Irradiated UAmO2 transmutation discs analyses: from dissolution to accurate isotopic analyses

Alexandre Quemet, Emilie Buravand, Jean-Gabriel Peres, Vincent Dalier, Syriac Bejaoui

Names of the authors: Alexandre Quemet[1], Emilie Buravand[1], Jean-Gabriel Peres[1], Vincent Dalier[1] and Syriac Bejaoui[2]

Title: Irradiated $UAmO_2$ transmutation discs analyses: from dissolution to isotopic analyses

Affiliation(s) and address(es) of the author(s):

- [1] CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France
- [2] CEA, DES, IRESNE, DEC, SESC, LECIM, F-13108 Saint-Paul-Lez-Durance, France

E-mail address of the corresponding author: alexandre.quemet@cea.fr

Irradiated $UAmO_2$ transmutation discs analyses: from dissolution to isotopic analyses

Alexandre Quemet[1], Emilie Buravand[1], Jean-Gabriel Peres[1], Vincent Dalier[1] and Syriac Bejaoui[2]

[1] CEA, DES, DMRC, Univ Montpellier, Marcoule, France

[2] CEA, DES, IRESNE, DEC, SESC, LECIM, F-13108 Saint-Paul-Lez-Durance, France

Abstract

This paper details the different steps for the isotopic determination of $UAmO_2$ discs from analytical irradiation. MARIOS and DIAMINO irradiations were performed in materials testing reactors to study the behaviour of americium bearing blanket samples in regard of heterogeneous recycling in sodium-cooled fast reactor. Six irradiated discs were dissolved in hot cells and were analyzed to determine isotope ratios of uranium, plutonium, americium and neodymium. The ratios were measured combining chemical separations and TIMS analyses. Using the double isotope dilution methodology helps measuring $^{238}Pu/^{238}U$, $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ ratios with uncertainty about a few per mil (k = 2).

Keywords

TIMS, isotope ratio, isotope dilution, transmutation, ion exchange resin, HPLC

Introduction

Since 2008, the French Alternative Energies and Atomic Energy Commission (CEA) started a program dedicated to study the americium recycling [1–4]. The R&D program is devoted to develop actinide bearing blankets for transmutation in sodium-cooled fast reactor. Two different kinds of fuel, containing americium, were manufactured in the ATALANTE facility: $U_{0.85}Am_{0.15}O_2$ discs with dense and tailored porosity [5]. Two separate-effect irradiation experiments were performed to understand the $UAmO_2$ discs behavior under irradiation and to determine the americium transmutation yield. The experiments were also devoted to study the influence of the microstructure on the gas release as a function of temperature [1]. Indeed, a large quantity of helium is produced under irradiation, mainly coming from the transmutation chain of ^{241}Am isotope, and could lead to significant swelling and a pellet-cladding interaction. The first irradiation experiment, called MARIOS, was implemented in the High Flux Reactor (Petten, Netherland) from March 2011 until May 2012, and investigated temperatures ranged between 1000 and 1200°C. The second experiment (DIAMINO irradiation) was irradiated in the OSIRIS reactor (Saclay, France) from February 2014 until December 2015 and focused on temperatures ranging between 600 and 800°C.

To obtain the transmutation yield and compare experimental results with neutronic simulation codes, isotopic analyses after quantitative dissolution of the irradiated discs were performed. Among these determinations, U, Pu, Am, Cm and Nd isotope compositions must be obtained accurately (*i.e.* measurement trueness and precision). Moreover, simulation codes require data on ^{238}Pu/^{238}U, ^{241}Am/^{238}U and ^{148}Nd/^{238}U ratios. In the nuclear fuel, the burn-up is monitored using stable or long-lived isotopes (*e.g.* ^{148}Nd/^{238}U ratio) that are invariantly produced under most conditions: a certain amount of each isotope is produced per fission occurring in the fuel. Six irradiated discs were dissolved and dissolution solutions were analyzed in the ATALANTE facility: 2 from MARIOS irradiation experiments [3] and 4 from DIAMINO irradiation experiments [1]. This study is focused on the U, Pu, ^{238}Pu/^{238}U, ^{241}Am/^{238}U and ^{148}Nd/^{238}U isotope ratio determination.

Spent fuels are commonly dissolved in hot nitric acid in reprocessing plants [6, 7]. Nevertheless, a mixture of nitric acid and hydrofluoric acid was used to ensure plutonium quantitative dissolution in this study [6–8].

Thermal Ionization Mass Spectrometry (TIMS) is an instrument of choice for actinides and lanthanides isotopic analysis with high accuracy [9–15]. Several artefacts disrupt the TIMS measurements: isotope fractionation, abundance sensitivity or isobaric interferences.

Isotope fractionation comes from an evaporation difference between the light and the heavy isotopes, causing a bias on measured isotope ratios. Different methodologies can be used to overcome the isotope fractionation: internal or external normalization or the total evaporation method (TE method). The TE method is generally used in the nuclear field to obtain reference values of all the measured isotope ratios [16]. It is based on the evaporation and the ionization of the entire sample. Therefore, the ion beam of the element is totally collected by a multi-collection system. This method is barely affected by the isotope fractionation and was successfully applied to U, Pu, Am or Nd [14, 17–19].

Minor isotope ratios analyses (*e.g.* $^{234}U/^{238}U$ or $^{236}U/^{238}U$) is more complicated due to low signal or abundance sensitivity contribution. The abundance sensitivity (or peak tailing effect) is the contribution of the major isotope peak tail (*e.g.* ^{235}U or ^{238}U) to the minor isotope detection (*e.g.* ^{234}U or ^{236}U). Using Faraday cups coupled to a 10^{12} or 10^{13} Ω current amplifier, instead of 10^{11} Ω, helps improving the TIMS sensibility [9]. For very low signal, using Secondary Electron Multiplier (SEM) improves dramatically the TIMS sensitivity., Using the SEM coupled to a Retarding Potential Quadrupole Lenses improves the measurement trueness by improving the abundance sensitivity. But, low SEM stability renders low uncertainty measurements difficult. The TE method limits the $^{234}U/^{238}U$ or $^{236}U/^{238}U$ ratios uncertainties to about few percent [17]. The development of a method with multi-dynamic sequences allowing mathematical correction of the abundance sensitivity, calibrating the SEM while the method is running and correcting isotope fractionation using internal normalization improve the measurement trueness, the repeatability as well as the uncertainties [17].

Isobaric interferences (*e.g.* $^{148}Nd/^{148}Sm$, $^{150}Nd/^{150}Sm$, $^{238}U/^{238}Pu$, $^{241}Am/^{241}Pu$ or $^{242m}Am/^{242}Pu$) are another bias observed for TIMS measurements. Chemical separation using ion exchange resin or High-Performance Liquid Chromatography (HPLC) is an efficient method to reduce them. The separation on resin takes advantage of ion exchange resins' different affinity with each element, according to its chemical species, its oxidation state and the environment acidity. By putting the resin in contact with wisely chosen eluents, it is possible to separate the species. The ion exchange resin TEVA (for TEtraValent Actinides) and UTEVA (for Uranium and TEtraValent Actinides) are well known to purify U, Pu and trivalent elements like Am [19–22]. The Am/Cm and the lanthanide separation can be achieved using HPLC [16, 19, 23, 24]. Using optimal separation conditions helps purifying Nd and Am in the same experiment [19].

