Nd, Am and Cm isotopic measurement after simultaneous separation in transmutation irradiated samples

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ARTICLE

Nd, Am and Cm isotopic measurement after simultaneous separation in transmutation irradiated samples.

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In this work, a High-Performance Liquid Chromatography (HPLC) separation followed by Thermal Ionization Mass spectrometry (TIMS) measurements was optimized to measure Am, Cm and Nd isotope ratios in irradiated samples. The method validation was performed on a natural Nd standard (JNdi-1 reference material). The literature JNdi-1 reference values are calculated using a conventional internal normalization. However, in nuclear science, such normalization is not possible as no isotope ratio can be considered as a reference. Measurements were compared to reference values using the Exponential Mass Fractionation Law, which is a powerful tool to detect drifts. The results show that the dominant bias comes from the isotope fractionation, that can be minimized using the TE method. Acquired data suggest the following absolute composition for the JNdi-1 reference standard: $^{142}Nd/^{144}Nd = 1.13950(47)$ $^{143}Nd/^{144}Nd = 0.51163(30)$, $^{145}Nd/^{144}Nd = 0.34876(17)$, $^{146}Nd/^{144}Nd = 0.72322(65)$, $^{148}Nd/^{144}Nd = 0.24264(46)$ and $^{150}Nd/^{144}Nd = 0.23789(68)$ (k = 2). These values suggest the need to revisit the agreed upon reference values when Nd absolute isotopic composition is required. The conditions of the HPLC separation were also optimized to obtain purified fractions of Nd, Am and Cm in one experiment using a cation exchange column. Separations were achieved on the LUNA SCX column and using 2-Hydroxy-MethylButyric Acid (HMB) as eluent, introduced in gradient mode. A difference below 0.03 % was observed between data obtained with separation and without separation. Compared to previous work that required three separations using two different HPLC conditions, improvements were made in terms of both duration and amount of radioactive effluents. The methodology was then successfully applied to irradiated discs coming from MARIOS and DIAMINO analytical irradiation.

Introduction

In 2008, the French Alternative Energies and Atomic Energy Commission (CEA) started an R&D program dedicated to the development of minor actinide-bearing blankets for transmutation in sodium-cooled fast reactor. In 2009-2010, fuel pellets containing Am were manufactured in the ATALANTE facility with either dense or tailored porosity[1]. Those $U_{0.85}Am_{0.15}O_2$ discs were obtained using pelletizing-sintering process. These fuel discs, were assembled in rods. Analytical irradiations, namely MARIOS and DIAMINO experiments, were performed to understand their behaviors under irradiation, to determine the americium transmutation yield and to study the influence of the microstructure on the gas release as a function of temperature[2]. The MARIOS experiment was implemented in the High Flux Reactor (Petten, Netherland) from March 2011 until May 2012, and investigated temperatures ranging between 1000 and 1200°C. The second experiment (DIAMINO) was irradiated in the OSIRIS reactor (Saclay, France) from February 2014 until December 2015 and focused on temperatures ranging between 600 and 800°C.

Post-irradiation examination were carried out to improve the knowledge of nuclear data. Elemental and isotopic analyses after quantitative dissolution of the irradiated discs were performed to obtain the accurate transmutation yield and to qualify the associated evolution calculation code for different isotopes. 2 discs from the MARIOS experiment and 4 discs from the DIAMINO experiment were analyzed. Among the different determinations, U, Pu, Am, Cm and Nd isotope ratios are the main elements of interest in terms of isotopic analysis. This study is focused on the Am, Cm and Nd isotope ratios determination.

Thermal Ionization Mass Spectrometry (TIMS) is one of the reference techniques for the determination of actinides and lanthanides isotopic composition[3–7]. The main sources of bias for TIMS measurements are the isotope fractionation and isobaric interferences.

Isotope fractionation comes from an evaporation difference between the light and the heavy isotopes, causing a bias on measured isotope ratios. The total evaporation method (hereafter referred to as TE method) was developed to overcome this phenomenon by evaporating, ionizing and collecting the deposited sample until it is fully consumed[6]. The TE method was previously successfully employed for Am measurements[8]. High accuracy results were obtained, typically

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total uncertainties about 0.1 % (k = 2) could be achieved for the major ^{243}Am/^{241}Am isotope ratio.

As for actinides measurement, the TE method applied to Nd minimizes the bias due to isotope fractionation[6,9]. However, the comparison between results obtained for methods developed in nuclear application and most of the published results is difficult. Isotope data are mostly published for geochemical studies using natural Nd. By convention, the isotope ratios are normalized to the ^{146}Nd/^{144}Nd with a value of 0.7219. This value is provided from a large Nd analysis lead by O'Nions $et\ al$.[10]. However, this value is subject to discussion: values of 0.72333(16)[9] and 0.7232(6)[6] were measured for natural Nd with the TE method. Normalization to one known isotope ratio is relevant for geochemical studies as it allows comparing isotope ratios with respect to a common reference: the data are compared relatively. In the nuclear field, a normalization is not suited as there is no invariant isotope ratio, the ^{146}Nd/^{144}Nd isotope ratio can have wide range of values and no Nd isotope ratios can be considered as a constant from one irradiated sample to another.

Another advantage of the TE method compared to the conventional method is that it helps to decrease the analyzable quantity: the deposit is entirely evaporated with the TE method whereas it is partly consumed with the conventional method, permitting the reduction of minimal analyzable quantities[9]. In addition, the use of higher resistance amplifiers improves the sensitivity allowing to analyze smaller quantities without loss of the accuracy[11].

The isobaric interferences (for instance ^{241}Pu-^{241}Am, ^{242}Pu-^{242m}Am, ^{243}Cm-^{243}Am, ^{148}Nd-^{148}Sm or ^{150}Nd-^{150}Sm) lead to analysis bias. In general, to avoid isobaric interferences it is required to purify each element to analyze. The Pu/Am separation is well known in the literature and is efficient using for example the TEVA resin[12]. One well-known method to purify Am, Cm and Nd in the laboratory consists of 2 different High-Performance Liquid Chromatography (HPLC) separations[13]. First, the Nd is purified using α-hydroxyisobutyric acid (HIBA) as eluent with the Vydac 201TP5415 column. The Am/Cm separation is performed using 2-Hydroxy-MethylButyric Acid (HMB) as an eluent with the Nucleosil 100-5SA column. The Cm fraction is depleted of Am and can be directly analyzed by TIMS. However, the Am fraction is not completely depleted of Cm and requires a second step of purification using the same HPLC condition[13]. Despite obtaining well purified fractions of Am, Cm and Nd, this protocol is tedious, generates a high quantity of radioactive effluent and uses a high quantity of sample. A new protocol was investigated to perform the separation in one step.

