

Recent improvements of actinides trace analysis in environmental samples for nuclear activities detection

F. Pointurier, O. Marie, A. Hubert, A.L. Fauré, A.C. Pottin

CEA, DAM, DIF, F-91297 Arpajon, France

fabien.pointurier@cea.fr

Abstract. In this paper, we present some results of R&D works conducted at CEA to improve on the one side the performance of the techniques already in use for detection of undeclared activities, and on the other side to develop new capabilities, either as alternative to the existing techniques or new methods that bring new information, complementary to the isotopic composition. For the trace analysis of plutonium in swipe samples by ICP-MS, we demonstrate that a thorough knowledge of the background in the actinide mass range is highly desirable. In order to avoid false plutonium detection in the femtogram range, correction from polyatomic interferences including mercury, lead or iridium atoms are in some case necessary. Efforts must be put on improving the purification procedure. Micro-Raman spectrometry allows determining the chemical composition of uranium compound at the scale of the microscopic object using a pre-location of the particles thanks to SEM and a relocation of these particles thanks to mathematical calculations. However, particles below 5 μm are hardly relocated and a coupling device between the SEM and the micro-Raman spectrometer for direct Raman analysis after location of a particle of interest is currently under testing. Lastly, laser ablation – ICP-MS is an interesting technique for direct isotopic or elemental analysis of various solid samples and proves to be a suitable alternative technique for particle analysis, although precision over isotopic ratio measurement is strongly limited by the short duration and irregularity of the signals. However, sensitivity and sample throughput are high and more developments are in progress to validate and improve this method.

1. Introduction

Environmental sampling and analysis is nowadays a key tool for nuclear safeguards. Environmental samples mainly consist in cotton cloth wiped on dusty surfaces, imprisoning particulate material representative of the various industrial activities – declared and undeclared – conducted in the facility. Bulk analysis and particle analysis are regularly carried out on these environmental samples by a few laboratories, members of the Network of the Analytical Laboratories (NWAL) that support the safeguards program of the IAEA. However, these laboratories now have to face new challenges. With this respects, we present here some results of R&D works conducted at CEA to cope with these challenges.

The first challenge arises from the increasing sensitivity of the mass spectrometers used for isotopic measurements of small amounts of actinides extracted from environmental samples. The counterpart of this higher performance is that greater care must be taken for correcting low intensity signals from artefacts, so as to obtain accurate results and to avoid false detections. We describe a methodology developed at CEA for reliably measuring extremely small amounts (femtograms) of plutonium in environmental samples by inductively coupled plasma – mass spectrometry (ICP-MS).

The second challenge is to extract more information from environmental samples, in addition to isotopic abundances, to obtain a more complete picture of activities carried out in the inspected facility. We present here the implementation of micro-Raman spectrometry coupled to scanning electron microscopy

with the aim of identifying the chemical composition (stoichiometry) of uranium compound contained in micrometer-size particles usually encountered in environmental samples.

Lastly, the third challenge is to shorten analytical delay and to develop faster analytical techniques. In relation to this goal, we describe the coupling of a laser ablation device with an ICP-MS to carry out direct isotopic analysis on micrometer-size particles extracted from environmental samples.

2. Avoiding false detection of plutonium in the femtogram range by ICP-MS

ICP-MS is now widely used for the measurement of low amounts of plutonium in various environmental samples (surface and underground waters, soil and biota samples, etc.). These measurements are performed after a chemical purification that allows elimination of the sample matrix and concentration of the plutonium in a few millilitres of solution. For these measurements, it is well known that some interfering effects must be corrected, like the tail of the ^{238}U peak on adjacent masses, the hydrides of ^{238}U (at mass 239) and the potential isotopic impurities of an isotopic dilution tracer ^{242}Pu or ^{244}Pu . By strongly reducing the remaining amount of uranium in the sample solutions and performing accurate corrections of the abovementioned effects, extremely low analytical detection limits and accurate results can be obtained [1-5].

However, determination of plutonium in the femtogram range using state-of-the-art high sensitivity ICP-MS may in some cases be biased by poly-atomic interferences made with a heavy element like lead, mercury, iridium, etc., and of atoms abundant in the plasma (oxygen, argon, nitrogen, hydrogen). Despite a thorough chemical purification based on ion-exchange chromatography, traces of these heavy elements, typically in the ppb ($\mu\text{g l}^{-1}$) range, can always be found in the sample solution, brought by the atmosphere and by some of the reagents used in the purification procedure itself. If not corrected, the resulting polyatomic interferences may lead to overestimation of the results and even to false plutonium detection. Therefore, we developed and successfully applied for now more than 3 years a method for correcting from these polyatomic interferences [6].