Combining TIMS measurement and isotope dilution methodology (ID-TIMS) is a powerful method for mass fraction determination [14, 25, 26]. $^{238}Pu/^{238}U$, $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ ratios can be calculated using U, Pu, Am and Nd mass fractions obtained by ID-TIMS, ^{238}U, ^{238}Pu, ^{241}Am and ^{148}Nd isotope abundances and molar masses. The $^{238}Pu/^{238}U$ ratio uncertainty can be, in first approximation, estimated by propagating U and Pu mass fraction uncertainties. Considering the U and Pu mass fraction measurement uncertainties in safeguards nuclear materials using ID-TIMS in hot cell condition (0.84 %, k = 2) [27], the $^{238}Pu/^{238}U$ ratio uncertainty will be estimated to 1.2 % (k = 2) using the propagation of uncertainty [28]. $^{238}Pu/^{238}U$, $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ ratios uncertainties will be limited to few percent using the ID-TIMS methodology, which is not enough for neutronic calculation validation.

The double isotope dilution (DID) methodology is another method to determine the ratio between two isotopes of two elements present in a sample, with one of them used as a reference [29]. As for the isotope dilution, this method is based on the addition of a spike to the sample. The spike solution contains the same analytes as the sample with a different isotope composition. For instance, for the $^{238}Pu/^{238}U$ ratio determination a spike enriched with ^{235}U and ^{242}Pu isotopes is required. This spike must be certified for the $^{242}Pu/^{235}U$ ratio. The $^{238}Pu/^{242}Pu$ and $^{238}U/^{235}U$ ratios determination of the (sample – spike) mixture reflect the $^{238}Pu/^{238}U$ ratio of the sample. The DID helps obtaining accurate measurements

as it is only based on isotope ratios determination. Separation yields and weights uncertainties are not to be taken into account in such case.

This paper aims at detailing the different steps for the isotopic analyses of the irradiated discs from the MARIOS and DIAMINO experiments. Methods and protocol optimization for the accurate isotopic measurements performed by TIMS measurements will be detailed. The same protocol was used for the 2 discs provided from the MARIOS irradiation experiment and for the 4 discs provided from the DIAMINO irradiation experiment. The results presented here focus more specifically on two of the discs: one from the MARIOS experiment (hereafter referred to as MARIOS disc) and one from the DIAMINO experiment (hereafter referred to as DIAMINO disc).

Experimental

Reagents and reference materials

The detailed information about reagents and reference materials can be seen in the supplementary information. The U spike solution, enriched in ^{235}U isotope (93 %), was the IRMM 054 certified reference material (CRM). The Pu spike solution, enriched in ^{242}Pu isotope (95 %), was the IRMM 049d CRM. The Am spike solution, enriched in ^{243}Am isotope (88 %), was the STAM CRM. The Nd spike solution, enriched in ^{150}Nd isotope, was prepared by dissolving a ^{150}Nd enriched (95%) non-radioactive neodymium oxide powder. This solution, hereafter referred to as ^{150}Nd spike solution, is not certified for isotope ratios or mass fraction. The 3135a CRM (natural Nd), was used to determine the ^{150}Nd spike mass fraction by reverse isotope dilution. The 3135a CRM is only certified for the mass fraction (and not for isotope ratios). The IRMM 187 CRM was used for the analytical method validation of ^{234}U/^{238}U and ^{236}U/^{238}U isotope ratios.

The samples analyzed during the “2017 Nuclear Material Round Robin” (hereafter referred to as 2017NMRoRo) and during the “2019 Nuclear Material Round Robin” (hereafter referred to as 2019NMRoRo) inter-laboratory comparisons (ILC) organized by the International Atomic Energy Agency (IAEA) were used to estimate the uncertainties.

These ILC aim at determining U and Pu isotope ratios in a dried mixed Pu-U nitrate samples for the 2019NMRoRo and in a Pu nitrate sample for the 2017NMRoRo. The Pu nitrate sample supplied during the 2017NMRoRo ILC is hereafter referred to as 2017PuNH sample. The Pu-U nitrate sample supplied during the 2019NMRoRo ILC is hereafter referred to as 2019UPuNH sample.

The isotope ratios determined in this study were updated on 2019/10/01 to correct the radioactive decay [30].

Separation experimental set-up

Three different separations using TEVA and UTEVA resins and HPLC were used. Each separation protocol is detailed in the supplementary information. The TEVA and UTEVA resins were used to obtain purified fractions of U, Pu and trivalent elements. The HPLC separation were used to obtain purified fractions of Am and Nd [19].

Thermal Ionization Mass Spectrometer

The measurements were performed with the Thermo Scientific Triton TIMS equipped with a glove box. The instrument is equipped with 9 Faraday cups (all are movables except the central denoted C) which can be coupled to 10^{11} Ω current amplifiers (8 available and hereafter referred to as FC 11), 10^{12} Ω current amplifier (1 available and hereafter referred to as FC 12) or 10^{13} Ω current amplifier (1 available and hereafter referred to as FC 13). 4 Faraday cups are positioned in low masses (noted L1–L4) and 4 Faraday cups are positioned in high masses (noted H1–H4). The TIMS is also equipped with one fixed SEM, equipped with a Retarding Potential Quadrupole Lenses and located behind the central Faraday cup.

A double Re-filament configuration was used to control independently the evaporation and the ionization temperature. These filaments (Re metal, purity 99.99 % and 99.999 %) are provided by ATES (France) and were outgassed for 20 min at 4.5 A in a high vacuum chamber ($<5 \times 10^{-6}$ mbar) before use. The 99.999 % purity was only dedicated for the

$^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios measurements. 1 µL was deposited onto the filament and was dried with a 0.4 A current. After deposition, the current increased progressively to 2 A in 10 seconds.

Isotopic analysis method

Total evaporation method

$^{235}U/^{238}U$, Pu, Am and Nd isotope ratios were measured using the TE method previously described [14, 17–19]. In a nutshell, the TE method is divided in 3 phases: adjustment, acquisition and shutdown phases. First, the ionization filament is heated to 5.5 A in 20 min for Nd analyses and in 10 min for U, Pu and Am analyses. Then, the evaporation filament is heated to obtain the major isotope ions beam of 1 mV. A "peak center" (mass calibration and ions beam centering in the detector) and the lenses optimization of the ion source are performed on the major isotope ion beam. In the second phase (acquisition phase), the data acquisition is started. The evaporation filament current starts to increase until the ion beam intensity of all measured isotopes reaches the target intensity. The evaporation filament is then controlled to keep the ions beam intensity constant, by increasing the evaporation current when necessary. When the evaporation filament current reaches a maximum value of 6.5 A and the ion beam decreases down to a 25 mV signal, the data acquisition is then finished (shutdown phase).

For the DID measurements, the isotopes (^{235}U, ^{238}U, ^{238}Pu, ^{242}Pu, ^{241}Am, ^{243}Am, ^{148}Nd and ^{150}Nd) were measured using FC 11. For the $^{235}U/^{238}U$ isotope ratio determination, ^{235}U isotope was detected using FC 12 and ^{238}U isotope was collected using FC 11. Mass 239 (^{239}Pu) was also measured to look for a possible Pu contamination using FC 11. For Pu isotope ratios determination, ^{238}Pu, ^{240}Pu and ^{242}Pu isotopes were measured using FC 11, ^{239}Pu isotope was detected with the FC 12 and ^{241}Pu was collected with the FC 13. Mass 235 (^{235}U) was also measured to look for a possible U contamination using FC 11.