In aqueous solution, the lanthanides are strongly hydrated trivalent cations and cannot be easily separated by ion exchange resins[14,15]. However, the separation selectivity can be increased using appropriate chelating agents such as HMB, HIBA or oxalic acid[14–21]. With oxalic acid, lanthanides form negatively charged complexes that can interact with a resin having positively charged functional groups (like IonPac CS5A column[15,17,18]). Heavier lanthanide ions ($e.g.$ Lu) have smaller ionic radii, thus higher charge densities, than the lighter one

($e.g.$ La) due to the lanthanide contraction[22]. So, complexes with heavier lanthanides have higher stability constant than complexes with lighter ones[23]. Heaviest lanthanides have more affinity with the resin: lanthanide elution is performed from La to Lu. With HMB and HIBA, lanthanides form neutral complexes that decrease the lanthanide affinity with resin which functional groups are negatively charged (like IonPac CS10[14], Shodex IC R-621[21], Supelcosil[16] or LUNA SCX[19,20] columns). Heavier lanthanides have stability constants of complexes higher than the lighter ones[24]. Therefore, lanthanides with the most stable complexes will elute first, whereas lanthanides with less stable complexes elute later: the elution order goes from Lu to La. The Am/Cm separation is more challenging due to similar chemical properties[25]. Recent studies showed that the combination HMB as the eluent and LUNA SCX as the column provides the most efficient separation[25]. The same combination eluent/column (HMB/LUNA SCX) with appropriate conditions described in the experimental section, was then selected to perform the lanthanide and the Am/Cm separation, in one step.

The present study is focused on the Nd, Am and Cm measurements of 2 irradiated samples: one from the DIAMINO experiment and one from the MARIOS experiment. The protocol implemented in glove box to separate lanthanides and Am/Cm was optimized and applied to these irradiated samples. In addition, this study proposes a method to obtain the Nd absolute isotope ratios. Suggested revised values for the JNdi-1 isotopic standard were also proposed and can be used for future studies.

Experimental

Reagents and reference materials

Ultrex II reagent grade nitric acid (w = 67-70 %, J.T. Baker) and Suprapur grade Hydrofluoric acid (w = 40 %, Merck) were used. Ammonia (w = 28 %, purity $\geq$ 99.99 %) and acetic acid (purity $\geq$ 99.99 %) were purchased from Sigma Aldrich and suitable for trace metal analysis. Deionised water was provided by a MilliQ system (resistivity: 18.2 MΩ cm, Millipore, Milford). Two HPLC eluents were prepared by dissolution of HMB (Sigma-Aldrich, Purity > 98 %) in deionized water and adjusted to the desired pH with 28 % ammonia: [HMB] = 0.1 mol L^{-1} / pH = 3.6 and [HMB] = 0.2 mol L^{-1} / pH = 4.5. A complexing solution was prepared by dissolution of 4-(2-pyridilazo) resorcinol (Sigma-Aldrich, Purity > 98 %) in acetic acid and ammonia (hereafter this solution is referred as PAR solution). The HPLC eluents and the PAR solution were filtered with Millipore filter with 0.22 μm pore diameter.

The JNdi-1 isotopic reference material was used as a reference for Nd isotope ratios measurements[26]. JNdi-1 solutions with 100, 10 and 1 ng μL^{-1} were prepared in 0.5 mol L^{-1} HNO$_3$ to load respectively 100, 10 and 1 ng on filaments.

Spex Certiprep mono-elemental standard solutions of La, Ce, Pr, Sm, Eu and Gd with lanthanide mass fraction of 1 mg g^{-1} were used. Mono-element solutions of ^{241}Am with Am mass fraction of 13 μg g^{-1} and a curium solution at 0.1 μg g^{-1} available in the laboratory were used.

Table 1: Detectors configuration for Nd, Am and Cm analyses. * and ** refer to the isotope that was measured using FC 12 and FC 13, respectively. All others masses were measured using FC 11.

Detector	Nd	Am	Cm
L4	140 mass		
L3	^{142}Nd		^{242}Cm
L2	^{143}Nd	239 mass	^{243}Cm*
L1	^{144}Nd	^{241}Am	^{244}Cm**
C	^{145}Nd	^{242m}Am**	^{245}Cm
H1	^{146}Nd	^{243}Am*	^{246}Cm
H2	147 mass		^{247}Cm
H3	^{148}Nd		^{248}Cm
H4	^{150}Nd*		

Two synthetic solutions were prepared from the previously described solutions. The first solution contained La, Ce, Nd, Pr, Sm, Eu and Gd at 50 mg L^{-1}, Am at 8 mg L^{-1} and Cm at 1 mg L^{-1} (hereafter referred to as Ln/Am/Cm synthetic solution). The second synthetic solution contained La, Ce, Nd, Pr, Sm, Eu and Gd at 8 mg L^{-1} (hereafter referred to as Ln synthetic solution).

Separation experimental set-up

Teva resin

A separation using TEVA resin (Triskem, 100–150 µm particle size in 2 mL prepackaged columns) was used to purify the trivalent elements (the lanthanides, Am and Cm) from U and Pu. The TEVA column was conditioned with 5 mL of 8 mol L^{-1} HNO$_3$. The sample, after HNO$_3$ concentration adjustment to 8 mol L^{-1}, was added to the column. The resin fixed U and Pu and did not retain the trivalent elements. This fraction was collected in a PFA vial. 4.5 mL of 8 mol L^{-1} HNO$_3$ were added to the column to elute any possible remaining trivalent elements and collected in the same PFA vial.

