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SIMS Analysis of Uranium and Actinides in Microparticles of Different Origin

Gabriele Tamborini*

European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340,
D-76125 Karlsruhe, Germany

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Abstract. In the framework of the projects "Environmental Sampling" and "High Performance Trace Analysis" in support to the International Atomic Energy Agency (IAEA) and the Euratom Safeguards Office (ESO), the research has been focused on the identification and characterisation of particles of interest containing mainly U and other actinides.

Multiple analyses, elemental and isotopic, of single radioactive particles in the µm-size range are key-tools in environmental research and in nuclear forensics. The main purpose in the analysis of single particles by SIMS is the determination of their isotopic composition that has been demonstrated successfully for uranium and plutonium particles. From these results, the enrichment of the material produced, the process used for the enrichment as well as the starting material employed (natural or reprocessed uranium) can be identified.

Key words: SIMS; radioactive microparticles; uranium; plutonium; environment.

The size and composition of radioactive particles determine the transport mechanisms of radionuclides in the environment as well as their bioavailability. Therefore, their characterisation as for elemental and isotopic composition is of great relevance. Considerable advances in secondary ion mass spectrometry (SIMS) have been made over the last decade to develop precise and accurate methods for the determination of the isotopic composition of individual radioactive particles [1–5]. These parameters are fundamental for the characterisation of such particles in safeguards as well as in environmental and forensic applications. Particularly, in nuclear forensics, the U and Pu isotope ratios give important information to trace the origin of nuclear fuel material.

In the aftermath of the Gulf War, the capability of analytical chemistry to reveal ongoing undeclared nuclear activities by the analysis of environmental samples was demonstrated [6, 7]. Immediately thereafter, the IAEA started the programme $93+2$ based on field trials to verify the effectiveness of environmental sampling in routine nuclear inspections, with the result that some years ago this methodology has been implemented in the Additional Protocol as complement to the existing safeguards agreement [8, 9]. Euratom jointed to this investigation developing the programme High Performance Trace Analysis (HPTA). In this framework, the Institute for Transuranium Elements (ITU) played an important role actively participating in the sampling during the field trials performed for the creation of baseline data for different nuclear installations. At the same time, ITU implemented new techniques able to detect nuclear

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* E-mail: tamborini@itu.fzk.de

activities by the characterisation of microparticles [1–4, 10]. It was the first civil laboratory in Europe to develop such technologies and entered in the Network of the Analytical Laboratory of IAEA for particle characterisation. The main method used at ITU for the characterisation of micro particles containing fissile material is based on secondary ion mass spectrometry, even though nuclear track technologies have been developed for their individuation.

Classical Swipe Sample Analysis

A large amount of information can be obtained from a small amount of collected material, such as a swipe sample on a 10×10-cm piece of cotton cloth. The samples are handled in a clean lab of class 100–10, where chemical treatments are performed in order to collect particles from the cotton swipe to the sample holder for further instrumental analysis. Sample preparation consists of the ultrasonic removal of particles from a piece of cotton swipe immersed in an organic solvent such as heptane. The particle suspension is then dried on a polished graphite planchet.

Scanning Electron Microscope-Energy Dispersive X-ray spectrometry (SEM-EDX) is used after sample preparation to measure the elemental composition of micrometer-sized particles removed from the cotton swipes. To search for uranium containing particles the samples are scanned automatically by SEM using the backscattered mode. From these analyses, the number of uranium particles deposited on the planchet, together with their elemental composition and their co-ordinates are obtained (Fig. 1).

