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Analytical developments for high precision isotope measurements on transmutation target in the Phenix fast neutron reactor

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The objective of the PROFIL-R (fast spectrum) and PROFIL-M (moderated spectrum) experiments, performed between 2003 and 2008 in the French fast neutron reactor Phénix, was to collect accurate information on the total capture integral cross sections of the principal heavy isotopes and some important fission products in the spectral range of fast reactor. The method consists of the irradiation of pure isotope samples and the determination of the composition change induced by irradiation. The elements present in powder form are representative of actinides and fission products present in irradiated fuels and cover all the applications for which accurate capture integral cross section are necessary. Then, accurate measurements of isotopic compositions and concentrations of the elements (actinides and fission products) before and after irradiation are required. The major difficulty for the analyses of products is the low quantity of the initial powder enclosed in steel container (3 to 5 mg) and the very low quantities of products formed (several μg) after irradiation. During several years developments have been performed in different laboratories of the CEA for the conception of a system implanted in shielded cell installations to open the steel container, collect the integrality of the powder and quantitatively dissolve each product. For several powders, like metallic ruthenium, metallic silver or metallic rhodium, this last step was a challenge due to the very high resistance of these metals to acid solutions. After recuperation and dissolution the second stage consists of mass spectrometric measurements in order to obtain isotope and elemental ratio at uncertainty of few per mil level. As very low measurement uncertainties are required for these applications, elemental and isotopic measurements are usually performed with state of the art mass spectrometric techniques such as thermal ionization mass spectrometry (TIMS) and multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) associated with the isotope dilution technique (ID). Furthermore it requires preliminary chemical separation to eliminate the elements which could prevent ionization and/or generate isobaric interferences in the mass spectrum of the analytes during measurements, thus leading to non-accurate isotopic analysis. We present the axes of analytical developments performed in the Nuclear, isotope and elemental analytical development laboratory (LANIE) to acquire accurate isotope ratios. Innovative method of separation like the hyphenation of liquid chromatography with ICPMS and MC-ICPMS or the use of collision reaction cell present in recent generation of ICPMS, have been developed. Several examples of analyses of irradiated transmutation targets will be presented. These various analytical developments demonstrate the considerable gains that can be expected in the near future in terms of sample amounts, handling time, and waste production associated to the high precision elemental and isotopic characterization of irradiated samples.

I. INTRODUCTION

The PROFIL-R and M experiments were performed between 2003 and 2008 in the French fast neutron reactor Phénix and took place after the earlier experimental program PROFIL and PROFIL-2¹.

PROFIL-R was performed in a standard fast neutron spectrum and PROFIL-M in a spectrum softened by a thick ¹¹B₄C sheath around the experimental pins. The

experiments consisted of the irradiation of pure isotope on powder form. Each enriched powder was enclosed in steel container inserted in individual pins of identical geometry for the two experiments. The elements present in powder form are representative of actinides and fission products present in irradiated Uox and Mox fuel samples and cover all the applications for which accurate capture integral cross section are necessary. The major difficulties for the analyses of these actinides and fissions products are the

low quantity of the initial powder enclosed in steel container (3 to 5 mg) and the very low quantities of activation products formed (several μg or ng) after irradiation.

The powders are recuperated in shielded cell installations and dissolved in different acid media. The development of the recuperation and dissolution operations has required research studies for several years conducted in different CEA laboratories of the Nuclear Energy Division. After dissolution accurate elemental and isotopic analysis were performed by mass spectrometry in the Nuclear, isotope and elemental analytical development laboratory (LANIE). It requires preliminary chemical separation to eliminate the elements which could prevent ionization and/or generate isobaric interferences in the mass spectrum of the analytes during measurements, thus leading to non-accurate isotopic analysis²⁻⁴. In order to guarantee the trueness and accuracy of the elemental and isotopic data, measurements are performed by Thermal Ionisation Mass Spectrometry (TIMS) or Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS).

This paper presents the main axes of analytical developments performed during the last few years that were applied to selected irradiated pure isotopes. Several examples of measurements performed in the irradiated targets of the PROFIL-R and M experiments will be presented.

II. PROFIL-R AND M PINS

The PROFIL-R experiment involved two experimental pins (labelled A and B) containing 55 separate samples each and loaded in the 4th fissile ring of the Phenix reactor core occupying a neutronicallly clean zone without control rods. Axially distributed ²³⁵U containers were used as fluence monitors for each pin. A standard fuel pin in the central assembly position was characterized to measure the fluence data.