To evaluate the extent of these interferences and their impact on the analyses of traces of plutonium, we give in Table 1 the average, maximum, and minimum contributions of polyatomic interferences made with iridium, mercury and lead on the background at masses 239 and 240 for plutonium measurements carried out for years 2007, 2008, and 2009 (i.e. 137 measurements). Contributions of the other heavy elements (Hf, Ta, W, Re, Pt, Au, Tl, Bi) are negligible ($<0.01 \text{ count s}^{-1}$) and are not reported. We also give in the Table 1 the average, maximum, and minimum values of the instrumental background (IB), obtained from the instrumental blanks (de-ionized water acidified with 2% HNO_3). For both masses 239 and 240, sums of polyatomic species induced-background are on average higher than average IB ($1.23 \text{ count s}^{-1}$ versus $0.41 \text{ count s}^{-1}$ at mass 239, and $1.95 \text{ count s}^{-1}$ versus $0.43 \text{ count s}^{-1}$ at mass 240). The additional polyatomic species induced-background is equivalent to plutonium concentrations of roughly 0.5 fg ml^{-1} .

Table 1 Average, maximum and minimum contributions of polyatomic interferences made with iridium, mercury and lead on the background at masses 239 and 240 for plutonium measurements carried out for years 2007-2009 (137 measurements); comparison with the instrumental background, referred as “IB” The sum of all polyatomic interferences is referred as “total”.

Heavy element	Mass 239			Mass 240		
	Average	Minimum value	Maximum value	Average	Minimum value	Maximum value
Ir	0.16	0.00	3.78	0.03	0.00	0.80
Hg	0.40	0.01	3.66	0.59	0.01	8.18
Pb	0.67	0.00	14.05	1.33	0.00	29.68
Total	1.23	0.01	14.34	1.95	0.01	30.10
IB	0.41	0.00	1.67	0.43	0.00	1.75

In addition to instrumental background and to polyatomic interference induced-background, other sources of background are on the one hand isotopic impurities of the isotopic dilution (ID) tracer ^{242}Pu , which contains small amounts of ^{239}Pu and ^{240}Pu , and on the other hand peak tail of ^{238}U at masses 239 and 240 plus hydrides of ^{238}U at mass 239. For each one of the measured samples, we determined the percentage of the background count rate which is due to each source of background. Then, from all these values, we calculated the average percentages, which are plotted in Figure 1. At mass 239, sum of polyatomic interference is one of the largest sources of background (~22%) with impurities of the ID tracer ^{242}Pu (~24%) and sum of ^{238}U hydrides and peak tail (~37%). Instrumental background at mass 239 only accounted for ~17% of the total background. At mass 240, sum of poly-atomic interference represents the

most important contribution to the total background (~50%) well above instrumental background, ID tracer impurities and ^{238}U peak tail. By calculating for each measurement the theoretical limit of detection only based on electronic background, ID tracer impurities, ^{238}U peak tail and ^{238}U hydrides, without taking into account the polyatomic interference, we show that false detections of ^{239}Pu and ^{240}Pu may have occurred for respectively 15% and 22% of the samples.