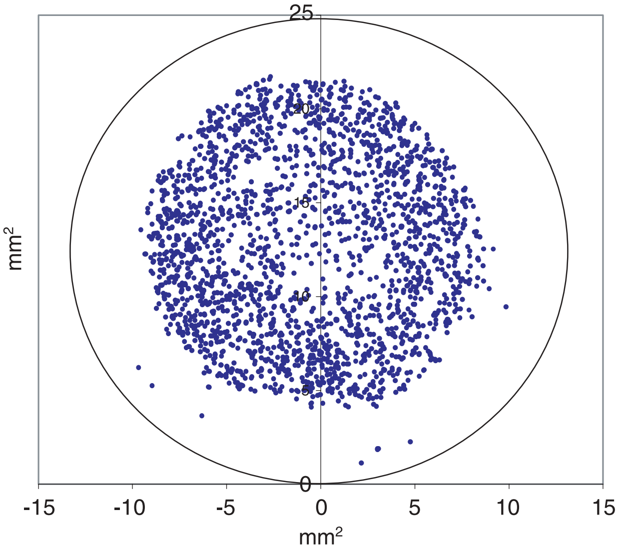


Fig. 1. Distribution of uranium particles (blue dots) on a SIMS planchet detected by the automated SEM analysis using a Gun-Shot Residue (*GSR*) program

SEM-EDX offers high elemental sensitivity and can screen large number of particles, but the technique does not give uranium or plutonium isotopic information, which can be of critical importance. For this purpose, SIMS that measures secondary ions of U and Pu isotopes by peak switching on an electron multiplier pulse-counting system or with an imaging detection system that produces spatially resolved images for each isotope, is exploited (CAMECA

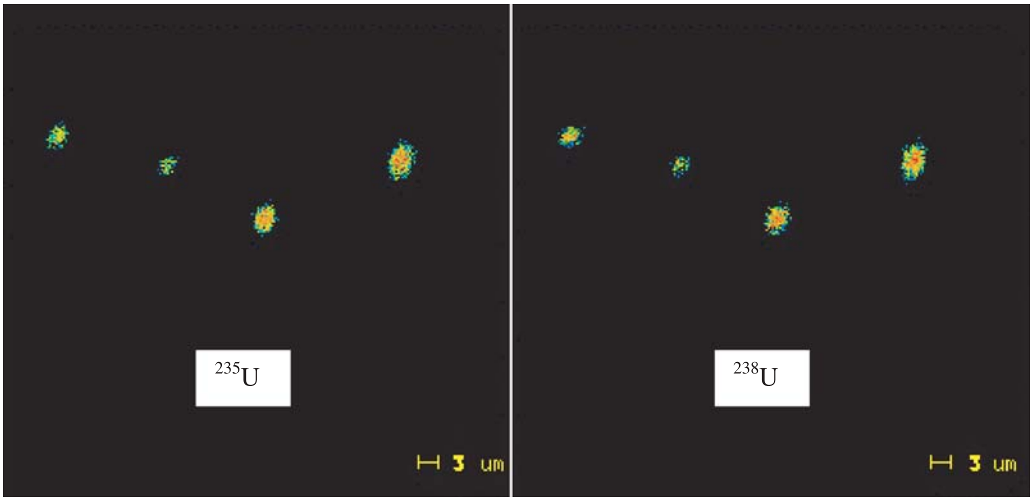


Fig. 2. Scanning ion images of HEU uranium particles (50% enriched in ^{235}U) by SIMS (O_2^+ primary beam) over a 50 µm^2 area

IMS 6f Paris, France). The particles deposited on a polished graphite planchet are bombarded with O^{2+} at an energy of 15 keV, which then provides a SIMS scanning ion image of the actinide particles present at the surface (Fig. 2). By reducing the size of the primary beam, the secondary ions from individual particles are mass analysed and detected.

The first information to be obtained for enrichment plants is to verify that enrichments no higher than the declared ones are produced. ^{235}U and ^{238}U are therefore measured to obtain the enrichment of uranium and to indicate whether the material produced was intended for civil uses or nuclear weapons purposes. The determination of the abundance of the minor U isotopes (^{234}U and ^{236}U) allows to recognise the feed material used and the technology used for the enrichment process. Figure 3 shows SIMS results for tens of particles analysed from an enrichment plant. Depleted, natural, and low enriched uranium (LEU) are the expected signatures for this installation. However, the linearity of the graph obtained by plotting ^{234}U atom% against ^{235}U atom% for these low enrichments can not suggest the type of enrichment system involved (in fact, the enrichment distribution from a centrifuge process shows always a linear behaviour up to the highest enrichments, i.e. 94%, while an exponential change is observed after ~55% for the gas diffusion) [11].