The PROFIL-M experiment used six experimental pins (labelled 1 to 6) containing 21 (pin 6), 22 or 23 (pin 1) separate samples each. Axially distributed ²³⁵U containers were also used as fluence monitors for each pin

The Table 1 give the number of different samples loaded in each experimental pin.

TABLE I
Number of experimental samples per isotope in the PROFIL-R and PROFIL-M pins.

	PROFIL			PROFIL	
	R	M		R	M
²³² Th	3	3	¹⁰² Ru	2	3
²³³ U	2	3	¹⁰⁴ Ru	2	3
²³⁴ U	2	3	¹⁰³ Rh	2	2
²³⁵ U	9	12	¹⁰⁴ Pd	2	2
²³⁸ U	3	5	¹⁰⁵ Pd	2	2
²³⁷ Np	4	2	¹⁰⁶ Pd	2	2
²³⁸ Pu	3	2	¹⁰⁷ Ag	2	2
²³⁹ Pu	2	4	¹⁰⁹ Ag	2	2
²⁴⁰ Pu	3	2	¹²⁹ I	3	2
²⁴² Pu	3		¹³³ Cs	2	3
²⁴² Pu*		4	¹⁴⁰ Ce	3	3
²⁴¹⁻²⁴³ Am	3	2	¹⁴¹ Pr	2	2
²⁴¹ Am		5	¹⁴³ Nd	2	2
²⁴³ Am		5	¹⁴⁵ Nd	2	2
²⁴⁴ Cm		6	¹⁴⁶ Nd	2	3
B	2	2	¹⁴⁷ Sm	2	2
⁸⁷ Rb	3	3	¹⁴⁹ Sm	2	2
⁹¹ Zr	3	3	¹⁵⁰ Sm	2	2
⁹² Zr	3	3	¹⁵² Sm	2	2
⁹⁵ Mo	2	2	¹⁵³ Eu	2	2
⁹⁷ Mo	2	2	¹⁵⁴ Gd	2	2
¹⁰⁰ Mo	3	3	¹⁵⁵ Gd	2	2
⁹⁹ Tc	3	2	¹⁵⁶ Gd	2	2
¹⁰¹ Ru	2	2	¹⁵⁷ Gd	2	2

* The enrichment of the powder in ²⁴²Pu was different between PROFIL-R and M

III. RECUPERATION AND DISSOLUTION OF THE POWDERS

All the operations of opening and recuperation were realized by teleoperation in shielded cell in two nuclear installations of the French Commission on Atomic Energy and Alternative Energies (CEA): the CHICADE hot cell facility located in Cadarache and the ATALANTE facility located in Marcoule. The main difficulty arises from the size of the telemanipulated container and the very small

quantity of the powder recovered. Furthermore it is major during these operations to avoid pollution by any radioelements or natural element that could be present in the hot cell.

Several containers were first opened using an Electro Chemical Discharge Machining⁵. However this technique was found to enable the introduction of the solution of electroerosion with preferential solubilisation of some elements (like Cs and Nd) in the container. To prevent this phenomenon and maximize the recuperation rate, a milling was further used to open the container by mechanical abrasion. Using this system the recuperation rate was maximal and permitted the recuperation of the powder without contamination with elements present in the steel.

The chemical forms for all elements of PROFIL-R experiments are presented in Table II.

TABLE II

Chemical form of the powders present in the PROFIL-R and M container.

Group	Element	Chemical form
Alkali metals	Rb	Rubidium carbonate
	Cs	Cesium sulfate
Transition metals	Zr	Zirconium oxide
	Mo	Metal and molybdenum oxide
	Tc	Technetium oxide
	Ru	Metal powder
	Rh	Metal powder
	Pd	Metal powder
Nonmetals	Ag	Metal powder
	B	Metal powder
	I	Sodium iodide
Lanthanides	Ce	Cerium oxide
	Pr	Praseodymium oxide
	Nd	Neodymium oxide
	Sm	Samarium oxide
	Eu	Europium oxide
	Gd	Metal powder and Gadolinium oxide
Actinides	U	Uranium metal and oxide
	Pu	Plutonium oxide
	Am	Americium metal and oxide
	Cm	Curium oxide
	Np	Neptunium oxide
	Th	Thorium oxide

The protocols of dissolution were developed by the Laboratoire d'Etude de Dissolution (LED) for actinides elements and by the Laboratoire d'Analyse Chimique et RadioChimique (LARC) for non-actinides elements. The digestion media used must avoid the introduction of pollutants and the loss of some elements by volatilisation (such as Ru in nitric media). Furthermore it must take into account the stability of all elements present after irradiation. For example, specific protocols have been developed to stabilize Ag, Cd and Pd in the dissolution solution of the ¹⁰⁹Ag irradiated target⁶.

