Dynamic SIMS Applications in Nuclear Safeguards

A New Methodology Improves the Accuracy of Pu Isotopic Analyses

Every nuclear process emits micrometric fragments of nuclear material that can be collected by inspectors from the International Atomic Energy Agency in the framework of the Non Proliferation Treaty. Elemental and isotopic analyses of such so-called particles provide useful information on the industrial origin of the nuclear material. Mainly focused on the characterization of uranium-bearing particles, it is also of great interest to determine the plutonium isotopic composition of such particulate matter. Actually, isotopic ratio measurements of Pu enable the identification of the Pu source, origin and potential use (irradiated fuel, mixed oxide fuel (MOX) for civilian reactors, nuclear weapons, etc.).

Dynamic Secondary Ion Mass Spectrometry (D-SIMS) is the only technique that can provide both particle location and isotopic measurements using a single instrument, with a high sensitivity and a high lateral resolution. However, Pu isotope analyses remain challenging due to isobaric interferences linked to hydride ions. Using their CAMECA IMS instrument, researchers at CEA developed a new methodology based on the extrapolation of the U hydride correction factor to Pu in order to improve the accuracy of $^{240}Pu/^{239}Pu$ isotopic ratio measurements conducted on both Pu oxide and MOX particles. Indeed, the U hydride correction factor can be easily measured in U oxide particles by calculating the $^{238}UH^+/^{238}U^+$ isotopic ratio. However, it is not possible to determine the Pu hydride formation rate because of the isotopic composition of this element (i.e. presence of ^{240}Pu that interferes with ^{239}PuH).

In the present study, the analysis of a Pu oxide reference material and two MOX samples demonstrated that:

- Thanks to the hydride correction, the $^{240}Pu/^{239}Pu$ isotopic ratios, presented in Figure 1 for Pu oxide particles containing very low amount of ^{240}Pu, can be measured more accurately. Without such correction, the ratios would be largely overestimated compared to the expected ratio (relative differences rising from 0,57% to 1,92% with/without correction).
- The double hydride corrections (^{238}UH on ^{239}Pu and ^{239}PuH on ^{240}Pu) also improved the accuracy of $^{240}Pu/^{239}Pu$ isotopic ratios in MOX particles containing 1 to 10 wt% of Pu (Table 1).

The researchers also proposed a method to determine the Relative Sensitivity Factor (RSF) based on the decay of Pu in order to quantify the Pu content in MOX samples, with an estimated lowest measurable $^{239}Pu/^{238}U$ atomic ratio in MOX particles around 1.6×10^{-3}.

Opening the way to the isotopic characterization of environmental particles containing U, Pu or both elements that may result from nuclear power plants and facilities, this new methodology is of particular interest for nuclear safeguards.

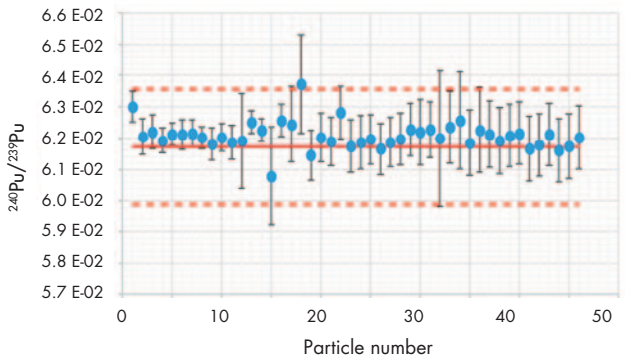


Figure 1:

$^{240}Pu/^{239}Pu$ isotopic ratios measured on individual Pu oxide particles over a nine month-period. Expanded uncertainties are given with a 95 % confidence level. The red line corresponds to the expected value. The red dashed lines correspond to the upper and lower uncertainties of the expected value.

Data obtained on CAMECA IMS 7f instrument, analytical conditions: O_2^+, IE 10keV, Energy pathway 75eV, CA 400, FA 1800, MR400, M. Area 75µm, Magnet peak jump sequence on EM.

It can be noted that applying the same methodology on a Large-Geometry SIMS such as the CAMECA IMS 1300-HR³, the accuracy could be further improved and the uncertainties lowered thanks to the multicollection device that offers the capability to collect up to five isotopes simultaneously.

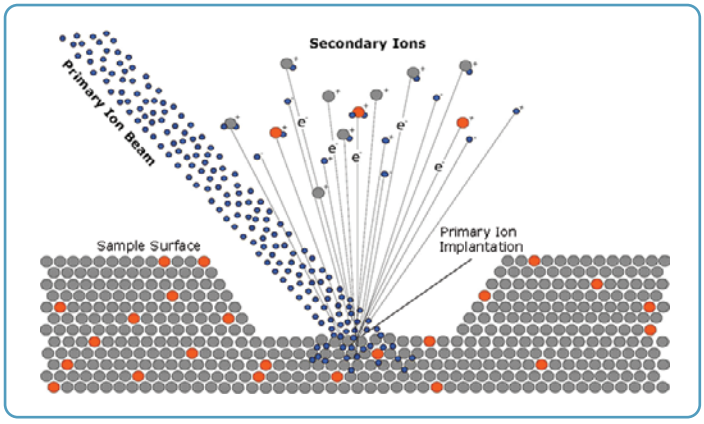
	UKMOX-010	UKMOX-100
$^{240}Pu/^{239}Pu$ with U and PuH corrections	$(2.859 \pm 0.046) \times 10^{-1}$ (0.06%)	$(2.859 \pm 0.058) \times 10^{-1}$ (0.03%)
$^{240}Pu/^{239}Pu$ without UH and PuH corrections	$(2.844 \pm 0.064) \times 10^{-1}$ (0.59%)	$(2.749 \pm 0.12) \times 10^{-1}$ (3.76%)
$^{235}U/^{238}U$	$(1.590 \pm 0.031) \times 10^{-2}$ (+0.03%)	$(1.584 \pm 0.034) \times 10^{-2}$ (−0.37%)
Number of analysed particles	23	15

Table 1:

Average $^{240}Pu/^{239}Pu$ atomic ratios measured on MOX particles. Expanded uncertainties are given with a coverage factor of 2 (confidence level of 95 %). Corresponding ratios without ^{238}PuH and ^{239}PuH corrections are also given. Values in parentheses below the atomic ratios are the relative difference with the expected ratio.