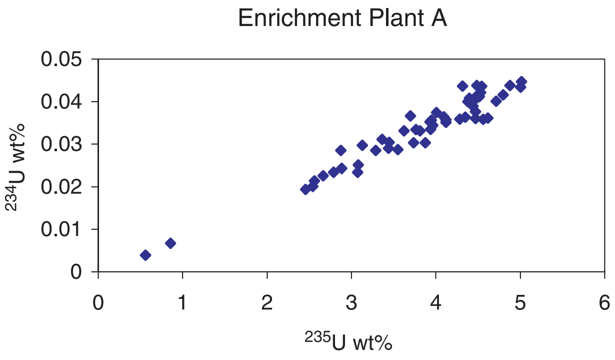


Fig. 3. Enrichment linearity graph for the particles from Plant A

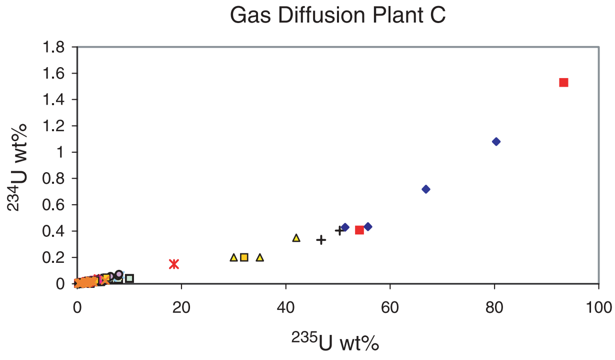


Fig. 4. Enrichment graph for the particles from Plant C

Figure 4 represents the enrichment curve obtained for another plant. Apart from the fact that in this case also highly enriched weapons grade particles were detected, the main feature, in respect to the information obtained for the plant A, is the indication that the enrichment was performed by gas diffusion technology. This is demonstrated by the exponential pattern of the curve.

Hot Cell Analyses

The samples are processed in a "clean glove-box" since they cannot be treated in the clean room laboratory. The main purpose of the analysis of samples from hot cells is to establish the absence of undeclared operations, and, depending on the declared status of the facility, to verify if separation of Pu or highly enriched uranium (HEU) or undeclared U or Pu production took place. Figure 5 shows the SIMS results obtained from the analysis of particles taken in two different locations inside a hot cell facility. The installation has clearly manipulated different enrichments. In fact, two main populations of enrichment in ^{235}U, the first centred on the low enrichment of uranium and the other around 37%, were found. The concentration of the ^{236}U resulted to be between 0.3 and 0.4% indicating fuel with low burnup [11]. The SEM analysis

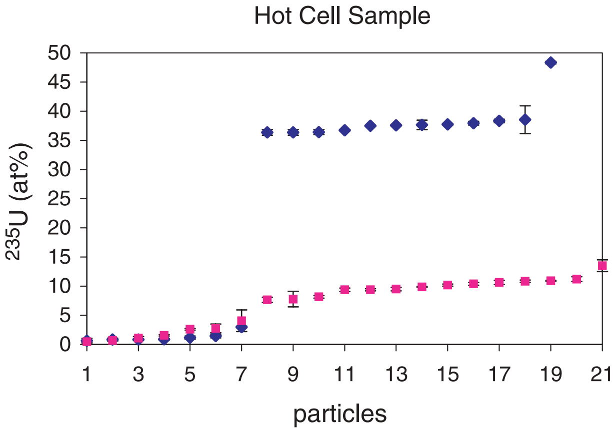


Fig. 5. Enrichments distribution found in the sample from hot cells for two different sets of sub-samples

and the related EDX spectra of some of the particles revealed the presence of Al associated with U. The U isotopic ratio results together with the detection of Al are fingerprints of few types of European research reactor, which use a mixture of Al/U fuel rods.