Classical method using multi-dynamic sequence

$^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios were measured with the classical method using multi-dynamic sequence (hereafter referred to as CMD method). The isotope fractionation was overcome with an internal normalization using the $^{235}U/^{238}U$ ratio previously measured with the TE method. The exponential law was used. Compare to the method previously described [17], some parameters (integration number, measurement time and idle time) were updated to take into account the use of the FC 13. Idle time using FC 13 must be increased compared to the method using FC 12, to ensure that the Faraday cups response return to their background level: time response of the FC 13 is slower than that of the FC 12.

The updated parameters of the CMD method are summarized in Table 1. The CMD method always includes 4 measurement sequences performed one after the other. In the first sequence, the ^{234}U isotope was collected on the FC 13, the ^{235}U isotope was measured on the FC 12, the ^{236}U isotope was collected on the SEM and the ^{238}U was collected on FC 11. The measurement was performed with 3 integrations of 8 s. Sequence 2, dedicated to the real-time SEM/FC inter-calibration, was performed using the SEM to measure the ^{234}U isotope and a FC 11 to detect the ^{235}U isotope. The measurement was performed with 3 integrations of 8 s. The sequence 3 and 4 used the same detector configuration as the sequence 1 and were dedicated to tailing contribution measurement. Each measurement corresponds to 6 blocks of 10 cycles. Each cycle corresponds to the acquisition of the 4 measurement sequences presented in the Table 1.

Equations to calculate the $^{234}U/^{238}U$ isotope ratio corrected from the peak tailing and the isotope fractionation, as well as the $^{236}U/^{238}U$ isotope ratio corrected from the peak tailing, the SEM/FC inter-calibration gain and the isotope fractionation were previously explained in details [17]. For the method validation with the updated parameters, 5 analyses were performed on the IRMM 187 CRM.

Double isotope dilution

Principle

The X/^{238}U ratios determination (X = ^{238}Pu, ^{241}Am or ^{148}Nd) required using a spike enriched with ^{235}U and Y isotopes (Y = ^{242}Pu, ^{243}Am or ^{150}Nd) [31]. The Y/^{235}U ratio of the spike must be known. Then, the spike is mixed with the sample. The X/^{238}U ratio in the sample is calculated with the measurements of the X/Y and ^{238}U/^{235}U mixture ratios (Eq. (1)).

$$\left(\frac{X}{^{238}U}\right)_S = \left(\frac{Y}{^{235}U}\right)_T \cdot \frac{\left[\left(\frac{X}{Y}\right)_M - \left(\frac{X}{Y}\right)_T\right] \cdot \left[1 - \left(\frac{^{238}U}{^{235}U}\right)_M \cdot \left(\frac{^{238}U}{^{235}U}\right)_S\right]}{\left[\left(\frac{^{238}U}{^{235}U}\right)_M - \left(\frac{^{238}U}{^{235}U}\right)_T\right] \cdot \left[1 - \left(\frac{X}{Y}\right)_M \cdot \left(\frac{Y}{X}\right)_S\right]} \quad (1)$$

Where *T* refers to the spike (or tracer), *M* refers to the (sample – spike) mixture and *S* refers to the sample.

^{242}Pu/^{235}U spike preparation

The spike enriched in ^{235}U and ^{242}Pu isotopes (hereafter referred to as ^{242}Pu/^{235}U spike), required to measure the ^{238}Pu/^{238}U sample ratio, was prepared gravimetrically from IRMM 054 and IRMM 49d CRM. The ^{242}Pu/^{235}U ratio in the spike was calculated using weighed CRM used for the preparation and the certified ^{235}U and ^{242}Pu isotope amount contents. The ^{242}Pu/^{235}U spike characteristics are: ^{238}U/^{235}U = 0.058065(69), ^{238}Pu/^{242}Pu = 0.0053313(35) and ^{242}Pu/^{235}U = 0.05074(14).

^{150}Nd spike solution characterization

^{148}Nd/^{238}U ratio determination required using a Nd/U spike. The first step was characterizing the ^{150}Nd spike solution. For the isotope ratios characterization, 5 deposits of about 10 ng were analyzed with the TE method.

The Nd mass fraction was measured by reverse isotope dilution using the NIST 3135a CRM as spike. 3 independent dilutions of the NIST 3135a CRM were performed to obtain Nd mass fraction about 10 µg g^{-1}. Then, 3 (diluted NIST 3135a CRM – ^{150}Nd spike solution) mixtures were prepared for each dilution cascade. The ^{144}Nd/^{150}Nd ratio of each

mixture was measured using the TE method to calculate the Nd mass fraction of the ^{150}Nd spike solution. The 3135a CRM being only certified for the mass fraction, these Nd isotope ratios were measured with 5 deposits of about 10 ng using the TE method.

^{150}Nd/^{243}Am/^{235}U spike preparation

^{241}Am/^{238}U and ^{148}Nd/^{238}U ratio were determined in the same experiment with a spike enriched in ^{235}U, ^{243}Am and ^{150}Nd isotopes. This spike, hereafter referred to as ^{150}Nd/^{243}Am/^{235}U spike, was prepared gravimetrically from IRMM 054, STAM and ^{150}Nd spike solution. The ^{150}Nd/^{243}Am/^{235}U spike characteristic are: ^{238}U/^{235}U = 0.058065(69), ^{241}Am/^{243}Am = 0.135574(54), ^{148}Nd/^{150}Nd = 0.009906(24), ^{243}Am/^{235}U = 0.028628(73) and ^{150}Nd/^{235}U = 0.005295(30).

Analytical protocol

An overview of the analytical protocol is summarized in Fig. 1.

Dissolution

The dissolution of MARIOS and DIAMINO discs was conducted in 2 steps in a closed vessel in a hot cell. The primary dissolution was performed in 11 mol L^{-1} HNO_3 to dissolve the uranium-based matrix, lanthanides and some of the fission products. The second dissolution step was the residue depletion using (11 mol L^{-1}/0.075 mol L^{-1}) HNO_3/HF mixture added to the primary dissolution solution to quantitatively dissolve the plutonium. Then, two independent 100-fold dilutions were performed for each of the dissolution solution in the hot cell to obtain a radiation level compatible with glove box operations (Fig. 1). Hereafter, the two diluted dissolution solutions are referred to as aliquot 1 and aliquot 2. 3 mL of aliquot 1 and 2 were transferred by pneumatic transfer to the isotopic analyses laboratory.

U isotope ratios measurements

The uranium isotope ratios were measured after a separation on UTEVA resin (Fig. 1). First, 2 mL of (6 mol L^{-1}/0.1 mol L^{-1}) HNO_3/H_2O_2 mixture were added to 300 µL of aliquot 1 and 2. This solution (aliquot + HNO_3/H_2O_2 mixture), containing about 15 µg of U, was separated with the UTEVA resin to obtain a purified fraction of U. This fraction was evaporated and dissolved again with 15 µL of 0.5 mol L^{-1} HNO_3 to obtain a solution with a U mass fraction about 1 µg $µL^{-1}$. 1 µL (about 1 µg of U) was deposited on 3 filaments for each aliquot to perform the $^{235}U/^{238}U$ ratio determination using the TE method. 4 µL (about 4 µg of U) were deposited on 3 filaments for each aliquot to perform the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios determination using the CMD method. U isotope ratios in each disc are the average from the values acquired for aliquot 1 and 2.