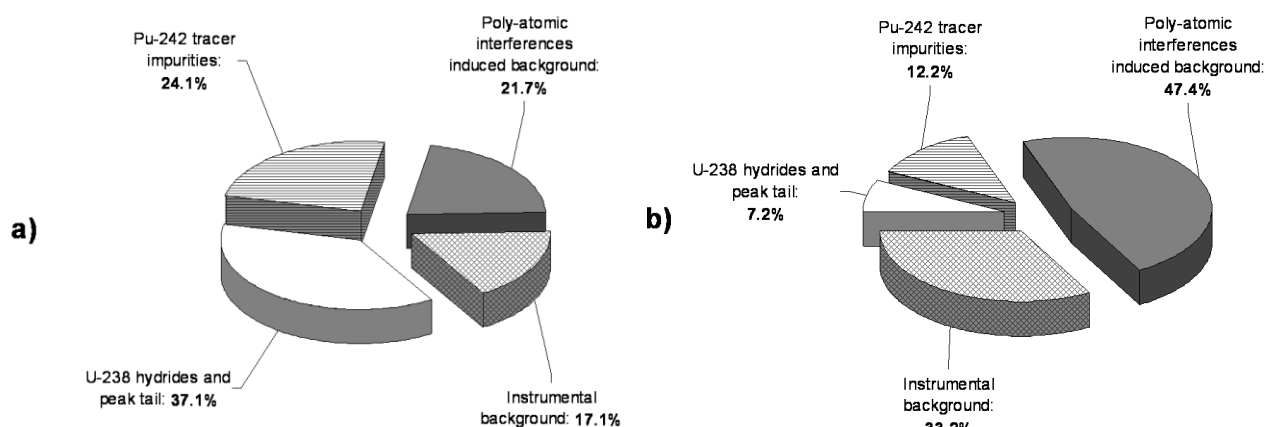


Fig.1 Drawing out of the composition of the total background budget at masses 239 (a) and 240 (b), average percentages over all plutonium measurements carried out for years 2007-2009 (137 measurements).

3. Determining the chemical composition of uranium compound by micro-Raman spectrometry

We used a micro-Raman spectrometer (MRS, “InVia”, Renishaw PLC, Wotton-Under-Edge, Gloucestershire, UK) with two different laser excitation sources (514 and 785 nm) and variable laser powers to identify some uranium chemical species contained in airborne particulate matter. For the analysis of particulate material, we typically acquire at least 3 spectra of 20 seconds each, from 100 cm^{-1} to 2000 cm^{-1} . Optimal laser powers are set to 1% of the maximal value for the 514 nm – laser (i.e. 0.5 mW) and to 0.5% of the maximal value for the 785 nm – laser (i.e. 1.5 mW). Lower powers do not provide enough sensitivity for micrometric targets whereas higher powers may lead to a quick thermal decomposition of the particle.

In the first part of this work [7], we demonstrated that characteristic Raman bands mentioned in the literature for several uranium compounds relevant in the nuclear industry can be identified in particles in the few μm to 30 μm size range. This step was necessary to ensure the applicability of MRS to identify relevant uranium compounds contained in micrometer-size particles coming from real samples. For this, we have to check our ability to recover characteristic bands identified by other authors for various uranium compounds. Small amounts of selected uranium compounds such as metallic uranium, U_3O_8 , $\text{UO}_4(4\text{H}_2\text{O})$, UO_3 , UO_2 , UO_2F_2 , UF_4 , and ADU (Ammonium Di-Uranate), produced by Areva (Pierrelatte, France) were collected with adhesive carbon disks from bulk materials (each disk containing only one compound). No specific precautions were taken for storing our samples. It should be kept in mind that these materials are not reference materials, although their bulk composition is reportedly well characterized and guaranteed by the producer. Our intention is to confirm (or not) the chemical compound present in the particles via confrontation with available Raman data on the same uranium compounds, obtained most of the time on significant amounts of materials (crystals, large particles, powder, bulk material, etc).

For these characterizations, particles were observed directly with the optical microscope of the MRS. Particle size distributions were large, but only particles in the size range of a few μm to a few tens of μm were studied. Raman bands regarded as the characteristic bands of a given uranium compound are the ones that are reproducibly observed for all particles. For each carbon disk we analysed 30 particles with each laser. For each particle, we acquired 4 to 10 spectra. Results are summarized in Table 2. Raman spectra are compliant with the literature, except for UO_3 , which exists in at least five crystalline phases, some of them not characterized by MRS. Consequently we assume that the crystalline phase of the UO_3 analysed is not the same as the phases studied by other authors. Moreover, we also observed that metallic uranium successfully oxidized under laser irradiation, to get U_3O_8 signal.

Table 2. Main Raman bands detected or predicted by various authors for different uranium compounds in bulk or particulate materials. s: strong band, m: medium-strength band, w: weak band.

U compounds	Wave-numbers of the main peaks (cm^{-1})	Lasers (nm)
UO_4	126 (w), 242 (w), 311 (w), 823 (s), 867 (m)	785 nm
UO_3	845 (s), 1052 (w)	785 nm
U_3O_8	185 (w), 351 (m), 412 (s), 487 (m), 810 (m)	785 nm
UO_2	445	514 & 785
UF_4	915 (w)	514