HPLC separation

The HPLC system is composed of an Agilent 1200 series quaternary pump, an isocratic pump, a vacuum degasser, a six-way manually operated rotary Rheodyne valve with 20 µL sample loop (model 7125), an injection syringe, the Phenomenex LUNA SCX column, a 10 mm Z-flow cell connected by optical fibres to the UV/Vis Agilent Cary 60 spectrophotometer (SEDI ATI SR600). The column has the following properties: internal diameter = 4.6 mm and column length = 250 mm. The resin properties are particle size = 5 µm and pore sizes = 100 Å. PEEK tubing with internal diameter of 0.25 mm was used. The Rheodyne valve, the syringe, the LUNA SCX column and the Z-flow cell were located inside the glove box. The Agilent 1200 series system, the eluents and the UV/Vis spectrophotometer were located outside the glove box. The separation was performed with a flow rate fixed at 1 mL min^{-1} for the quaternary pump (HMB solutions) and at 0.5 mL min^{-1} for the isocratic pump (PAR or 0.5 mol L^{-1} HNO$_3$ solution). The HMB eluent was introduced in gradient mode: starting at 100 % [HMB] = 0.1 mol L^{-1} / pH = 3.6, the final elution conditions at

t = 30 min are 50 % v/v [HMB] = 0.1 mol L^{-1} / pH = 3.6 and 50 % [HMB] = 0.2 mol L^{-1} / pH = 4.5. The pressures were about 100 bars for the quaternary pump and 8 bars for the isocratic pump. The PAR solution complexed the lanthanides, and to a lesser extent Am and Cm, for their detection with the spectrophotometer and subsequent measurement at their respective retention time. After the retention times determination, the PAR solution was substituted by 0.5 mol L^{-1} HNO$_3$ for the separation dedicated to isotope ratios analysis. Indeed, this avoids the formation of a large crust on the TIMS filaments due to the PAR. The separation is therefore "blind" using only the retention times determined previously with the presence of PAR, to collect the different fractions.

Thermal Ionization Mass Spectrometry

The Thermo Scientific Triton TIMS is equipped with 9 Faraday cups (all are movable 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). A relay matrix helps to easily select as required which amplifiers are connected to which Faraday cup. Due to the differences in the signal response of the different amplifiers, a tau decay constant, implemented by the manufacturer, equal to 0, 0.294 and 0.540 for FC 11, FC 12 and FC 13, respectively, was applied. The measurements were performed in multi-collection and positive modes. Intercalibration gains of the Faraday cup detectors were measured daily by an automated process of the TIMS software. The baselines were measured every half day during 20 min.

A double Re-filament configuration was used to control independently the evaporation and the ionization filament temperature. These filaments (Re metal, purity 99.99 %) are provided by ATES and were outgassed 20 min at 4.5 A in a Thermo Scientific vacuum chamber (< 5.10^{-6} mbar). 1 µL of Am or Nd solutions, or 2 µL of Cm solutions was deposited on the filament and dried with a 0.4 A current. After dryness, the current was increased progressively to 2 A in 10 s.

TE method measurements

All the measurements were performed with the TE method. This method, divided in 3 steps, was previously described for Th, U or Am and was applied to Nd, Am and Cm[8,27,28]. The filaments heating process can slightly differ depending on the element to analyze. In the first step, the ionization filament current is increased from 0 A to 5.5 A in 20 min for Nd analyses and in 10 min for Am and Cm analyses. Then, the evaporation filament is heated to obtain a major isotope ion beam of 1 mV intensity. A "peak center" (mass calibration and ions beam centering in the detector) and the lens optimization of the ion source are performed on the major isotope ion beam. In the second step (acquisition step), the data acquisition is started. The evaporation filament current is increased until the ion beam intensity of the sum of all measured isotopes reaches the target

intensity: about 42 V, 4.2 V and 0.6 V for 100 ng, 10 ng and 1 ng of the JNdi-1 measurements without separation respectively, about 3.5 V for the JNdi-1 measurement after separation and about 1.2 V, 5V and 0.04 V for the DIAMINO and MARIOS discs Nd, Am and Cm measurements, respectively. The evaporation filament is then controlled to keep the ion 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 (step 3 - shutdown phase).

The detector configuration for Nd, Am and Cm analyses were summarized in the Table 1. During Nd measurement, masses 140 (^{140}Ce) and 147 (^{147}Sm and ^{147}Pm) were measured to monitor any possible contamination. No mathematical correction for the Ce or for the Sm isobaric interferences were performed on ^{142}Nd, ^{144}Nd, ^{148}Nd and ^{150}Nd isotopes measurement. For Am analysis, mass 239 (^{239}Pu) was measured to monitor any possible Pu contamination.

Nd validation method

JNdi-1 measurements using the TE method

5, 7 and 14 loaded filaments of respectively 100, 10 and 1 ng of JNdi-1 standard were analyzed to validate the Nd isotope ratios determination method.

JNdi-1 measurements after separation

In the DIAMINO and MARIOS samples, the Nd analysis might be subject to the following interferences: ^{142}Ce-^{142}Nd, ^{144}Ce-^{144}Nd, ^{148}Sm-^{148}Nd and ^{150}Ce-^{150}Nd. In the case of the Ln synthetic solution, the isobaric interferences are: ^{142}Ce-^{142}Nd, ^{144}Sm-^{144}Nd, ^{148}Sm-^{148}Nd and ^{150}Ce-^{150}Nd. As a neutronic simulation code was available for the DIAMINO sample, it was possible to evaluate the level of isobaric interferences (no neutronic simulation data were available for the MARIOS disc). For the DIAMINO discs, the amount ratios before separation were estimated to be 4 for the Nd/Sm ratio and 1.7 for the Nd/Ce ratio. The samples contained more Nd compared to Ce and Sm whereas the amount ratios were about 1 for the Ln synthetic solution. Therefore, the DIAMINO disc has an ^{142}Nd/^{142}Ce ratio estimated at 0.004, an ^{144}Nd/^{144}Ce ratio estimated at 54, an ^{148}Nd/^{148}Sm ratio estimated at 14 and an ^{150}Nd/^{150}Sm estimated at 0.8. In the Ln synthetic solution before separation, the ratios were about 2.4 for the ^{142}Nd/^{142}Ce, 0.5 for the ^{148}Nd/^{148}Sm ratio and 0.8 for the ^{150}Nd/^{150}Sm. ^{144}Ce isotope is not present in the non-radioactive Ln synthetic solution.

9 independent injections of the Ln synthetic solution were performed before and after each series of the DIAMINO and MARIOS samples separation to evaluate the HPLC performance separation. 20 µL of the Ln synthetic solution was injected in the HPLC system. The Nd purified fraction containing about 160 ng of Nd was then evaporated. The residue was dissolved again with 16 µL of 0.5 mol L^{-1} HNO$_3$ to obtain a [Nd] ≈ 10 ng µL^{-1} solution. 1 µL was deposited on a filament to be analyzed.

