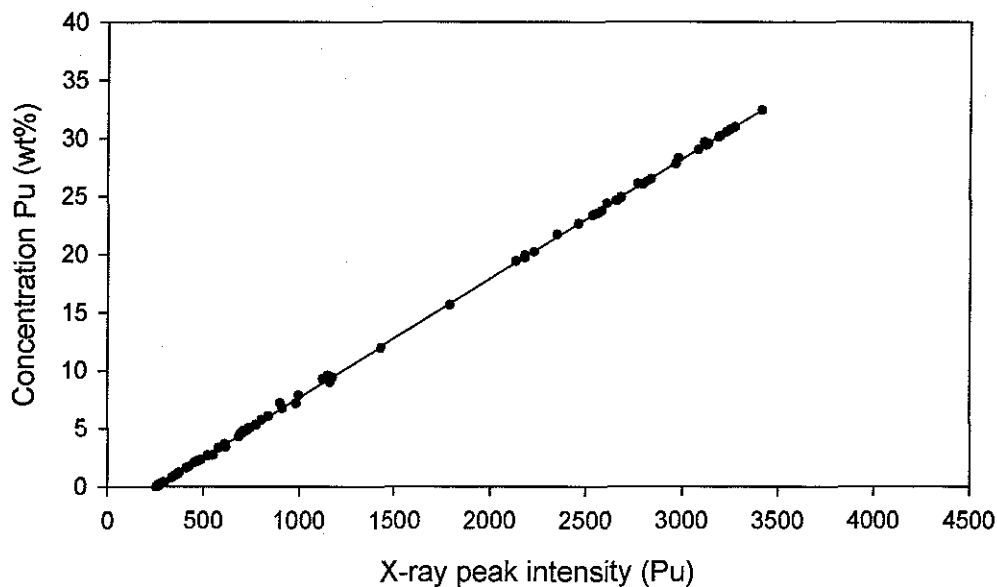

Fig.2. Under the applied experimental conditions the relation between uncorrected Pu peak intensity and local Pu concentration is highly linear.

3.2. Acquisition :

With an accelerating voltage of 15 kV and a beam current of 100 nA, a probesize of 1 μm and an intensity of a 1000 counts per second (cps) on $Pu_{M\beta}$ for a Pu concentration of 10wt% is obtained.

For the quantitative Pu distribution analysis, a large area x-ray map of $Pu_{M\beta}$, $U_{M\alpha}$ and $O_{K\alpha}$ is taken (fig.3.). The specimen is scanned in both X and Y direction in 1024 steps of 1 μm, resulting in a scanned area of 1 mm^2. The scan speed is fixed in such a way that the acquisition time per point or pixel is 17ms. With the instrumental setting of 15 kV and 100 nA the resulting yield of Pu will never exceed a 255-threshold value, which is convenient when exporting the x-ray map to an 8-bit image.

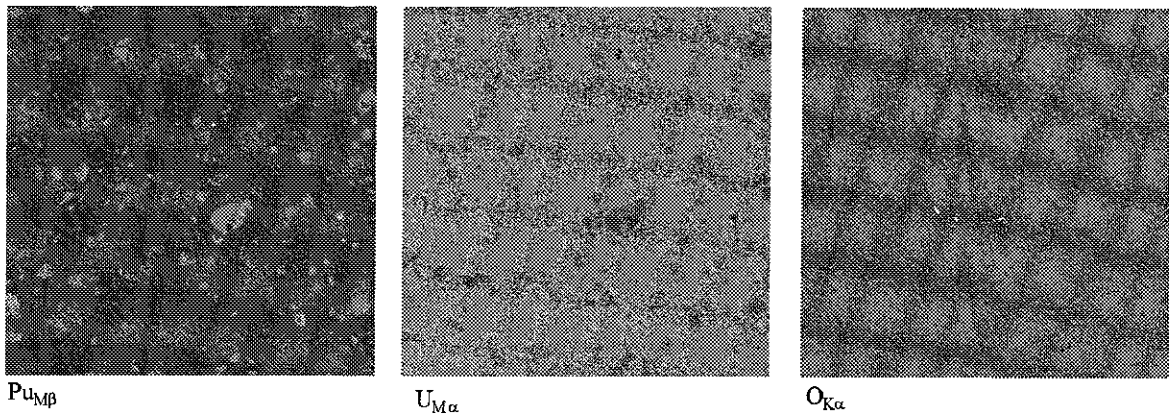In this way, the resulting pixel value of the image file is equal to the raw x-ray intensity measured.

$Pu_{M\beta}$ $U_{M\alpha}$ $O_{K\alpha}$

Fig.3. X-ray intensity map of $Pu_{M\beta}$, $U_{M\alpha}$ and $O_{K\alpha}$.