For samples taken inside hot cells, the U/Pu and the Am/Pu ratios are of particular interest. In case of many lines in a relatively narrow energy range, as for mixtures of U, Pu and Am, the use of a wavelength dispersive x-ray (WDX, LiF 220 as crystal) system with a detection limit about 50 times lower than EDX, is of great help in determining the elemental composition of particles.

Analysis of Particles from the Environment

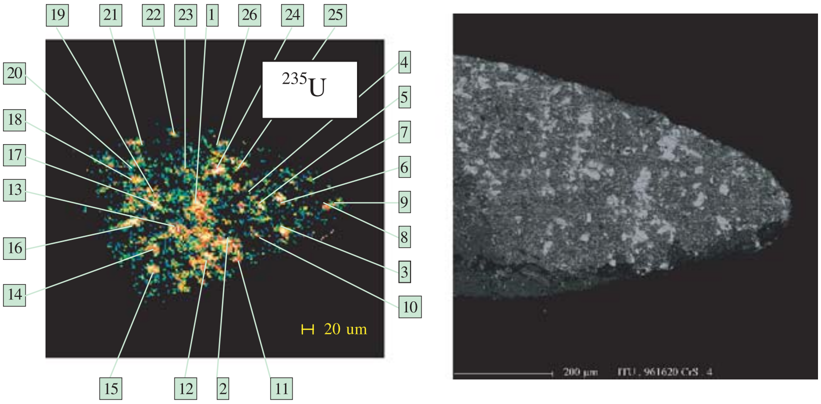
Following an accidental discharge, highly radioactive particles of few millimetres in size have been found for more than ten years on the seabed and occasionally on beaches in the neighbourhood of a nuclear establishment in Scotland. The particles were identified as an Al/U matrix fuel from a material test reactor. A double-focusing secondary ion mass spectrometer was used. The instrument has been previously described [3]. To search for U particles in the sample, the SIMS mass spectrometer was set to mass ^{238}U and alternatively to mass ^{235}U to obtain a mapped distribution of the U particles. The sample was scanned across the surface with a field of view of 500×500-µm and the analysis performed is shown in Fig. 6. This SIMS image of the ^{235}U secondary ion signal distribution in the sample reproduces exactly the same uranium spots found by the scanning electron microscope laboratory, as shown in Fig. 7. The primary beam was then focused on a single U particle and the isotope ratios were calculated from the measured ion beam intensities at the mass positions of the different U isotopes.

Few micrograms of the sample were also dissolved and measured by inductively coupled plasma mass spectrometry (ICPMS). The measurements were performed with a double focusing multi-collector ICPMS from NU Instruments.

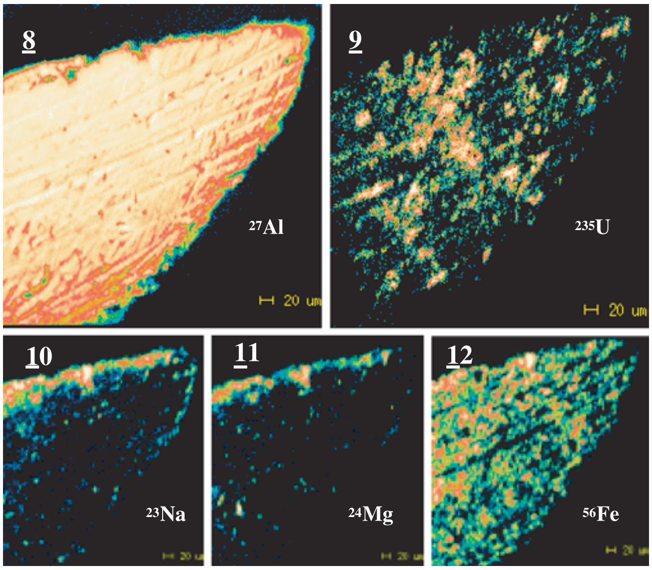
The typical imaging distribution analysis of the Al and U elements in the sample performed by SIMS is shown on Figs. 8 and 9. To check whether the uranium spots found in the particle were located at the same place with some other elements, a series of images was recorded during the same analysis scanning consecutively the analysed area for the masses ^{23}Na, ^{24}Mg, ^{27}Al, ^{31}P, ^{40}Ca, ^{56}Fe and ^{235}U. The SIMS analysis found the nature of the matrix to be Al (this result was also confirmed by the SEM analysis) and showed also that the other major elements present in the sample were not directly located with the uranium spots. In fact, no evident contribution of any uranium in the same area of analysis of the detected iron particles, for instance, was found (Figs. 10–12).