In the second part of this study [7], we developed a method to carry out Raman analysis on airborne uranium particles sampled along with a majority of other kinds of particles simply by dabbing adhesive carbon disks on dusty surfaces. This methodology involves a SEM (XL30 ESEM, FEI, Eindhoven, The Netherlands) equipped with an energy dispersive X-ray analyser and software for automated detection of particles specifically to locate uranium particles on the substrate before the Raman analysis (the so-called “gun shot residue” (GSR) which allows detecting automatically particles whose average atomic number is above a given threshold – usually 20 to 25). To relocate the particles located beforehand by SEM inside the MRS’s measurement chamber, we apply a relocation method based on the identification of landmarks on the sample holder and on suitable calculations. Landmarks are given features on two copper grids currently used in transmission electron microscopy (TEM). These two copper grids are glued on two sticky carbon disks which are set out on each side of the sticky carbon disks on which the particles are deposited. The coordinates of a particle inside the MRS are calculated using rather straightforward arithmetical operations since we know the positions of landmarks both inside the SEM and the MRS and the position of the particle inside the SEM with respect to the internal reference systems of each instrument. This method of relocation, based on the use of 2 reference marks, was used previously in our laboratory to relocate particles detected by SEM before isotopic analysis by SIMS [8]. The precision of the SEM to MRS relocation is $\pm 20 \mu\text{m}$. After localization of the particles, the sample holder is transferred to the micro-Raman spectrometer and particles are relocated using landmarks and simple geometric calculations. Raman analyses are carried out with the laser that gives the best signal to noise ratio. With such a method particles as small as $5 \mu\text{m}$ can be efficiently analysed, although most of the smaller particles cannot be analysed due to limited precision of the relocation process.

This relocation method was applied to 20 uranium real-life particles, with sizes ranging from $5 \mu\text{m}$ to $30 \mu\text{m}$, which do not present initially characteristic Raman bands. After irradiation, U_3O_8 spectra were collected, showing that these airborne particles might be metallic uranium. In the near future, we planned to implement a coupling interface between the SEM and the MRS, which allows the Raman analysis to be carried out inside the SEM measurement chamber, thereby eliminating the need of the relocation process.

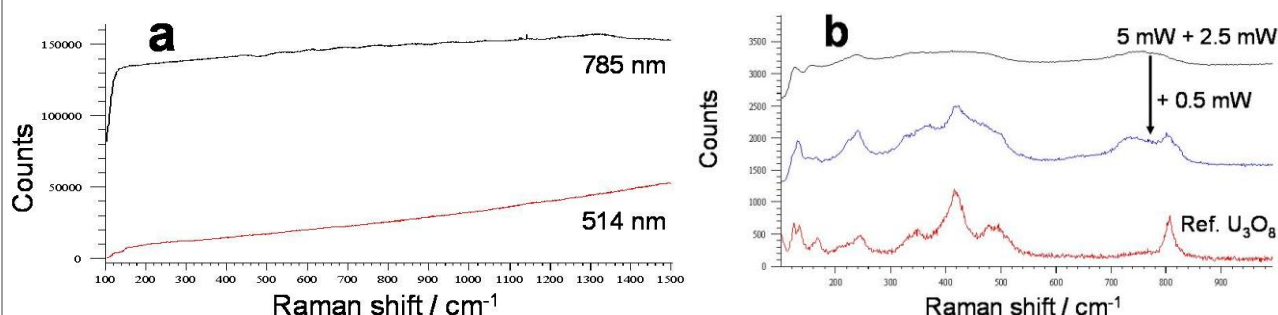


Fig. 2. (a): first spectra obtained with the 514 and 785 nm lasers for a uranium particle of unknown composition ($3 \times 20 \text{ s}$, 0.5 mW at 514 nm , 1.5 mW at 785 nm). (b): spectra obtained with the 514 nm – laser after successive irradiations with laser powers of 5 mW and 2.5 mW (upper spectrum) and after an additional irradiation of 0.5 mW (middle spectrum). This latter spectrum can be compared to the reference spectrum for U_3O_8 (lower spectrum). Vertical axes are shifted for better legibility of the spectra.

4. Developing alternative method for particle analysis: coupling of laser ablation with ICP-MS

Laser ablation provides a good spatial resolution (a few μm at best) and a correct introduction yield

of ablation debris into the plasma. Besides, ICP-MS is a very sensitive technique. The coupling LA-ICP-MS proves to be an efficient technique for the direct analysis of solid samples. Therefore, we estimated that the coupling of ICP-MS and of a laser ablation device deserved to be tested as a potential alternative technique for particle analysis.