Pu isotope ratios measurements

The Pu isotope ratios were measured after a separation on TEVA resin followed by a separation on UTEVA resin (Fig. 1). First, 2 mL of 8 mol L^{-1} HNO_3 were added to 300 µL of aliquot 1 and 2. This solution (aliquot + 8 mol L^{-1} HNO_3), containing about 1 µg of Pu, was separated using the TEVA resin to obtain a Pu fraction purified from Am. The separation on TEVA is also able to purify Pu from U and can be enough to purify Pu from U and Am. However, U traces are commonly observed in the Pu fraction: the decontamination factor is not high enough.

The Pu fraction, obtained from the TEVA resin, was evaporated and dissolved again with 1 mL of the (6 mol L^{-1}/0.1 mol L^{-1}) HNO_3/H_2O_2 mixture. The UTEVA resin separation protocol was applied to obtain a purified fraction of Pu. This fraction was evaporated and dissolved again with 6 µL of 0.5 mol L^{-1} HNO_3 to obtain a Pu mass fraction of about 200 ng $µL^{-1}$. 1 µL (about 200 ng of Pu) was deposited on 3 filaments for each aliquot. Pu isotope ratios in each disc are the average from the values acquired for aliquot 1 and 2.

$^{238}Pu/^{238}U$ ratio measurements

First each aliquot was diluted 10-fold (Fig. 1). Then, 3 (diluted aliquot - $^{242}Pu/^{235}U$ spike) mixtures were prepared and separated using the UTEVA resin to obtain purified fractions of U and Pu. Theses fractions were evaporated and dissolved again using 10 µL of 0.5 mol L^{-1} HNO_3 for the U fraction to obtain U mass fraction about 500 ng μL^{-1} and using 1 µL of 0.5 mol L^{-1} HNO_3 for the Pu fraction to obtain Pu mass fraction about 400 ng μL^{-1}. 1 µL (about 500 ng of U and 400 ng of Pu) was deposited on a filament. $^{238}Pu/^{238}U$ ratio in each disc is the average value of aliquot 1 and 2.

$^{148}Nd/^{238}U$ and $^{241}Am/^{238}U$ ratios measurements

2 (aliquot - $^{150}Nd/^{243}Am/^{235}U$ spike) mixtures were prepared for each aliquot. These mixtures, containing about 17 µg of U, 1 µg of Am and 50 ng of Nd, were purified using the TEVA resin to obtain purified fractions of trivalent elements and U (Fig. 1). The trivalent elements fraction was evaporated and then dissolved again in 30 µL of 0.5 mol L^{-1} HNO_3. This 30 µL was then used to inject 20 µL in the HPLC system. Purified fractions of Am and Nd were obtained and then evaporated. The residue of the Am and Nd fractions was dissolved again with 6 µL and 5 µL of 0.5 mol L^{-1} HNO_3, respectively, to obtain a solution with [Am] ≈ 100 ng μL^{-1} and [Nd] ≈ 6 ng μL^{-1}. 1 µL of solution (about 100 ng of Am and about 6 ng of Nd) was deposited.

The U fraction, obtained from the TEVA resin separation, was not well purified against Pu, that interferes the ^{238}U isotope measurement. The U fraction was evaporated and dissolved again with 1 mL of 6 mol L^{-1}/0.1 mol L^{-1} HNO_3/H_2O_2 mixture. The UTEVA resin separation protocol was applied to obtain a purified fraction of U. This fraction was evaporated and dissolved again with 10 µL of 0.5 mol L^{-1} HNO_3 to obtain [U] ≈ 500 ng μL^{-1} solution. 1 µL of solution (about 500 ng of U) was deposited. $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ ratios in each disc are the average value of aliquot 1 and 2.

Results evaluation

Bias, or trueness, was calculated using Eq. (2).

$$Bias\ (\%) = \frac{Z - ref}{ref} \tag{2}$$

Where Z is the experimental value and ref is the reference value.

Eq. (3) was used to determine if the analytical method has a statistically significant bias. If the normalized error (E_N) is lower than 2, the method is considered having no statistically significant bias [32].

$$E_N = \frac{|Z - ref|}{\sqrt{u_z^2 + u_{ref}^2}} \tag{3}$$

Where u_z is the measurement uncertainty and u_{ref} is the reference value uncertainty with a coverage factor at k = 1.

Uncertainties estimation

Isotope ratio uncertainty

The isotope ratio (R) uncertainty (u) at k = 1 was estimated using Eq. (4) [14].

$$\frac{u^2(R)}{(R)^2} = \frac{u_{\bar{x}}^2}{(\bar{x})^2} + \frac{u_{trueness}^2}{(trueness)^2} + \frac{u_{ref}^2}{(ref)^2} \tag{4}$$

$$\frac{u_{trueness}}{trueness} = \frac{maximum\ bias\ in\ CRM}{\sqrt{3}} \tag{5}$$

The first term of Eq. (4) on right hand side is given by the Relative Standard Deviation (RSD, *i.e.* random effects). The second and third terms take into account the systematic effect. The measurement trueness is calculated using Eq. (5) with a reference material. The optimal reference material is the same element as the analyte with similar isotope ratio. The 2019UPuNH sample was used to evaluate the $^{235}U/^{238}U$ isotope ratio: ratio about

0.0074 for the material and about 0.004 for both discs. The IRMM 187 was used for the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios.

The Pu isotope ratios were evaluated with the 2017PuNH and 2019UPuNH materials. The choice of the material is not very important in this case as similar biases were observed during ILC: the only difference is 2019UPuNH has lowest assigned values uncertainties than 2017PuNH. The choice of the material was only made to be as close as possible to the measurement values of the discs. The $^{242}Pu/^{239}Pu$ ratio of the 2019UPuNH (about 0.03) was used for the $^{242}Pu/^{238}Pu$ uncertainty estimation in the discs (about 0.2). The $^{240}Pu/^{239}Pu$ ratio of 2017PuNH sample (about 0.1) was used for the $^{239}Pu/^{238}Pu$ (0.1-0.2) and $^{240}Pu/^{238}Pu$ (0.01-0.03) uncertainty estimations in the discs. The $^{241}Pu/^{239}Pu$ ratio of 2017PuNH sample (about 0.002) was used for the $^{241}Pu/^{238}Pu$ ratio in the discs (0.002-0.01).

Double isotope dilution uncertainty

$^{238}Pu/^{238}U$, $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ ratios uncertainties were estimated by combining the uncertainties from each term of the DID equation. A precision component was added and corresponds to the RSD obtained for the two aliquots divided by the square root of the number of aliquots (here 2).

Results and discussion

Analytical optimization

Pu purification against Am

Routinely the Pu purification is performed in one separation step with the UTEVA resin first. This protocol was applied for one of the DIAMINO aliquot. The repeatability observed for the 3 measurements of the $^{241}Pu/^{238}Pu$ ratio coming from the same separation was 16 %, which is important for isotope ratio about 0.002. Fig. 2.a shows the $^{241}Pu/^{238}Pu$

ratio evolution as a function of time (or cycle number) while using the TE method. The ratio mainly decrease during the TE method, which is not in agreement with the isotope fractionation law. Lighter isotopes mainly evaporate at the beginning of the TE method compared to the heavier isotopes: the $^{241}Pu/^{238}Pu$ ratio need to increase during the TE method to respect the isotope fractionation law. These informations (repeatability and profile) showed ^{241}Pu isotope measurement is interfered by the ^{241}Am isotope after one separation step with UTEVA resin.