For all the U particles analysed, homogeneous distribution of the isotopes was proven. The abundance of the minor isotopes is much higher than in irradiated low enriched uranium fuels. Therefore any possible molecular interference at mass position 236 arising from ^{235}UH^{+} can be neglected. To confirm the SIMS results, a few micrograms of the sample were dissolved and measured by ICPMS. The ICPMS results are consistent with the values obtained by SIMS as shown in Table 1.

For the plutonium measurements, the primary beam was focused on a single spot and the isotope ratios (^{239}Pu/^{240}Pu, ^{239}Pu/^{238}U) were calculated from the measured ion currents of the different Pu and U isotopes.



Figs. 6 and 7. Uranium spots analysed by SIMS scanning ion image system (left) and SEM-EDX (right)



Figs. 8–12. SIMS scanning ion map distributions of the particles on the main elements present in the sample

Table 1. Mean values and relative standard uncertainties (1σ) for the U measurements

Isotopes	SIMS	ICPMS	Calculated (Scale)
^{234}U at%	1.49 ± 0.02	1.49 ± 0.01	1.4
^{235}U at%	82.9 ± 1.0	82.7 ± 0.9	83.5
^{236}U at%	7.63 ± 0.19	7.56 ± 0.08	7.6
^{238}U at%	7.96 ± 0.21	8.20 ± 0.08	7.5

Table 2. Mean values and relative standard uncertainties (1σ) for the Pu and Pu/U ratios

Ratio	SIMS	ICPMS
^{239}Pu/^{240}Pu	6.0 ± 0.3	5.9 ± 0.3
^{239}Pu/^{238}U	1.51E-02 ± 0.0004	1.43E-02 ± 0.0007

Pu has generally a considerably higher ionisation efficiency than U. Therefore the measured Pu/U ratios have to be corrected with the "relative sensitivity factor" (RSF) for Pu/U, which takes into account the differences in the ionisation efficiencies of the elements at the fixed conditions (e.g. constant primary ion beam energy and current) of the measurement. The RSF of 2.41 previously determined [10] is applied in this work for the correction of the ^{239}Pu/^{238}U ratio. In Table 2, the value of the ratio ^{239}Pu/^{238}U has been corrected with the RSF for Pu/U ratio.

In the same table, the ICPMS results of one scan measurement are given for comparison. Accordingly to the theoretical calculations, due to the negligible amount of ^{238}Pu, no U/Pu separation has been performed. The results of the two techniques agree quite well demonstrating a good reliability of the results. The uranium and plutonium isotope ratio results were used for the identification of the sample. The results of SCALE programme calculations (software for the computation on radionuclides) of HEU fuels are in good agreement with the SIMS and ICPMS measured values. Another information supplied from the analysis of this sample is the Al/U ratio in the alloy. Taking into account that Al has a considerable higher ionisation efficiency than U by SIMS, the RSF of 50.36 obtained from the literature [12] was applied in this work for the correction of the Al/U ratio. A value of 6.9 was obtained by SIMS and this result was confirmed by ICP-MS ($Al/U = 7$).

This method permitted the identification of the reactor and fuel type from U and Pu/U isotopic results obtained by SIMS and ICPMS. The measured isotopic composition is consistent with the calculated composition of a HEU fuel (enrichment $>90\%$) irradiated in an MTR reactor to a burnup of 25 to 30%. The calculated parameters confirm the experimental values within calculation uncertainty.