Tests were made through collaboration with a laboratory already equipped with a performing laser ablation system (Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, IPREM, UMR 5254 CNRS/Université de Pau et des Pays de l'Adour, Pau, France). We used a femtosecond – infra-red laser with a high repetition rate laser source (till 10 kHz) (“Alphamet”, Amplitude System and Novalase, Bordeaux, France). This device was coupled with a quadrupole-based ICP-MS (“X-Series II”, Thermo-Fischer, Les Ulis, France). Optimisation of sensitivity and reproducibility were carried on glass standard (IRMM541) and on natural uranium particles. Use of a femtosecond laser provides a significant advantage over other laser ablation systems as ablation results in almost no deposition of ablation debris around the crater. Therefore, we do not observe the “cross-contamination” phenomenon in the vicinity of the ablated area reported by other authors. Use of high repetition rate of the ablation and of fast scanning preserves the advantages of conventional fs laser ablation in terms of very low thermal effects and elemental fractionation [9,10].

The developed methodology for particle consists in: i) a pre-localization of uranium particles by fission tracks or SEM; ii) relocation of the particles on the sample holder inside the ablation cell; iii) ablation of the particles using the optimum conditions (repetition rate, spot size, ablation pattern, pulse energy and duration, dwell time of the ICP-MS, etc.) previously defined. Very noisy, short and transient signals were obtained, mainly because of irregular arrivals of ablation debris of various sizes into the plasma. Therefore, a limited precision over isotopic ratios was obtained, with RSD over $^{235}\text{U}/^{238}\text{U}$ ratios for natural uranium particles around 2% at best. Moreover, minor isotopes (^{234}U , ^{236}U) were not measured during our test experiments. However, an excellent sensitivity was obtained, with detection limits estimated to 10-20 fg for ^{235}U . Indeed, significant signals were measured for the ^{235}U and ^{238}U isotopes for almost all the particles localized by fission tracks (see Figure 3). Tests performed on standard particles and on a real sample already analyzed by FT-TIMS and SIMS showed that isotopic signatures evidenced by SIMS and FT-TIMS were recovered, as well as intermediate signatures probably due to the fact that more than one particle may stand in the ablated area. Due to very irregular and noisy signal, uncertainties were in some cases very high (RSD > 10% over $^{235}\text{U}/^{238}\text{U}$ ratios).

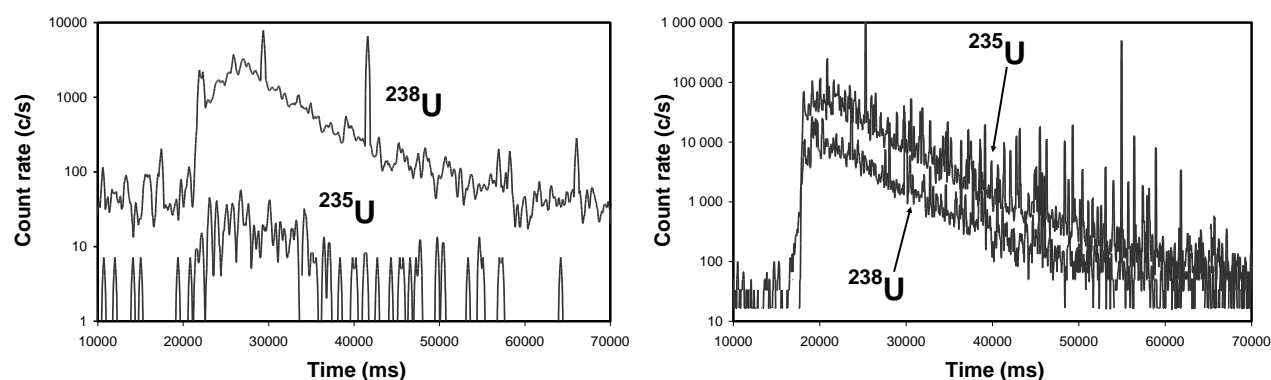


Fig. 3. Examples of laser ablation – ICP-MS measurements for uranium particles: for a small natural uranium particle (graph on the left) and for a highly enriched uranium particle (graph on the right). These spectra were obtained with “Alphamet” ablation device coupled with a quadrupole-based ICP-MS “X-Series”.

A few tests were also made with a multi-collector ICP-MS equipped with several ion counters (“Nu-Plasma”, Nu-Instruments, UK). First results showed a significant improvement of the precision over isotopic ratio measurement, but also some bias effects when two different kinds of detector were used (a Faraday cup for ^{238}U and an ion counter for ^{235}U , for instance).