Exponential Mass Fractionation Law (EMFL)

The quality of the Nd isotope ratios measurements was investigated using the three-isotope plot and the EMFL. This indicator of data quality investigates unresolved interferences and others drifts (like peak tailing effect) that could cause ratios to deviate from the EMFL. The EMFL expresses the kinetics of the isotope fractionation[29,30]. The EMFL curve in which one ^XNd isotope (X = 142, 143, 145, 148 or 150) is plotted against the others (^{144}Nd and ^{146}Nd) is given in Eq. (1)[29].

$$\left(\frac{^XNd}{^{144}Nd}\right) = \left(\frac{^{146}Nd}{^{144}Nd}\right)^\beta \cdot \left[\frac{\left(\frac{^XNd}{^{144}Nd}\right)_{ref}}{\left(\frac{^{146}Nd}{^{144}Nd}\right)_{ref}^\beta}\right] \qquad (1)$$

Where ^XNd/^{144}Nd and ^{146}Nd/^{144}Nd are the isotope ratios for each data on the EMFL curve and (^XNd/^{144}Nd)$_{ref}$ and (^{146}Nd/^{144}Nd)$_{ref}$ are the reference isotope ratios. The data obtained by Garçon et al.[7], who measured all Nd isotope ratios and not only the ^{143}Nd/^{144}Nd certified ratio[26], were used as reference values, and are hereafter referred to as such. These reference values were obtained after conventional normalization (^{146}Nd/^{144}Nd = 0.7219). β represents the kinetic fractionation factor and is calculated with Eq. (2).

$$\beta = \frac{ln\left(\frac{M(^XNd)}{M(^{144}Nd)}\right)}{ln\left(\frac{M(^{146}Nd)}{M(^{144}Nd)}\right)} \qquad (2)$$

Where $M(^XNd)$, $M(^{144}Nd)$ and $M(^{146}Nd)$ are the atomic masses of ^XNd, ^{144}Nd and ^{146}Nd isotopes, respectively. The data acquired with the TE method are then compared to the EMFL. Data fitted with the EMFL indicates whether the only possible bias comes from the isotope fractionation or not.

Samples preparation

The analytical protocol scheme of the discs is presented in Fig. S1 in the supplementary material. The dissolution of each of the irradiated UAmO$_2$ transmutation discs was conducted in 2 steps in a closed vessel in a hot cell. The primary dissolution was performed at 11 mol L^{-1} HNO$_3$ leading to a uranium based solution, containing lanthanides and some of the fission products. The second dissolution step was the residue depletion by adding a 11 mol L^{-1}/0.075 mol L^{-1} HNO$_3$/HF mixture to the primary dissolution solution to finalize the dissolution of the plutonium.

Dissolution solutions were diluted 100 times in the hot cell to obtain a radiation level compatible with glove box environment where the TIMS are located. Two independent dilutions were performed for each of MARIOS and DIAMINO discs dissolution solution. 1 mL of each diluted dissolution solution was transferred by pneumatic transfer to the isotopic analysis laboratory. The characteristic of the diluted solution for the DIAMINO sample was: [U] ≈ 55 µg mL^{-1}, [Pu] ≈ 3.7 µg mL^{-1}, [Am] ≈ 4.8 µg mL^{-1}, [Cm] ≈ 0.02 µg mL^{-1} and [Nd] ≈ 0.10 µg mL^{-1}. The characteristic of the diluted solution for the MARIOS sample was: [U] ≈ 58 µg mL^{-1}, [Pu] ≈ 6.8 µg mL^{-1}, [Am] ≈ 4.0 µg mL^{-1}, [Cm] ≈ 0.08 µg mL^{-1} and [Nd] ≈ 0.26 µg mL^{-1}.

2 mL of 8 mol L^{-1} HNO$_3$ was added to the diluted dissolution solutions. Then, the separation using the TEVA resin was applied to obtain a purified fraction of trivalent elements (see Separation experimental set-up section). 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, Cm and Nd were obtained and then evaporated. The residues of the respectively purified Am, Cm and Nd were dissolved again with respectively 20 μL, 5 μL and 10 μL of 0.5 mol L^{-1} HNO$_3$ to obtain [Am] ≈ 100 ng μL^{-1}, [Cm] ≈ 2.4 ng μL^{-1} and [Nd] ≈ 11 ng μL^{-1} solutions for the DIAMINO disc, and [Am] ≈ 100 ng μL^{-1}, [Cm] ≈ 11 ng μL^{-1} and [Nd] ≈ 26 ng μL^{-1} solutions for the MARIOS disc. 3 deposits were analyzed for Am. 2 deposits were analyzed for Cm and Nd.

Results evaluation

The relative bias was calculated using Eq. (3).

$$\text{Bias (\%)} = \frac{Z - ref}{ref} \qquad (3)$$

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

Eq. (4) 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[31].

$$E_N = \frac{|z - ref|}{\sqrt{u_z^2 + u_{ref}^2}} \qquad (4)$$

with u_z being the measurement uncertainty and u_{ref} the reference value uncertainty with a coverage factor $k = 1$.

The precision was evaluated by calculating the Relative Standard Deviation (RSD) of all the measurements.

The HPLC separation performance was evaluated by calculating the resolution (R_S) between 2 peaks (Eq. (5))[32].

$$R_S = 1.177 \cdot \frac{t_{r,n+1} - t_{r,n}}{\omega_{n+1} - \omega_n} \qquad (5)$$

with $t_{r,n}$ (resp. $t_{r,n+1}$) the retention time of the compound n (resp. n+1) corresponding to the peak n (resp. n+1) and ω_n (resp. ω_{n+1}) the width at half maximum of the peak n (resp. n+1). The separation is optimal if the resolution is higher than 1.5.[32]