To solve this Pu/Am interference, a separation using a TEVA resin was added before the UTEVA resin separation. The $^{241}Pu/^{238}Pu$ ratio thus obtained is 27 % lower than the value obtained after only a UTEVA resin separation. The repeatability observed for the 3 measurements coming from the same separation improves to 0.2 % for DIAMINO and MARIOS measurements (Table 2). Fig. 2.b shows the $^{241}Pu/^{238}Pu$ ratio evolution as a function of time while using the TE method for a DIAMINO aliquot after TEVA and UTEVA separation. The ratio increases slowly, which is in agreement with the isotope fractionation law. The repeatability and the $^{241}Pu/^{238}Pu$ ratio evolution during the TE method showed combining TEVA and UTEVA resins is efficient to overcome the $^{241}Am/^{241}Pu$ isobaric interference.

This behavior difference between the routine samples and the MARIOS/DIAMINO discs can be explained by the Am/Pu ratio. The routine samples contained more Pu than Am: the Am/Pu ratio is mainly below 0.1. For the DIAMINO and MARIOS discs, the Am/Pu ratio was about 1. The trivalent elements decontamination used routinely using the UTEVA resin separation is probably not sufficient to eliminate this higher Am quantity.

U purification against Pu

The absence of Pu in the U fraction was verified by measuring the ^{239}Pu isotope for each U analysis. The $^{239}Pu/^{238}U$ ratio is an indicator of the U/Pu purification efficacy. The highest $^{239}Pu/^{238}U$ ratio observed during the measurements was 3×10^{-5} (Table 2) which is slightly higher than the detection limit estimated to 1×10^{-5} [17]. Combining the $^{239}Pu/^{238}Pu$ ratio measured during the Pu isotope ratios determination (about 0.1 for DIAMINO disc

and 0.2 for MARIOS disc) and the $^{239}Pu/^{238}U$ ratio measured here, the contribution of the ^{238}Pu isotope to the signal measured at mass 238 amu has been calculated at about 0.02 % and is negligible compared to the repeatability (RSD about 0.1 % for both discs, Table 2) and the estimated uncertainty (relative uncertainty is over 0.16 % for all U isotope ratios). $^{235}U/^{238}U$ isotope ratio evolution during the TE method was also verified for each analysis and confirmed the separation efficiency.

Pu purification against U

The absence of U in the Pu fraction can be verified by measuring the ^{235}U isotope for each Pu analysis. The highest $^{235}U/^{238}Pu$ ratio observed was lower than the detection limit and estimated to 5.10^{-5} (Table 2). This value gives a first approximation of the Pu purification quality. However, ^{235}U isotope is not abundant enough ($^{235}U/^{238}U$ ratio of about 0.004 for both discs) to make sure the Pu fraction contained no traces of U. $^{235}U/^{238}Pu$ ratio is not the perfect indicator as was, previously, the $^{239}Pu/^{238}U$ ratio for the U purification control. Pu isotope ratios evolution while using the TE method was verified for each Pu analysis and for each Pu isotope ratio to make sure the ratio evolution are in agreement with the isotope fractionation law. These observations confirmed the separation quality to obtain a Pu purified from U.

Method validation for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios determination using the CMD method with the FC 13

The updated parameters for the CMD method were validated using the IRMM 187 CRM. The biases obtained are equal to -0.003 % for the $^{234}U/^{238}U$ ratio and to -0.004 % for the $^{236}U/^{238}U$ ratio. The RSD for the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios are equal to 0.04 % and 0.06 %, respectively. The normalized error calculated for both isotope ratios (E_N = 0.07 for $^{234}U/^{238}U$ ratio and E_N = 0.05 for $^{236}U/^{238}U$ ratio) were below 2, showing the method has no significant bias and validating the updated parameters for minor U isotope ratios determination.

^{150}Nd spike calibration

The ^{150}Nd spike calibration is composed of 3 steps: isotope ratios determination of the NIST 3135a CRM used as spike, isotope ratios determination of the ^{150}Nd spike and mass fraction determination of the ^{150}Nd spike by reserve isotope dilution.

The Nd isotope ratios of the NIST 3135a CRM correspond to a natural Nd (see Table S1 in the supplementary information). The repeatability observed for all isotope ratios were below 0.05 %. The uncertainties were estimated between 0.1 and 0.3 % (k = 2).

The Nd isotope ratios of the ^{150}Nd spike were summarized in Table S2 in the supplementary information. The repeatability observed for all isotope ratios (RSD between 0.1% to 0.7 %) were higher than the ones observed for natural uranium (RSD < 0.1 %), due to lower isotope ratios in the case of the ^{150}Nd spike. The uncertainty were estimated between 0.3 % and 1.3 % (k = 2).

The Nd mass fraction of the ^{150}Nd spike was determined at 7.468(40) µg g^{-1}. The repeatability among the 3 independent determinations was 0.13 %. The uncertainty was estimated to 0.53 % (k = 2). The study of the main uncertainty sources shows the total uncertainty is mainly due to the Nd mass fraction uncertainty of the NIST 3135a CRM (69 % of the total uncertainty). The others uncertainty sources are the mixture isotope ratio uncertainty (11 % of the total uncertainty), the masses uncertainties (10 % of the total uncertainty) and the repeatability (10 % of the total uncertainty). The other uncertainty sources, like Nd isotope ratios of the 3135a CRM and ^{150}Nd spike, are negligible (below 1 % of the total uncertainty). These measurements calibrated the ^{150}Nd spike for isotope ratios and mass fraction.

Results of MARIOS and DIAMINO discs

Results are summarized in Table 3.

U isotope ratios

The $^{235}U/^{238}U$ ratio was 0.0045960(85) for the DIAMINO disc and 0.0041534(69) for the MARIOS discs. The repeatability between the two aliquots were equal to 0.06 % for the DIAMINO disc and 0.01 % for the MARIOS disc. The relative uncertainties were 0.18 % and 0.17 % for DIAMINO and MARIOS discs, respectively.

The $^{234}U/^{238}U$ ratio was 0.0019338(37) for the DIAMINO disc and 0.005052(12) for the MARIOS discs. The $^{236}U/^{238}U$ ratio was 0.0004201(11) for the DIAMINO disc and 0.0005800(19) for the MARIOS disc. The repeatabilities were below 0.2 %. The relative uncertainties were estimated between 0.19 % and 0.33 %.

Pu isotope ratios

$^{239}Pu/^{238}Pu$, $^{240}Pu/^{238}Pu$ and $^{242}Pu/^{238}Pu$ ratios were 0.12101(17), 0.015288(54) and 0.21275(45), respectively, for the DIAMINO disc and 0.20247(17), 0.030771(29) and 0.20240(36), respectively, for the MARIOS disc. The relative uncertainties were between 0.09 % and 0.35 %.

$^{241}Pu/^{238}Pu$ ratio were measured at 0.002129(13) and 0.011497(66) for DIAMINO and MARIOS discs, respectively. The relative uncertainty (about 0.6 % for both disc) were higher than the other Pu isotope ratios (below 0.35 %). This is explained by the material chosen to calculate the systematic effect in the uncertainty equation: this material (*i.e.* 2017PuNH sample) have an uncertainty of 0.53 % (k = 2) whereas the material used to calculate the systematic effect for others isotope ratios have an uncertainty below 0.04 % (k = 2).

$^{238}Pu/^{238}U$, $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ isotope ratios

The $^{238}Pu/^{238}U$ ratio is 0.04887(18) for the DIAMINO disc and 0.07980(30) for the MARIOS disc. The repeatabilities are below 0.1 % for both disc. The relative uncertainties were estimated at 0.35 % for the DIAMINO disc and 0.37 % for the MARIOS disc (k = 2). The study of the main uncertainty sources shows that the total uncertainty is mainly come from the $^{242}Pu/^{235}U$ ratio of the spike (about 58 % of the total uncertainty), the $^{238}U/^{235}U$

464 mixture ratio (about 18 % of the total uncertainty) and $^{238}Pu/^{242}Pu$ mixture ratio (about
465 22 % of the total uncertainty). The others uncertainty sources (sample and spike isotope
466 ratios) are negligible (below 2 % of the total uncertainty).