5. Conclusion

Significant efforts are made by the CEA analytical laboratory to improve on the one side the performance of the techniques already in use, and on the other side to develop new capabilities, either as alternative techniques to the existing ones or new methods that bring new information, complementary to the isotopic composition.

For the trace analysis of plutonium in swipe samples by ICP-MS, we demonstrate that a thorough knowledge of the background is desirable. In order to avoid false plutonium detection in the femtogram range, correction from polyatomic interferences including mercury, lead or iridium atoms are in some case necessary. Efforts must be put on improving the purification procedure.

Micro-Raman spectrometry allows determining the chemical composition of uranium compound at the scale of the particle using a pre-location of the particles using SEM and a relocation thanks to mathematical calculations. However, particles below 5 μm are hardly relocated and a coupling device between the SEM and the micro-Raman spectrometer for direct Raman analysis after location of a particle of interest is currently under testing.

Lastly, laser ablation – ICP-MS is an interesting technique for direct isotopic or elemental analysis of various solid samples and proves to be an alternative technique for particle analysis, although precision over isotopic ratio measurement is strongly limited by the short duration and irregularity of the signals. However, sensitivity and sample throughput are high and more developments are in progress to validate and improve this method.

References

- [1] F. Pointurier, N. Baglan, P. Hémet, “Ultra Low Level Measurements of Actinides by Sector Field ICP-MS”, *Applied Radiation and Isotopes* **60** (2004) 561-566.
- [2] N. Baglan, P. Hemet, F. Pointurier, R. Chiappini, “Evaluation of a Single Collector, Double Focusing Sector Field Inductively Coupled Plasma Mass Spectrometer for the determination of U and Pu concentrations and isotopic compositions at trace level”, *Journal of Radioanalytical and Nuclear Chemistry* **261** (2004) 609-617.
- [3] F. Pointurier, N. Baglan., P. Hémet., Measurement of actinides at ultra-trace level by double-focusing sector-field ICP-MS: instrumental performances and analytical difficulties, Proceedings of 9th International Conference on Plasma Source Mass spectrometry, Durham, UK (12-17 September 2004), in “Plasma Source Mass Spectrometry – Current Trends and Future Developments”, ed. by G. Holland and D.R. Bandura, RSC Publishing, Cambridge, UK (2005), pp.130-142.
- [4] J.S. Becker, M. Zoriy, L. Halicz, N. Teplyakov, C. Müller, I. Segal, C. Pickhardt, T. Platzner, “Environmental monitoring of plutonium at ultratrace level in natural water (Sea of Galilée – Israel) by ICP-SFMS and MC-ICP-MS, *Journal of Analytical Atomic Spectrometry* **19** (2004) 1257-1261.
- [5] J. Zheng, M. Yamada, “ICP-SFMS with a high efficiency sample introduction system for the determination of Pu isotopes in settling particles at femtogram levels”, *Talanta* **69** (2006) 1246-1253.
- [6] F. Pointurier, P. Hémet, A. Hubert, “Assessment of plutonium measurement in the femtogram range by ICP-MS; correction from interfering polyatomic species”, *Journal of Analytical Atomic Spectrometry* **23** (2008) 104-112.
- [7] F. Pointurier, O. Marie, “Identification of the chemical forms of uranium compounds in micrometer-size particles by means of micro-Raman spectrometry and scanning electron microscopy”, To be published in *Spectrochimica Acta Part B*, doi: 10.1016/j.sab.2010.06.008.
- [8] L. Sangély, O. Marie, S. Baude, F. Pointurier, “Combined SIMS / SEM technique for environmental monitoring of nuclear facilities: detection, analysis, and characterization of radionuclide in micrometer-sized particles”, Proceedings of the IAEA Symposium on International Safeguards - Addressing Verification Challenges, Vienna, Austria (16-20 October 2006), pp.813-819, IAEA-CN-148/119.
- [9] B. Fernandez, F. Claverie, C. Pécheyran, J. Alexis, O.F.X. Donard, “Direct determination of trace elements in powdered samples by in-cell isotope dilution femtosecond laser ablation ICP-MS”, *Anal. Chem.* **80** (2008) 6981-6994.
- [10] B. Fernandez, F. Claverie, C. Pécheyran, J. Alexis, O.F.X. Donard, “Solid-skipping isotope dilution laser ablation ICP-MS for the direct and simultaneous determination of trace elements in soils and sediments”, *Journal of Analytical Atomic Spectrometry* **23** (2008) 367-377.