Adapted from: A. Diacre et al. $^{240}Pu/^{239}Pu$ isotopic ratio measurements in micrometric Pu and MOX particles using Secondary Ion Mass Spectrometry. Talanta 252 (2023)

The Technique Behind

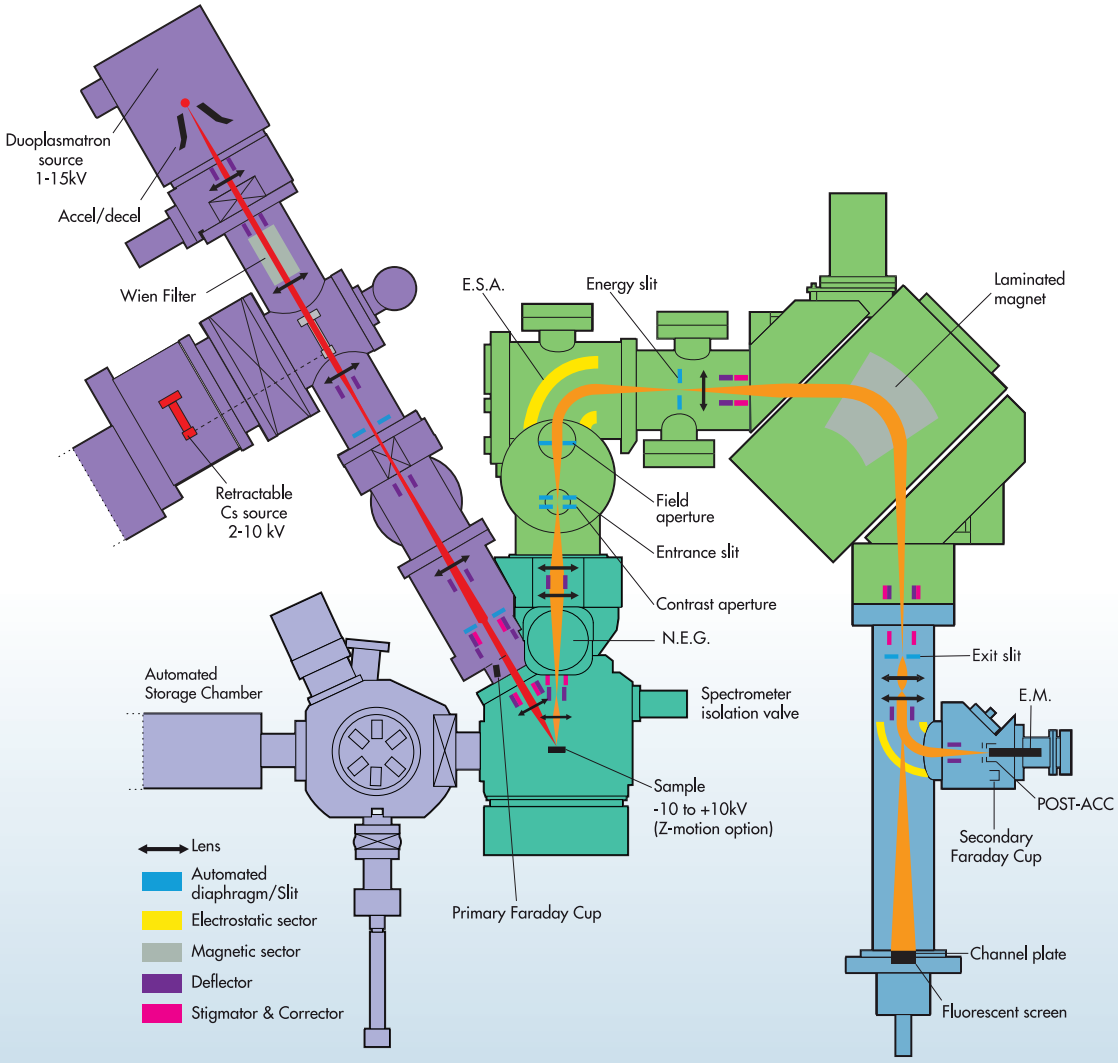


Dynamic SIMS

When a solid sample is sputtered by primary ions of few keV energy, a fraction of the particles emitted from the target is ionized. Secondary Ion Mass Spectrometry consists of analyzing these secondary ions with a mass spectrometer.

The SIMS technique is "destructive" by its nature (sputtering of material). It can be applied to any type of flat, solid material that can be kept under vacuum.

In dynamic SIMS, bulk composition and in-depth distribution of trace elements are investigated with a depth resolution ranging from sub-nm to tens of nm. SIMS is recognized as the most sensitive elemental and isotopic surface analysis technique.



CAMECA IMS 7f-Auto

The IMS 7f-Auto is a versatile SIMS tool offering reference detection sensitivity with high throughput and full automation. Its motorized storage chamber and sample transfer allows the analysis of multiple samples in chained or remote mode.

For more information please visit www.cameca.com/products/sims/ims7f-auto

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