Uranium Oxide Control Particles

In order to reduce the measurement uncertainty and to improve the accuracy of the various particle analysis techniques, standard particles with a well-known content of uranium are needed. These particles can allow the detection efficiency to be determined. Furthermore, reference particles with well-defined isotopic composition are required, for the quality control of SIMS analyses. Since no such particles are commercially available, it was decided to produce them at ITU. Monodisperse uranium oxide particles have been produced starting from certified standard reference materials of different uranium isotopic composition. The particles were obtained by aerosol generation methodology starting from a solution of a standard reference uranium oxide powders. The morphology of the monodisperse uranium oxide particles was studied by scanning electron microscopy. A SEM image of four such particles on the collecting filter is shown in Fig. 13.

Secondary ion mass spectrometry was used to verify the isotopic composition of the produced particles.

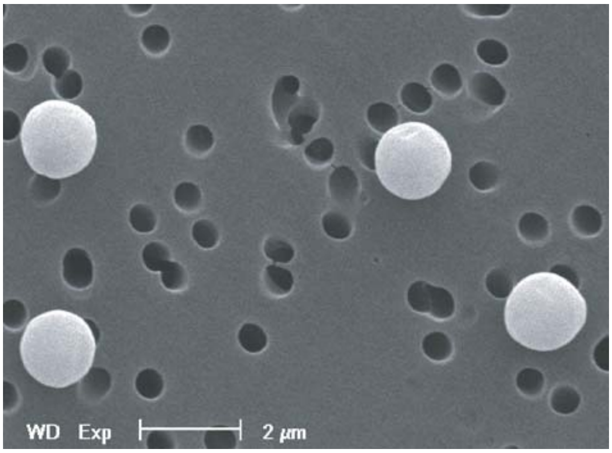


Fig. 13. SEM image of four monodisperse uranium oxide particles on a Nucleopore filter

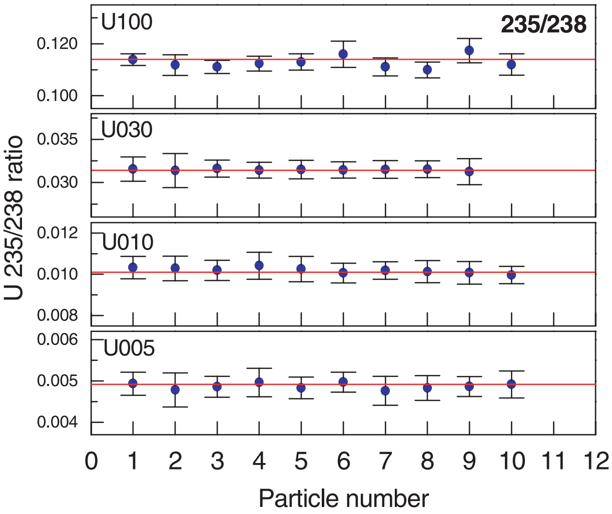


Fig. 14. SIMS experimental values with error bars for the 235/238 from 4 different isotopic compositions

Figure 14 shows as an example the mean 235/238 isotopic ratios values and the error bars relevant to 9 measurements for the individual particles and for each isotopic composition. The certified values are plotted as horizontal lines for comparison.

Conclusion

Tiny single particles, stemming from nuclear material, collected in the environment (often less than 1 µm in size) can give information on the history of nuclear sample itself and reveal undeclared nuclear activities. The analysis by secondary ion mass spectrometry of these particles is done with the respect to their isotopic composition. In many cases scanning electron microscopy can be used as complementary technique to study the morphology of the particles.

Monodisperse standard uranium oxide particles have been produced for calibration and performance testing of isotope-ratio secondary ion mass spectrometer. The method developed at ITU represents a powerful technique to be applied for the analysis and characterisation of particles found in environmental samples or swipes characterised by different matrices.

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