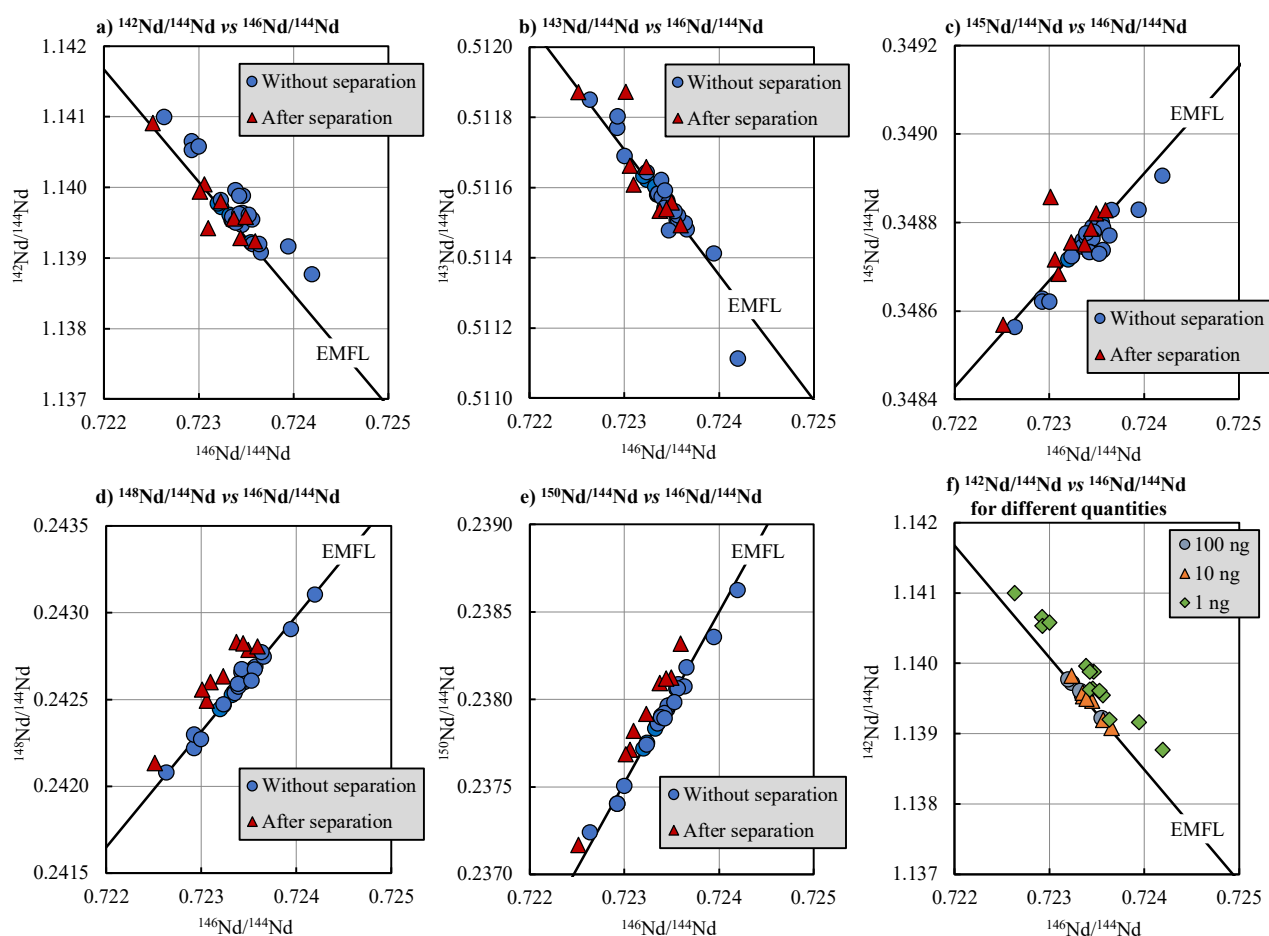
Figure 1: ^{X}Nd/^{144}Nd (X = 142, 143, 145, 148, 150) in comparison to the ^{146}Nd/^{144}Nd ratio for the JNdi-1 standard without and after separation (figure a to e, respectively) and ^{142}Nd/^{144}Nd vs ^{146}Nd/^{144}Nd ratios for different Nd quantities without separation (f). The solid line represents the Exponential Mass Fractionation Law calculated with the Garçon et al.[8] reference values.

Table 2: Suggested revised JNdi-1 standard reference values and isotope ratios of the Ln synthetic solution after HPLC separation. The bias was calculated in regard of the revised reference values. E_N corresponds to the normalized error.

	$^{142}Nd/^{144}Nd$	$^{143}Nd/^{144}Nd$	$^{145}Nd/^{144}Nd$	$^{146}Nd/^{144}Nd$	$^{148}Nd/^{144}Nd$	$^{150}Nd/^{144}Nd$
This work: Suggested revised reference values						
Value	1.13950(47)	0.51157(28)	0.34874(15)	0.72339(63)	0.24258(43)	0.23789(59)
RSD	0.02 %	0.03 %	0.02 %	0.04 %	0.09 %	0.12 %
Values after separation						
Value	1.1400(13)	0.51164(29)	0.34875(18)	0.72320(66)	0.24263(45)	0.23788(69)
RSD	0.05 %	0.03 %	0.03 %	0.05 %	0.09 %	0.14 %
Bias	0.02 %	0.01 %	0.002 %	-0.03 %	0.02 %	-0.002 %
E_N	0.44	0.37	0.07	0.42	0.17	0.01

Uncertainty estimation

The isotope ratio (R) uncertainty ($u(R)$) at k = 1 was described in previous work[8] and was estimated using Eq. (6).

$$\frac{u^2(R)}{(R)^2} = \frac{u^2(\bar{x})}{\bar{x}^2} + \frac{u^2(trueness)}{(trueness)^2} + \frac{u_{ref}^2}{(ref)^2} \qquad (6)$$

$$\frac{u(trueness)}{trueness} = \frac{maximum\ bias\ in\ CRM}{\sqrt{3}} \qquad (7)$$

The first term of Eq. (6) is given by the RSD (random effects). The second and third terms take into account the systematic effect. The measurement trueness is calculated using Eq. (7) by measuring the maximum bias observed on a reference material. The choice of the reference material will be discussed in the results and discussion part.

Results and discussion

JNdi-1 measurement

The data acquired on the JNdi-1 standard with the TE method was compared to the reference values (Table S1 in supplementary material). A bias was observed for all isotope ratios: $\approx$ -0.2 % for $^{142}Nd/^{144}Nd$; $\approx$ -0.1 % for $^{143}Nd/^{144}Nd$; $\approx$ 0.1 % for $^{145}Nd/^{144}Nd$; $\approx$ 0.2 % for $^{146}Nd/^{144}Nd$; $\approx$ 0.4 % for $^{148}Nd/^{144}Nd$ and $\approx$ 0.6 % for $^{150}Nd/^{144}Nd$. The measured values are not in agreement with the reference values (E_N > 2). The bias is negative for isotope ratios involving an isotope with a mass below 144 and is positive for isotope ratios involving an isotope with a mass higher than 144.

The reference values were obtained after an internal normalization. The acquired data were reprocessed applying the conventional internal normalization using the exponential law and the conventional value ($^{146}Nd/^{144}Nd$ = 0.7219, Table S2 in the supplementary material). Recalculated data are now in excellent agreement with the reference values (bias < 0.02 % and E_N < 2) for all isotope ratios and deposited quantities except for the $^{142}Nd/^{144}Nd$ were a normalized error of 3.0 is observed for 1 ng quantity: these $^{142}Nd/^{144}Nd$ data stay statistically different to the reference value. These results suggest that the

bias previously observed is due to the internal normalization used for the reference values.