467 The $^{241}Am/^{238}U$ ratios were measured at 0.08545(29) and 0.06242(23) for DIAMNIO and
468 MARIOS discs, respectively. The repeatabilities are below 0.1 % for both discs. The
469 relative uncertainties are estimated at 0.34 % and 0.37 % for DIAMNIO and MARIOS
470 discs, respectively. As for the $^{238}Pu/^{238}U$, the study of the main uncertainty sources shows
471 that the total uncertainty is mostly come from the $^{243}Am/^{235}U$ ratio of the spike (about 57 %
472 of the total uncertainty), the $^{238}U/^{235}U$ mixture ratio (about 19 % of the total uncertainty)
473 and the $^{241}Am/^{243}Am$ mixture ratio (about 23 % of the total uncertainty). The others
474 uncertainty sources are negligible (below 1 % of the total uncertainty).

475 The $^{148}Nd/^{238}U$ ratio was determined at 0.0002153(14) for the DIAMINO disc and
476 0.0004805(33) for the MARIOS disc. The repeatabilities are about 0.2 % for both disc. The
477 relative uncertainties were estimated at 0.65 % and 0.68 % for DIAMNIO and MARIOS
478 discs, respectively. These uncertainties are about twice higher than the ones estimated for
479 $^{238}Pu/^{238}U$ and $^{241}Am/^{238}U$ ratios (about 0.35 %). This is mainly due to the $^{150}Nd/^{235}U$ ratio
480 uncertainty of the spike that is estimated to 0.57 % (k = 2). It is mathematically impossible
481 to obtain a $^{148}Nd/^{238}U$ ratio uncertainty below the $^{150}Nd/^{235}U$ spike ratio uncertainty. The
482 study of the main uncertainty sources shows that the contribution linked to the $^{150}Nd/^{235}U$
483 spike ratio increased: about 75 % of the total uncertainty for the $^{148}Nd/^{238}U$ ratio compared
484 to about 60 % for $^{238}Pu/^{238}U$ and $^{241}Am/^{238}U$ ratios.

485 Comparison between analysis results and neutron simulation ones

486 The information provided in Table 3 indicate a rather good agreement between analysis
487 results and neutron simulation ones.

488 In the case of DIAMINO, almost all the deviations remain below 20 % which is satisfactory
489 considering all uncertainties associated to both neutron simulations and analysis
490 measurements. Only the deviation related to the ratio $^{241}Pu/^{238}Pu$ is higher (34 %), possibly

due to uncertainties in some specific neutron cross-sections used in neutron simulations where the neutron flux has the OSIRIS reactor particular energy spectrum.

As for MARIOS, more deviations exceed 20 %. The ones related to specific isotopes in the isotopic vector of an element (*i.e.* $^{234}U/^{238}U$, $^{240}Pu/^{238}Pu$ and $^{241}Pu/^{238}Pu$) could also be due to neutron cross-section uncertainties. Regarding the $^{148}Nd/^{238}U$ and $^{241}Am/^{238}U$ ratios, the slight lack of neodymium and excess of americium as-calculated suggest that neutron calculations were run up till a slightly lower fluence compared to the experimental one. In addition, it is mentioned that the fluence used in the MARIOS neutron calculations corresponds to the one determined from measurements performed on the activation monitor set of the irradiation device, some uncertainties being also associated to these measurements.

Conclusions

Six discs from MARIOS and DIAMINO irradiations experiments were dissolved in a hot cell before analysis. These analyses are part of an R&D program initiated in 2008 at the CEA on minor actinides transmutation. Isotopic analyses were carried out with high accuracy to help interpreting the experiments and to qualify the associated evolution calculation code for different isotopes. Several analytical optimizations of the protocol were performed.

The Pu purification was optimized to ensure an optimal Pu/Am separation. Adding a TEVA resin separation before the usually employed UTEVA resin separation helps measuring the ^{241}Pu isotope without any interference from the ^{241}Am isotope. The DID showed its potential for the $^{238}Pu/^{238}U$, $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ ratios determination. Compared to the conventional ID-TIMS methodology, the DID showed lower uncertainties: estimated to a few percent for the ID-TIMS and to a few per mil for the double isotope dilution. The DID is also faster as no gravimetrically preparation are required as this step is tedious in hot cell or in glove box.

Uncertainties, estimated about a few per mil for the main determination, showed significant difference between discs of the same irradiation. The burnup of each disc is slightly different depending on the position of the disc in the needle (bottom, middle or high), that produce different transmutation yield and isotope ratios.

Acknowledgements

We are grateful to Dr. S. Baghdadi (CEA/DES/ISEC/DMRC/SASP/L2AT) for her precious advice on the present paper. We would like to thank Dr. Eric Esbelin, Dr. Steve Jan, Ms Barbara Caniffi, Ms Corinne Deshoux, Ms Delphine Vantalon, Mr Bruce Charles, Mr Regis Joulia, Mr Laurent Lancial, Mr Lyonel Trintignac (CEA/DES/ISEC/DMRC/SASP/L2AT) and Mr Ygor Davrain (CEA/DES/ISEC/CETAMA) who have taken part in this work.

528 **Table**

529 Table 1: Summarized description of one cycle of the CMD method

Cups Detectors	L2 FC 13	L1 FC 12	C SEM	H1 FC 11	H2 FC 11	Integration number	Measurement time (s)	Idle time (s)
Sequence 1	^{234}U	^{235}U	^{236}U		^{238}U	3	8	1
Sequence 2			^{234}U	^{235}U		3	8	1
Sequence 3	233.7	234.7	235.7		237.7	3	4	5
Sequence 4	234.4	235.4	236.4		238.4	3	4	1

530

531

532

533 Table 2: ^{239}Pu/^{238}U maximal ratio and RSD obtained for the ^{235}U/^{238}U ratio during U
534 analysis and ^{235}U/^{238}Pu maximal ratio and RSD obtained for the ^{241}Pu/^{238}Pu ratio during
535 Pu analysis for aliquot 1 and 2 of DIAMINO and MARIOS discs

Disc	Aliquot	U analysis		Pu analysis	
		^{239}Pu/^{238}U	RSD ^{235}U/^{238}U	^{235}U/^{238}Pu	RSD ^{241}Pu/^{238}Pu
DIAMINO	1	2.1×10^{-5}	0.14 %	$< 1\times10^{-5}$	0.12 %
	2	3.0×10^{-5}	0.10 %	$< 1\times10^{-5}$	0.14 %
MARIOS	1	2.3×10^{-5}	0.04 %	$< 1\times10^{-5}$	0.01 %
	2	2.0×10^{-5}	0.05 %	$< 1\times10^{-5}$	0.04 %

536

537

538

Table 3: Experimental and neutronic simulation results for the DIAMINO and MARIOS discs. Values in parenthesis are the estimated uncertainties expressed at k = 2