To avoid introduction of pollutants, powders were dissolved in Teflon vials with ultrapure acid certified for their very low impurities contents. The procedures were based on wet digestion using single acid (HNO₃) or some combinations (HNO₃, HCl, HF...). Actinides, lanthanides and alkali metals, are dissolved on a hot plate at ambient pressure. For transition metals, techniques of high pressure microwave were developed.

IV. ANALYTICAL DEVELOPMENT FOR MASS SPECTROMETRIC MEASUREMENTS

For each target, isotopic compositions and elemental ratios are required with a low level of uncertainty. In the major case uncertainties on isotope ratio are less than 0,5% and uncertainties on elemental ratio are less than 1%.

Isotope ratio measurements are performed by mass spectrometry using Thermal Ionisation Mass Spectrometry (TIMS), Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) or in some cases using Quadrupole Inductively Coupled Plasma Mass Spectrometry (Q ICPMS)⁷⁻¹⁰. To be able to obtain uncertainty less than 1% on elemental ratios the isotope dilution (ID) technique associated with isotopic measurements were used. This method is based on the addition to the sample of a known quantity of the same element but with a different isotopic composition¹¹. In

addition, the sources of uncertainties of the isotope dilution method are well understood and controlled and this technique has been also used for different nuclear applications^{7,12}.

Prior to mass spectrometric measurements, chemical separation steps are required in order to avoid matrix effects and isobaric interferences. Innovative methods of separation based on the hyphenation of liquid chromatography with ICPMS or the use of the collision reaction cell present in some ICPMS instruments, have been developed.

IV. A. Chromatographic separation and hyphenated techniques

On-line coupling of liquid chromatography to an inductively coupled plasma mass spectrometer (ICP-MS) is a well-established method to reduce the handling time and consequently the analyst's exposure to radiation in the case of radioactive samples. For the two targets ¹⁰⁹Ag and ¹⁵³Eu on-line coupling of High Performance Liquid Chromatography (HPLC) for separation of Ag-Pd-Cd and Eu-Gd-Sm, respectively, and Q-ICPMS were developed^{4,6}. In the case of the ¹⁵³Eu target, measurement of the ¹⁵²Sm/¹⁵³Eu ratio after irradiation is of prime interest in relation with the determination of the capture integral cross section of ¹⁵¹Eu. To determine this ratio and due to isobaric interferences at m/z=152, Sm had to be separated from Gd and Eu. The separation was performed by HPLC using a silica sulphonated support as stationary phase and hydroxy-methyl butyric acid (HMBA) as eluent solution. The column was directly coupled to a high sensitive Q-ICPMS. In order to obtain a low uncertainty, this coupling has been associated with the method of the double isotope dilution. The external reproducibility of Sm isotope ratios was determined to be around 0.5% (2σ) resulting to a final uncertainty on the ¹⁵²Sm/¹⁵³Eu ratio around 1% (2σ). These on-line measurements present a robust and high-throughput alternative to the thermal-ionisation mass

spectrometry technique used so far in combination with off-line chromatographic separation.

To decrease the uncertainty on isotope ratios, the coupling between LC and multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) was developed for Nd isotope ratios on ²³⁵U irradiated targets¹³. The reproducibility obtained on all Nd isotope ratios on a simulated ²³⁵U fission product fraction, after appropriate data treatment, was lower than 0.2%.

The feasibility and performances on such on-line Nd isotope ratio measurements have been demonstrated as an alternative to off-line methods for nuclear samples and can now be applied to real samples.

IV.B. Direct separation using collision-reaction cell

Chemical purification has the major disadvantage for trace and ultra-trace elemental analysis to increase the risk of introducing natural contamination and lose a significant amount of the analytes during the chemical separation. Several analytical developments were then conducted with the collision reaction cell implanted on a Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) to perform separations directly within the cell by using a reaction gas. When the analyte and the interfering ions enter inside the cell, the gas reacts selectively with one of the species to reduce or suppress the interference¹⁴. If the ion-molecule reactions between the interfering ions and the reaction gas are thermodynamically and kinetically allowed, they will react quickly and specifically¹⁵.

For three targets (¹⁵³Eu, ²³⁵U and ⁹⁵Mo) analytical methods were developed to perform direct separation in the collision reaction cell of a MC ICPMS. An estimation of the quantity of products formed and the major isobaric interferences are presented in Table III.