However, the acquired data (TE method without normalization) are in good agreement with the data obtained by Wakaki *et al.*[6] using the TE method without normalization as well. Biases below 0.07 % and normalized errors below 2 in comparison to Wakaki et al.[6] are observed, regardless the isotope ratio or the analytical quantity (Table S1 in the supplementary material).

The acquired isotope ratios were reported in a three-isotope plot and compared to the EMFL. As can be seen in Figure 1, the $^{X}Nd/^{144}Nd$ (X = 143, 145, 146, 148 and 148) ratios (blue circle in the figures) fitted well the EMFL, regardless of the Nd amount. The observed bias compared to the reference values only come from the isotope fractionation. However, the $^{142}Nd/^{144}Nd$ data has a different behavior.

Investigation of the $^{142}Nd/^{144}Nd$ ratio

For the $^{142}Nd/^{144}Nd$ ratio, it seems that two groups of values can be found in the three-isotope plot (Figure 1.a). The first group of 13 values fits the EMFL. The second group of another 13 values does not fit the EMFL. Figure 1.f represents the three-isotope plot for $^{142}Nd/^{144}Nd$ and $^{146}Nd/^{144}Nd$ distinguishing the different analyzed quantities (*i.e.* 100 ng, 10 ng and 1 ng). This plot shows that the data obtained with amounts of 100 ng and 10 ng fit the EMFL. The data obtained with the smallest quantity (*i.e.* 1 ng) does not fit the EMFL. This indicates a drift that is not attributed to isotope fractionation in the case of 1 ng.

During the measurements, a low signal was observed at mass 140 due to ^{140}Ce. Cerium has another isotope (^{142}Ce) that could interfere with ^{142}Nd. The $^{140}Ce/^{142}Nd$ ratio was below 0.00004 for 100 ng and below 0.0004 for 10 ng. Assuming the Ce isotope composition provided by IUPAC[33] (^{140}Ce and ^{142}Ce isotope abundance of 88.45 % and 11.11 %, respectively), the ^{142}Ce isotope contribution on the measured signal at mass 142 was below 0.0005 % for 100 ng and below 0.005 % for 10 ng and is small compared to the repeatability (RSD = 0.02 % for 100 ng and 0.01 % for 10 ng). For 1 ng, the $^{140}Ce/^{142}Nd$ ratio (between 0.001 and 0.006) is higher than for 10 ng and 100 ng. The ^{142}Ce isotope contribution (between 0.01 % and 0.07 %) on the signal measured at mass 142 is in this case not negligible compared to

the repeatability (RSD = 0.06 %). This Ce impurity seems to be the cause of the bias observed for 1 ng.

The data acquired for the ^{142}Nd isotope for 1 ng was corrected from the ^{142}Ce isotope contribution using isobaric interference correction[34]. . As can be seen in Figure 2 (three-isotope plot for ^{142}Nd/^{144}Nd and ^{146}Nd/^{144}Nd ratios for both the corrected and uncorrected data), the corrected data (purple circle in figure) are in good agreement with the EMFL. This confirms that the observed bias comes from a small amount of Ce impurities, which becomes significant when low signal is detected. The EMFL confirms that the mathematical correction suppresses efficiently these interferences. The small presence of cerium impurities was investigated but no explanations were found: in particular, blank filament were analyzed without observed significant signal at mass 140.

Suggested revised JNdi-1 standard reference values

The TE method, developed to correct the mass fractionation, is often used in the nuclear field to obtain reference values and analyte isotope composition[6,20]. As showed by the three-isotope plot, no drift were observed for Nd isotope ratios, which are, moreover, in agreement with Wakaki *et al*.[6] data using the TE method. The difference between the acquired data and the reference values is attributed to the procedure to correct the isotope fractionation: TE method for this study and internal normalization for the reference values. The data acquired here with the JNdi-1 standard using the TE method without normalization suggests the need to revisit the agreed upon reference values when absolute isotope ratios determination are required. The revised reference values uncertainties were estimated using Eq. (6) taking into account the repeatability and the reference values uncertainty. The measurement trueness term (Eq. (7)) was not taken into account as no drift were observed. The suggested revised reference values for JNdi-1 standard were chosen as the average of all the measurements (Table 2): ^{143}Nd/^{144}Nd = 0.51163(30), ^{145}Nd/^{144}Nd = 0.34876(17), ^{146}Nd/^{144}Nd = 0.72322(65), ^{148}Nd/^{144}Nd = 0.24264(46) and ^{150}Nd/^{144}Nd = 0.23789(68). For the ^{142}Nd/^{144}Nd ratio, as a bias was observed for 1 ng quantity, the suggested revised reference value was the average of the values for 100 ng and 10 ng quantities (1.13950(47)).

Optimization of the lanthanides/Am/Cm separation condition using HPLC

The first HPLC separation experiments were performed in isocratic mode using only the [HMB] = 0.1 mol L^{-1} / pH = 3.6 eluent. The lanthanides separation was excellent but required 3 h, which is too long for routine use and generates too much effluents for a single separation.

The second tested condition was similar to Goutelard *et al*.[19] studies: [HMB] = 0.13 mol L^{-1} / pH = 3.6 for 20 min, then [HMB] = 0.22 mol L^{-1} / pH = 4.5. The rapid change of elution condition lead to blocking the column. This method was therefore not selected.

The next experimental condition was the concentration gradient proposed by Gueguen *et al*.[20]: initial elution with 100 % [HMB] = 0.1 mol L^{-1} / pH = 3.6 and end at t = 35 min with 100 %

[HMB] = 0.2 mol L^{-1} / pH = 4.5. This condition leads to a resolution higher than 1.5 with a short analysis time (about 20 min). Separation conditions using concentration gradient are required to decrease progressively the lanthanides affinity with the column with a continuous pH increase of the solution. As a consequence, the retention times are decreased. However, despite the good separation performance (R$_s$ > 1.5), Nd, Am and Cm were eluted in about 2 min which was too short to collect manually properly the fractions in a glove box.