Isotope ratio	DIAMINO disc	DIAMINO neutronic simulation	MARIOS disc	MARIOS neutronic simulation
$^{234}U/^{238}U$	0.0019338(37)	0.00232	0.005052(12)	0.00281
$^{235}U/^{238}U$	0.0045960(85)	0.00490	0.0041534(69)	0.00433
$^{236}U/^{238}U$	0.0004201(11)	0.00045	0.0005800(19)	0.00053
$^{239}Pu/^{238}Pu$	0.12101(17)	0.114	0.20247(17)	0.185
$^{240}Pu/^{238}Pu$	0.015288(54)	0.0187	0.030771(29)	0.0223
$^{241}Pu/^{238}Pu$	0.002129(13)	0.0030	0.011497(66)	0.0094
$^{242}Pu/^{238}Pu$	0.21275(45)	0.214	0.20240(36)	0.208
$^{238}Pu/^{238}U$	0.04887(18)	0.0497	0.07980(30)	0.0690
$^{241}Am/^{238}U$	0.08545(29)	0.0873	0.06242(23)	0.0845
$^{148}Nd/^{238}U$	0.0002153(14)	0.00022	0.0004805(33)	0.00035

Figure

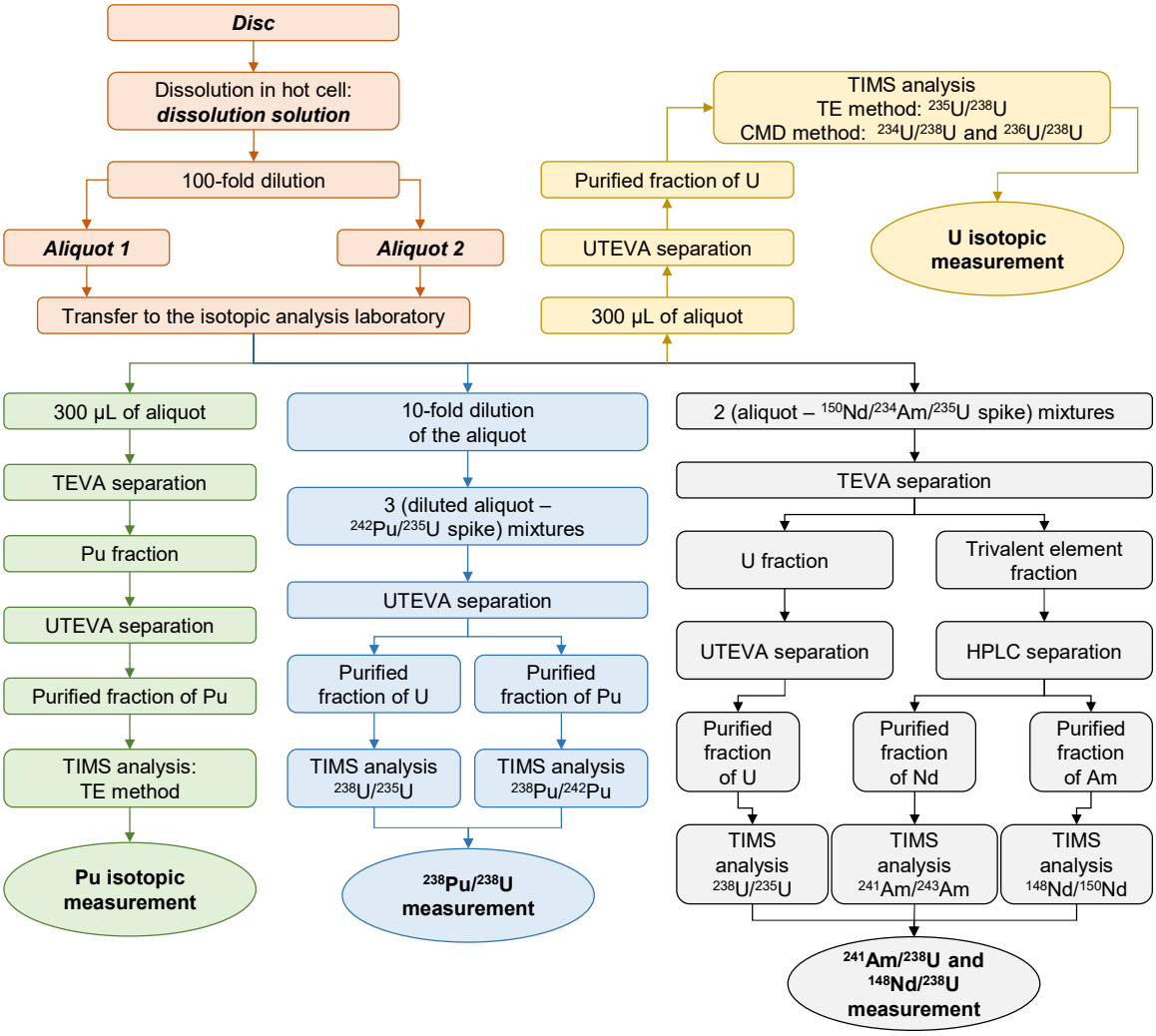

Fig. 1: Schematics of the analytical protocol

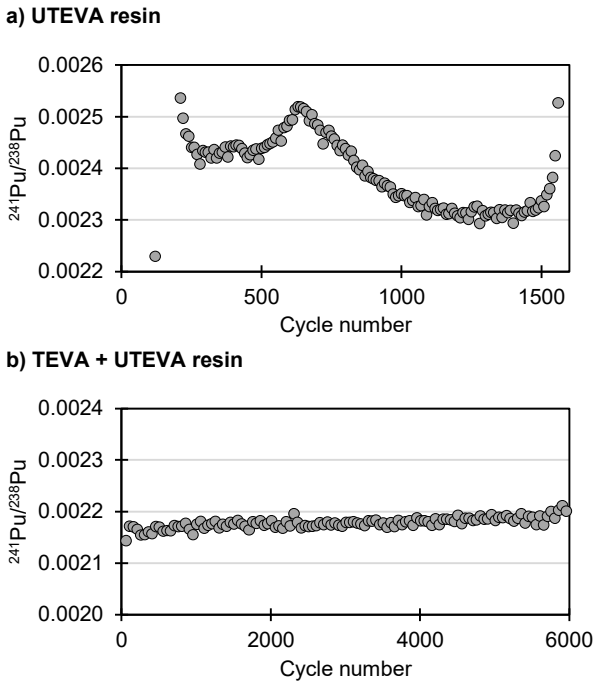

Fig. 2: $^{241}Pu/^{238}Pu$ isotope ratio evolution through an analysis by the TE method for the DIAMINO aliquot 1 after a UTEVA resin separation (a) and after a TEVA resin separation following by UTEVA resin separation (b). For better clarity only 1 in 10 points (a) and 1 in 50 points (b) were plotted

References

1. Bejaoui S, Helfer T, Bendotti S, Lambert T (2019) Description and thermal simulation of the DIAMINO irradiation experiment of transmutation fuel in the OSIRIS reactor. Prog Nucl Energy 113:28–44. https://doi.org/10.1016/j.pnucene.2019.01.012

2. Bejaoui S, Bendotti S, Lambert T, Helfer T (2017) Status of the DIAMINO experiment irradiated in the OSIRIS reactor. In: Proceedings of GLOBAL 2017. Seoul (Korea)

3. D'Agata E, Hania PR, Bejaoui S, Sciolla C, Wyatt T, Hannink MHC, Herlet N, Jankowiak A, Klaassen FC, Lapetite JM, Boomstra DA, Phelip M, Delage F (2013) The results of the irradiation experiment MARIOS on americium transmutation. Ann Nucl Energy 62:40–49. https://doi.org/10.1016/j.anucene.2013.05.043