TABLE III

Isobaric interferences and mass products formed for ^{235}U , ^{153}Eu and ^{95}Mo target

Target	Elements present after irradiation	Mass present after a 3-year cooling (μg)	Isobaric interferences
^{235}U	U	1587	$m/z=238$ (U, Pu)
	Pu	0.9	"
	Nd	50	$m/z= 148, 150$ (Nd, Sm)
	Cs	30	$m/z= 134, 135, 137$ (Cs, Ba)
^{153}Eu	Eu	4745	$m/z= 154$ (Eu, Gd, Sm)
	Gd	262	$m/z= 155$ (Eu, Gd)
	Sm	2.3	$m/z= 152$ (Eu, Gd, Sm)
^{95}Mo	Mo	5000	$m/z= 92$ (Mo, Zr)
	Zr	0.2	"

The interference resolutions for these targets were Eu/Gd-Sm, U-Pu and Mo-Zr, respectively. The three gases selected for the interference resolution were O_2 for Eu/Gd-Sm, CO_2 for U-Pu and N_2O for Mo-Zr.

In the case of the ^{235}U target, it was demonstrated that Pu and U react differently towards CO_2 gas, which allows accurate and precise Pu and U isotopic measurements on Pu^+ and UO_2^+ forms, by using two different CO_2 gas flows (Fig. 1). A good agreement between isotope ratios of U and Pu measured with CO_2 in the cell and U and Pu measured after chemical separation was obtained. The relative difference of the average isotope ratio values between the purified fractions and the direct CO_2 measurements was found to be 0.38% and 0.11% for U and Pu, respectively¹⁷.

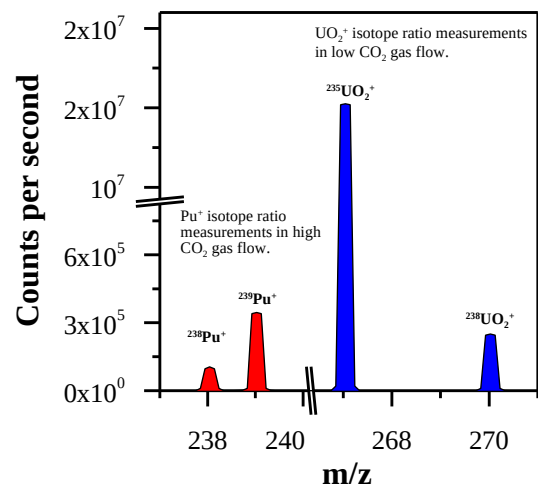


Fig. 1. Sensitivity of U and Pu by MC-ICPMS using different gas flow rates. The strong reactivity of U^+ towards CO_2 gas allows recovering high precision Pu isotope ratios despite U isobaric interference for a high CO_2 gas flow. Furthermore, uranium isotope ratio could also be measured as double oxide species at low CO_2 gas flow¹⁷

For the ^{153}Eu target the results obtained on the Eu isotope ratios obtained by direct separation in the cell with O_2 are compared to results obtained after chromatographic separation classically used in the laboratory¹⁹ (Table IV)

TABLE IV

Eu isotope ratio measurements in the ^{153}Eu target by direct separation in the cell with O_2 compared to results obtain after Eu chemical purification¹⁹

	Direct separation in the cell with O_2 gas	After chemical separation in the cell
$^{151}\text{Eu}/^{153}\text{Eu}$	0.007842 (16)	0.007826 (10)
$^{152}\text{Eu}/^{153}\text{Eu}$	0.001249 (5)	0.001244 (3)
$^{154}\text{Eu}/^{153}\text{Eu}$	0.13313 (4)	0.13315 (16)
$^{155}\text{Eu}/^{153}\text{Eu}$	0.012238 (4)	0.012241 (24)

The excellent agreement of the results confirms the ability of the in-situ Eu-Gd-Sm separation by O_2 addition in the collision reaction cell to produce accurate and highly reproducible Eu isotope ratios.

Several studies have demonstrated the capability of the collision-reaction cell of a MC-ICPMS to resolve in-situ

isobaric interference and provide accurate and reproducible isotope ratios in irradiated transmutation targets. This approach offers a great interest for trace element determination when natural contamination is critical and in the case of high activity sample in which minimal quantity of elements has to be analyzed.

V. CONCLUSIONS

PROFIL-R and M experiments irradiated in the French fast neutron reactor Phénix is providing a collection of accurate information on the total capture integral cross sections of the principal heavy isotopes and some important fission products. This program has required many developments, for the irradiated powder recovery, the dissolution, and the analysis by mass spectrometry. They have been implemented in several laboratories of the French Commission on Atomic Energy and Alternative Energies (CEA) for the past few years. At this stage of the project 22 targets of PROFIL-R experiment and 9 targets of PROFIL-M experiment, have been completely analysed.

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Put acknowledgments here.

NOMENCLATURE

Put nomenclature here.

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