3.3. Calibration :

Since the transformation of a $Pu_{M\beta}$ intensity map into an enrichment map is a linear function, the calibration line can be determined using two standards with a known Pu concentration (fig.4.). In the present case, a pure UO_2 and a homogenous MOX sample (with known composition) were used. One has to keep in mind that the measurement of the standards can not be done by the normal calibration procedure, since there will be an automatic correction of the result for dead time and background. In such a case, it would not be correct to correlate the corrected standards measurements to the uncorrected raw data obtained by the x-ray maps. To obtain good accuracy, several measurements on the standards are conducted and the average values (cps/nA) are calculated. These values are then converted to a yield that meet the acquisition parameters of the x-ray maps (i.e. nominal beam current 100 nA, acquisition time 17ms).

As one can see in fig.4. that the calibration line does not cross the origin. This is due to both the continuous background and an overlap of the $U_{M\gamma}$ line with the $Pu_{M\beta}$ line. The pure UO_2 standard (enrichment = 0) still yields an intensity of 4.8 counts for an acquisition time of 17ms.
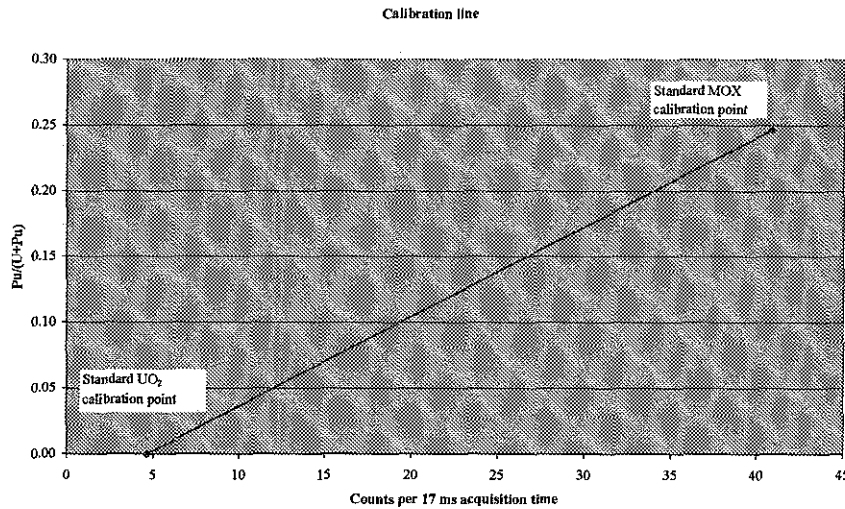
Calibration line

Fig.4. Calibration line obtained from measuring UO_2 and MOX standard.

A linear regression analysis on the calibration line will provide the parameters a and b, that are required in the calculation of the local and global enrichment :

$$y = a.x + b$$

with x the measured number of counts at each pixel (acquisition time 17ms) and y the enrichment expressed as $\dfrac{Pu}{U+Pu}$.

3.4. Quantification :

All quantification is done using the exported image files and image processing software.
In order to calculate an accurate average enrichment, the Pu intensity map first has to be corrected for pores.
To define a mask, containing the size and distribution of the pores in the measured area, the $O_{K\alpha}$ x-ray map can be used. This is justified by the fact that $O_{K\alpha}$ has a low escape-depth, and therefore the measured $O_{K\alpha}$ x-ray map resembles a topographical image of the area. The pixelpositions of this mask (defining the pore position) can be used to set the complementary pixelvalue in the Pu distribution image to zero. In this way, it is possible to omit these values while calculating an average enrichment (cq. average pixelvalue) of the image.

Finally the local and global enrichment can be calculated using the parameter a and b obtained by the calibration. The resulting enrichment image can be seen in fig.5. The accuracy on the mean enrichment of this image is ± 5%.
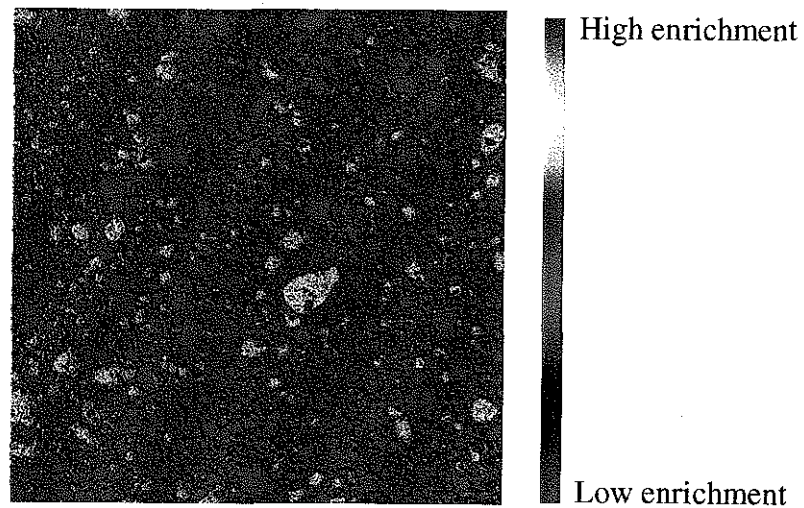
High enrichment