To have more time to collect the purified fraction, the elution gradient duration was increased: the gradient started at t = 0 min with 100 % [HMB] = 0.1 mol L^{-1} / pH = 3.6 and finished at t = 30 min with 50 % *v/v* [HMB] = 0.1 mol L^{-1} / pH = 3.6 and 50 % [HMB] = 0.2 mol L^{-1} / pH = 4.5. These elution conditions resulted in the lanthanides exiting the column from Gd to La. Cm then Am are eluted between Sm and Nd (Figure 3). The resolutions were excellent: 3.9 for Am and Cm, 5.8 for Pr and Nd, 11 for Ce and Nd and 15.6 for Sm and Nd. The retention times for Cm, Am and Nd were 12.7 min, 14.3 min and 16.3 min, respectively.

Our historical method to obtain purified fractions of Nd, Am and Cm was performed with three HPLC separations using two different resins and elution conditions[13]. Each separation took about 30-40 min. Therefore, obtaining the purified fractions required at least 120 min (not including the time consuming change of the column and the elution condition). Moreover, this protocol generated at least 100 mL of radioactive effluent. The optimized HPLC conditions developed in this study helped separating the lanthanides, Am and Cm in one step (suppressing the time necessary to change the condition elution and the column) and required 30 min. This reduces the analyst exposition to irradiating samples as only 1 HPLC injection is required instead of 3. Finally, the volume of radioactive effluent (about 45 mL) is reduced by a factor 2.

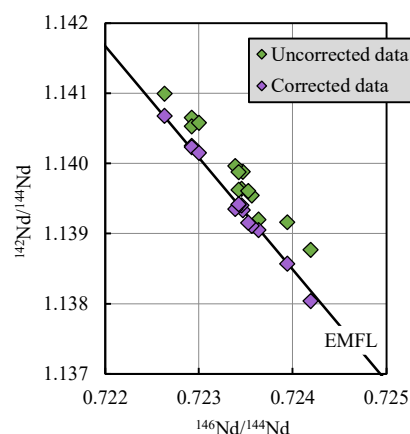**Validation of the HPLC separation for measuring Nd isotope ratios**

Figure 2: Three-isotope plot for ^{142}Nd/^{144}Nd and ^{146}Nd/^{144}Nd ratios for uncorrected and ^{142}Ce isotope contribution corrected data for 1 ng JNdi-1 standard. The solid line represents the Exponential Mass Fractionation Law (EMFL) calculated from Garçon *et al*.[7] reference values.

The data acquired on the JNdi-1 standard after separation were compared to the suggested revised reference values (Table 2). Repeatabilities are similar to the ones observed for the suggested revised reference values: for instance RSD = 0.03 % for the ^{143}Nd/^{144}Nd ratio with and without separation or RSD = 0.09 % for ^{148}Nd/^{144}Nd ratio with and without separation. The data obtained after separation are statistically identical to the suggested revised reference values ($E_N < 2$). Biases were below 0.03 % for all the isotope ratios. It should be noted that for 3 measurements a short signal at mass 140 was observed at the very beginning of the acquisition. The data acquired at the beginning for these 3 measurements of the TE method were not taken into account for the integration of the ^{142}Nd isotope signal. The three-isotope plots (Figure 1) showed that all the isotope ratios (red triangle) are in good agreement with the EMFL. These data validated the separation protocol: no bias attributed to the separation was observed.

Nd isotope ratios for the DIAMINO and MARIOS discs

Reference isotope

The ^{144}Nd isotope measurement in the irradiated discs can have a bias due to the presence of the ^{144}Ce non-natural radioisotope. In the case ^{144}Nd measurement has a bias, all isotope ratios relative to ^{144}Nd would have a bias as well. It is therefore preferable to use another isotope without interference as a reference isotope. The ^{145}Nd isotope was therefore arbitrarily chosen when reporting DIAMINO and MARIOS results (Table S3 in the supplementary materials).

Uncertainty estimation for Nd isotope ratios

The Nd isotope ratios uncertainties were estimated using Eq. (6). The systematic effect term was calculated considering the suggested revised reference value uncertainties and the trueness term was the maximum bias observed for the JNdi-1 after separation compared to the suggested revised reference value.

Nd isotope ratios in the discs

The ^{143}Nd/^{145}Nd, ^{144}Nd/^{145}Nd, ^{146}Nd/^{145}Nd, ^{148}Nd/^{145}Nd and ^{150}Nd/^{145}Nd ratios were 1.2877(15), 1.3840(77), 0.8562(21), 0.5705(17) and 0.3445(21), respectively, for the DIAMINO disc. These data are in agreement with the simulation code data: about 1.2, 1.4, 0.84, 0.56 and 0.31 for ^{143}Nd/^{145}Nd, ^{144}Nd/^{145}Nd, ^{146}Nd/^{145}Nd, ^{148}Nd/^{145}Nd and ^{150}Nd/^{145}Nd ratios, respectively. For the MARIOS disc, the isotope ratios were 1.2860(14), 1.4086(67), 0.8992(14), 0.5892(17) and 0.3626(16) for ^{143}Nd/^{145}Nd, ^{144}Nd/^{145}Nd, ^{146}Nd/^{145}Nd, ^{148}Nd/^{145}Nd and ^{150}Nd/^{145}Nd respectively. The repeatability observed for both discs were similar to the JNdi-1 measurements. The uncertainty estimation were below 0.62 % for all isotope ratios.

The ^{142}Nd/^{145}Nd was 0.0180(72) for the DIAMINO disc and was 0.0128(37) for the MARIOS disc. The uncertainty estimations (40 % for DIAMINO disc and 29 % for MARIOS disc) were significantly higher than for all other Nd isotope ratios (always below 0.62 %) due to the low signal measured at mass 142 (about 4 mV) increasing the repeatability and consequently the uncertainties.

Am isotope ratios for the DIAMINO and MARIOS discs

Pu/Am separation performance verification

The absence of Pu in the Am fraction, that could lead to ^{241}Am-^{241}Pu and ^{242m}Am- ^{242}Pu isobaric interferences, was verified by measuring the isotope ^{239}Pu for each analysis. The measured ^{239}Pu/^{241}Am maximum signal ratio was 5.10^{-5} for the DIAMINO disc and 2.10^{-4} for the MARIOS disc. This ratio is slightly above the detection limit estimated at 3.10^{-5}. If we consider the ^{241}Pu/^{239}Pu ratio measured during the Pu isotope ratios determination[35] (about 0.002 for DIAMINO disc and 0.01 for MARIOS disc), the contribution of the ^{241}Pu isotope to the signal measured at mass 241 can be estimated to be below 0.001 % and is negligible compared to the repeatability (RSD = 0.02 % for DIAMINO disc and RSD = 0.06 % for MARIOS disc). Similarly, it is possible to estimate the contribution of the ^{242}Pu isotope to the signal measured at mass 242. This contribution represented 0.19 % for the DIAMINO disc and 0.23 % for MARIOS disc and is similar to the repeatability (RSD = 0.2 % for DIAMINO disc and RSD = 0.3 % for MARIOS disc). To take into account this potential bias, this contribution was added to the calculation of the uncertainty estimation for the ^{242m}Am/^{243}Am ratio.