4. Horlait D, Lebreton F, Delahaye T, Herlet N, Dehaudt P (2012) U1-xAmxO2±δ MABB Fabrication in the Frame of the DIAMINO Irradiation Experiment. Procedia Chem 7:485–492. https://doi.org/10.1016/j.proche.2012.10.074

5. Prieur D, Jankowiak A, Delahaye T, Herlet N, Dehaudt P, Blanchart P (2011) Fabrication and characterisation of U0.85Am0.15O2-x discs for MARIOS irradiation program. J Nucl Mater 414:503–507. https://doi.org/10.1016/j.jnucmat.2011.05.036

6. Beauvy M, Berthoud G, Defranceschi M, Ducros G, Guérin Y, Latgé C, Limoge Y, Madic C, Moisy P, Santarani G, Seiler J-M, Sollogoub P, Vernaz E (2008) Treatment and recycling of spent nuclear fuel, Actinide partitioning - application to waste management, Le Moniteur Editions, Paris, France

7. (2018) State-of-the-art Report on the Progress of Nuclear Fuel Cycle Chemistry. OECD

8. Quemet A, Sevilla J, Vauchy R (2021) A combined TIMS and ICP-MS study for

Th0.5Np0.5O2 thorium neptunium mixed oxide analysis. Int J Mass Spectrom 460:116479. https://doi.org/10.1016/j.ijms.2020.116479

9. Quemet A, Maloubier M, Ruas A (2016) Contribution of the Faraday cup coupled to 1012 ohms current amplifier to uranium 235/238 and 234/238 isotope ratio measurements by Thermal Ionization Mass Spectrometry. Int J Mass Spectrom 404:35–39. https://doi.org/10.1016/j.ijms.2016.04.005

10. Quemet A, Maloubier M, Dalier V, Ruas A (2014) Development of an analysis method of minor uranium isotope ratio measurements using electron multipliers in thermal ionization mass spectrometry. Int J Mass Spectrom 374:26–32. https://doi.org/10.1016/j.ijms.2014.10.008

11. Bürger S, Riciputi LR, Bostick DA, Turgeon S, McBay EH, Lavelle M (2009) Isotope ratio analysis of actinides, fission products, and geolocators by high-efficiency multi-collector thermal ionization mass spectrometry. Int J Mass Spectrom 286:70–82

12. Bürger S, Balsley SD, Baumann S, Berger J, Boulyga SF, Cunningham JA, Kappel S, Koepf A, Poths J (2012) Uranium and plutonium analysis of nuclear material samples by multi-collector thermal ionisation mass spectrometry: Quality control, measurement uncertainty, and metrological traceability. Int J Mass Spectrom 311:40–50

13. Aggarwal SK (2016) Thermal ionisation mass spectrometry (TIMS) in nuclear science and technology – a review. Anal Methods 8:942–957. https://doi.org/10.1039/c5ay02816g

14. Quemet A, Ruas A, Dalier V, Rivier C (2018) Americium isotope analysis by Thermal Ionization Mass Spectrometry using the Total Evaporation Method. Int J Mass Spectrom 431:8–14. https://doi.org/10.1016/j.ijms.2018.05.017

15. Aggarwal SK (2018) A review on the mass spectrometric studies of americium: Present status and future perspective. Mass Spectrom Rev 37:43–56.

https://doi.org/10.1002/mas.21506

16. Guéguen F, Isnard H, Nonell A, Vio L, Vercouter T, Chartier F (2015) Neodymium isotope ratio measurements by LC-MC-ICPMS for nuclear applications: investigation of isotopic fractionation and mass bias correction. J Anal At Spectrom 30:443–452. https://doi.org/10.1039/C4JA00361F

17. Quemet A, Ruas A, Dalier V, Rivier C (2019) Development and comparison of high accuracy thermal ionization methods for uranium isotope ratios determination in nuclear fuel. Int J Mass Spectrom 438:166–174. https://doi.org/10.1016/j.ijms.2019.01.008

18. Quemet A, Buravand E, Catanese B, Huot P, Dalier V, Ruas A (2020) Monitoring the dissolution of a uranium-plutonium oxide from a spent fuel solution: using plutonium ratio and TIMS for isotope ratio measurements. J Radioanal Nucl Chem 326:255–260. https://doi.org/10.1007/s10967-020-07311-5

19. Quemet A, Angenieux M, Ruas A (2021) Nd, Am and Cm isotopic measurement after simultaneous separation in transmutation irradiated samples. J Anal At Spectrom 36:1758. https://doi.org/10.1039/D1JA00165E

20. Horwitz EP, Dietz ML, Chiarizia R, Diamond H, Maxwell SL, Nelson MR (1995) Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion-Exchanger - Application to the Characterization of High-Level Nuclear Waste Solutions. Anal Chim Acta 310:63–78. https://doi.org/10.1016/0003-2670(95)00144-O

21. Morgenstern A, Apostolidis C, Carlos-Marquez R, Mayer K, Molinet R (2002) Single-column extraction chromatographic separation of U, Pu, Np and Am. Radiochim Acta 90:81–85. https://doi.org/10.1524/ract.2002.90.2_2002.81

22. Apostolidis C, Molinet R, Richir P, Ougier M, Mayer K (1998) Development and Validation of a Simple, Rapid and Robust Method for the Chemical Separation of Uranium and Plutonium. Radiochim Acta 83:21–25.

https://doi.org/10.1524/ract.1998.83.1.21

23. Goutelard F, Caussignac C, Brennetot R, Stadelmann G, Gautier C (2009) Optimization conditions for the separation of rare earth elements, americium, curium and cesium with HPLC technique. J Radioanal Nucl Chem 282:669–675. https://doi.org/10.1007/s10967-009-0308-z

24. Banik N lal, Lützenkirchen K, Malmbeck R, Nichol A (2019) A method for the mg scale separation of curium(III) from americium(III) by HPLC using a SCX column. J Radioanal Nucl Chem 321:841–849. https://doi.org/10.1007/s10967-019-06653-z

25. Quemet A, Maillard C, Ruas A (2015) Determination of zirconium isotope composition and concentration for nuclear sample analysis using Thermal Ionization Mass Spectrometry. Int J Mass Spectrom 392:34–40. https://doi.org/10.1016/j.ijms.2015.08.023

26. Quemet A, Ruas A, Esbelin E, Dalier V, Rivier C (2019) Development and comparison of two high accuracy methods for uranium concentration in nuclear fuel: ID-TIMS and K-edge densitometry. J Radioanal Nucl Chem 321:997–1004. https://doi.org/10.1007/s10967-019-06670-y

27. International Atomic Energy Agency (2010) International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials - STR368. Vienna, Austria

28. Désenfant M, Priel M (2017) Reference and additional methods for measurement uncertainty evaluation. Measurement 95:339–344. https://doi.org/10.1016/j.measurement.2016.10.022

29. Chartier F, Aubert M, Pilier M (1999) Determination of Am and Cm in spent nuclear fuels by isotope dilution inductively coupled plasma mass spectrometry and isotope dilution thermal ionization mass spectrometry after separation by high-performance liquid chromatography. Fresenius J Anal Chem 364:320–327

30. Henri Becquerel National Laboratory (2015) Mini Table of radionucleides, First

edition. EDP Sciences

31. Quemet A, Baghdadi S (2021) Optimization of the double isotope dilution. J Anal At Spectrom under peer review

32. Désenfant M, Priel M, Rivier C (2005) Evaluation des incertitudes des résultats d'analyse. Ref P105 V1. Les Tech l'Ingénieur 1–17