Low enrichment

Fig.5. Resulting enrichment image, showing the Pu enrichment distribution in a MOX pellet.

It should be noted that in case the specimen or standards have a gold coating, an additional and appropriate correction has to be made.

3.5. Verification

The result of the calculation of the 2D Pu enrichment map can be verified by comparing a conventional quantitative linescan to a linescan obtained from the enrichment map (fig.6.).
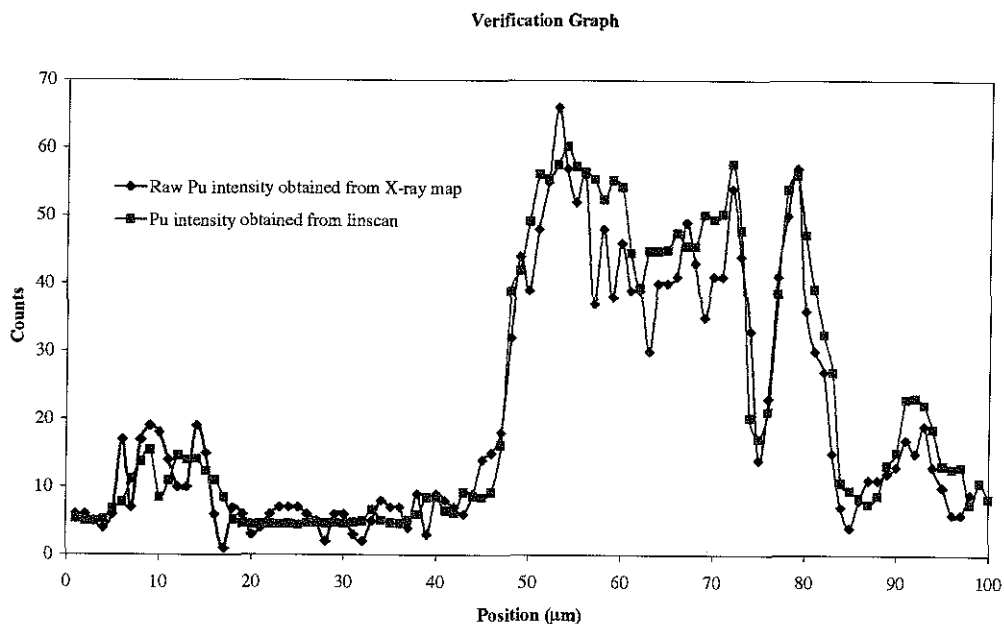

Fig.6. Comparison of Pu intensity obtained from X-ray map and linescan, over a Pu grain.

As one can see, the two curves are in good agreement, but the scatter on the data points retrieved from the 2D map is larger. Such a higher degree of statistical scatter (noise) can be

expected, since the acquisition time per point of the 2D map is much lower (17 ms) than those of a linescan (10 s). However, as stated before, the lower accuracy per point in the 2D map is compensated by the larger number of data points measured.

To improve the accuracy of the global enrichment several maps on different positions on the MOX pellet can be taken. It should be noted however that each acquisition should be accompanied with the appropriate calibration.

4. Conclusion

The transformation of qualitative Pu x-ray intensity maps, using the described method, results in an accurate quantitative two-dimensional enrichment map.
The method has been successfully applied on samples from different productions and having different enrichment levels. The resolution of the obtained x-ray maps is superior to the resolution of alpha-autographs and in addition, the local Pu enrichment can be readily quantified. The values of the global enrichment of the samples obtained by this method have been confirmed by wet chemical analysis.
In conclusion, it can be stated that for this type of analysis, where numerous sampling is needed to acquire accurate results, the described approach is better than conventional EPMA quantification methods.

Reference

[1] D. Haas, J. van Vliet and A. Vandergheynst : Experience with MOX fuel, The Nuclear Energy Institute – Fuel Cycle 95, 2-5 April 1995 – San Diego, Ca.
[2] S.J.B. Reed, Electron Microprobe Analysis, Cambridge University Press, 1993