Uncertainty estimation parameters

The data obtained on the STAM reference material was used for the ^{243}Am/^{241}Am ratio uncertainty estimation, in particular to calculate the measurement trueness[8]. In the absence of certified values for the ^{242m}Am/^{241}Am ratio, the ^{234}U/^{238}U isotope ratio of the U500 NBL reference material was used to estimate the measurement trueness: the ^{234}U/^{238}U isotope ratio is close to the ^{242m}Am/^{241}Am ratio (about 0.01). Also, both ^{234}U and ^{242m}Am isotopes are close to a major peak (^{235}U and ^{241}Am isotopes, respectively). Then U500 ^{234}U/^{238}U ratio simulates correctly any bias coming from peak tailing. For the ^{234}U/^{238}U ratio of the U500 NBL standard, the maximum bias was measured at 0.56 % and the reference uncertainty was 0.1 % ($k = 1$). These values were considered for the uncertainty estimation of ^{242m}Am/^{241}Am ratio.

Am isotope ratios in the discs

The ^{243}Am/^{241}Am isotope ratio was 0.016730(22) for the DIAMINO disc and 0.061149(93) for the MARIOS discs (Table S3 in the supplementary materials). The uncertainty estimations
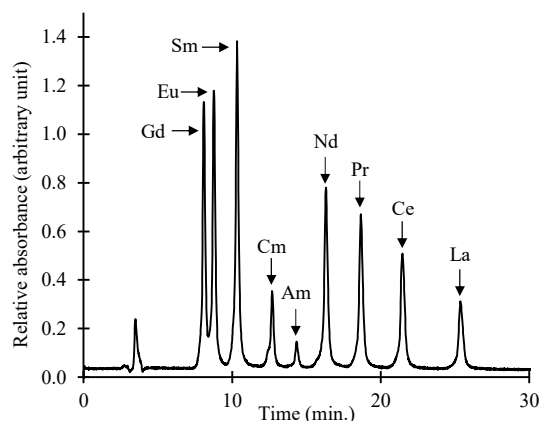

Figure 3: Separation chromatogram of Am, Cm and the lanthanides in a synthetic mixture.

were below 0.2 % (k = 2). The data acquired for the DIAMINO experiment seems slightly different to the data obtained with the simulation code (^{243}Am/^{241}Am about 0.024).

The ^{242m}Am/^{241}Am isotope ratio was 0.01164(21) for the DIAMINO disc and 0.02173(36) for the MARIOS discs. The uncertainty estimations were 1.6 % for the DIAMINO disc and 1.8 % for the MARIOS disc. These uncertainty estimations were 10 times higher than the one obtained for ^{243}Am/^{241}Am ratio, mainly due the contribution of the peak tailing and the separation in the final uncertainty. The data acquired for the DIAMINO experiment seems slightly different to the data obtained with the simulation code (about 0.0061).

Cm isotope ratios for the DIAMINO and MARIOS discs

The Cm measurements were more difficult to obtain due to the low analyte quantity. Low measured signal limited the counting statistics. The signal collected for all the Cm isotopes was between 100 and 1000 times lower than the signal obtained for the Am isotopes. As a consequence the repeatability is higher than the ones observed for Am and the uncertainties are higher than the uncertainties commonly observed for others actinides. The ^{242}Cm isotope measurement showed the presence of an interference attributed to ^{242}Pu. The ^{242}Cm/^{244}Cm ratios were reported as a detection limit as the presumably real ratios are below the measured ratios. This ratios were < 0.6 for the DIAMINO disc and < 0.1 for the MARIOS disc.

The ^{243}Cm/^{244}Cm was 3.167(69) for the DIAMINO disc and 1.314(28) for the MARIOS discs. The data acquired for the DIAMINO experiment seems slightly different to the data obtained with the simulation code (about 2.1). The uncertainty estimations were about 2 % for both discs.

The ^{245}Cm/^{244}Cm was 0.00821(80) for the DIAMINO disc and 0.0451(12) for the MARIOS discs. The signal measured at mass 245 was close to the detection limit (estimated to 0.1 mV for a measurement with FC11) for the DIAMINO disc and was about 0.8 mV for the MARIOS disc (higher than the estimated detection limit by a factor 8 only). The repeatability observed for the DIAMINO disc is important (RSD = 6 %).

The ^{246}Cm/^{244}Cm was below 0.02 (detection limit) for the DIAMINO disc and 0.024(12) for the MARIOS disc. The signal measured at mass 245 for the MARIOS disc, approaching the detection limit, explained the high uncertainty estimation of 50 %. The ^{247}Cm/^{244}Cm and ^{248}Cm/^{244}Cm ratio are below the detection limit for both discs.

Conclusions

The Nd, Am and Cm isotope ratios determination in irradiated samples provided from the MARIOS and DIAMINO analytical experiments were performed combining HPLC separation and TIMS measurements.

The data evaluation for the Nd validation method, performed with natural Nd standard, was investigated to determine all the Nd isotope ratios. The acquired data were compared to the EMFL demonstrating that the only bias comes from the isotope fractionation which can be minimized using the TE method. The EMFL is a powerful tool to detect isobaric interference and to

confirm if mathematical correction can suppress efficiently interferences. Suggested revised reference values without normalization for JNdi-1 standard were proposed: ^{142}Nd/^{144}Nd = 1.13950(47), ^{143}Nd/^{144}Nd = 0.51163(30), ^{145}Nd/^{144}Nd = 0.34876(17), ^{146}Nd/^{144}Nd ratio = 0.72322(65), ^{148}Nd/^{144}Nd = 0.24264(46) and ^{150}Nd/^{144}Nd = 0.23789(68).

The lanthanides, Am and Cm were separated in the same experiment using optimized HPLC conditions. The duration of the separation was improved compared to previous experiments that required 3 different separation steps. This helped generating less radioactive effluent and reduces the analyst exposure to irradiating samples.

Author Contributions

Alexandre Quemet: Methodology, Experiments, Writing - original draft. Mathilde Angenieux: Bibliography review. Alexandre Ruas: Writing - review & editing.

Conflicts of interest

There are no conflicts to declare.

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