



HAL
open science

A combined TIMS and ICP-MS study for Th 0.5 Np 0.5 O 2 thorium neptunium mixed oxide analysis

Alexandre Quemet, Jean-Robert Sevilla, Romain Vauchy

► To cite this version:

Alexandre Quemet, Jean-Robert Sevilla, Romain Vauchy. A combined TIMS and ICP-MS study for Th 0.5 Np 0.5 O 2 thorium neptunium mixed oxide analysis. *International Journal of Mass Spectrometry*, 2021, 460, pp.116479. 10.1016/j.ijms.2020.116479 . cea-03470774

HAL Id: cea-03470774

<https://cea.hal.science/cea-03470774v1>

Submitted on 8 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

A combined TIMS and ICP-MS study for $\text{Th}_{0.5}\text{Np}_{0.5}\text{O}_2$ thorium neptunium mixed oxide analysis

Alexandre Quemet¹, Jean-Robert Sevilla¹ and Romain Vauchy¹

¹*CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France*

Abstract

This paper presented thorium and neptunium quantification of a new synthesized powder, a (Th,Np)O₂ mixed oxide. Thorium was quantified by Thermal Ionization Mass Spectrometry using Isotope Dilution (ID-TIMS) which is one of the most accurate methodology to determine actinide mass fraction. The (sample-spike) mixture isotope ratio was measured using the TIMS reference method for major isotope ratio determination, *i.e.* the total evaporation method. An expanded uncertainty below 1 % was estimated for the Th mass fraction. The study of the uncertainty sources showed that the main one comes from the spike mass fraction uncertainty. As Np quantification with ID-TIMS is difficult due to the lack of commercially-available spike solution, the Np mass fraction was obtained by ICP-MS measurements using a gravimetric standard addition method combined with an analytical internal standard. The developed method used an element initially present in the sample, here Th, as an internal standard for ICP-MS measurements. This helps reducing the number of manipulation as well as cross contamination, which is an important risk when experiments are performed in glove boxes. Also, equations are simplified. An expected uncertainty about 1.8 % was estimated for Np. Finally, the Th-Np mixed oxide was found to have a $\text{Th}_{0.4836(50)}\text{Np}_{0.5164(50)}\text{O}_2$ stoichiometry. This study can be extended to other complicated samples or to the characterization of in-house certified reference material.

Keywords

TIMS; ICP-MS; uncertainty evaluation; isotope dilution; gravimetric standard addition method

I. Introduction

The material science of uranium-plutonium, uranium-actinides or plutonium-actinides oxides is well known as they were used for decades as nuclear fuels or as transmutation targets [1–4]. The study of others actinide mixed oxides is a niche field. A thorium and neptunium mixed oxide ((Th,Np)O₂) was synthesized by a powder metallurgy process in ATALANTE facility of the French Alternative Energies and Atomic Energy Commission (CEA) to improve the knowledge of these singular materials [5]. The microstructure and structure of this mixed oxide were characterized by optical microscopy, Secondary Electron Microscopy, Electron Probe MicroAnalysis, X-Ray powder Diffraction and Raman spectroscopy [5]. In order to characterize its chemical stoichiometry to the best of our capability, the determination of a low uncertainty elemental composition is mandatory. The stoichiometry obtained validates the powder metallurgy process, the methodology used for the synthesis and is useful to observe the stoichiometry variation in future study. The powder purity can also be computed combining the elemental composition and the oxygen/metal ratio measured by X-ray powder diffraction.

Thermal Ionization Mass Spectrometry (TIMS) is one of the reference techniques for the determination of actinides isotopic measurements [6–9]. TIMS measurements coupled to Isotope Dilution (ID-TIMS) is a powerful methodology for a highly accurate determination of actinides mass fraction (*i.e.* measurement trueness and precision) [6,10,11]. The principle of ID is adding to the sample a known amount of spike with a known mass fraction and a known isotopic composition (that must be different than that of the sample analyzed) [12,13]. The sample – spike mixture isotope ratio reflects the sample analyte mass fraction. This methodology was successfully used for the determination of thorium mass fraction with high accuracy [7,14].

Quantifying neptunium containing a single isotope (^{237}Np) using ID-TIMS requires a neptunium spike enriched other than ^{237}Np isotope. ID-TIMS is not a suitable technique as spike solution enriched in another isotope is not commercially available [6,15]. The full elemental characterization of the (Th,Np) O_2 powder needs to be done by combining ID-TIMS to measure Th and another technique to quantify Np. Many methodologies are available to determine the neptunium mass fraction: controlled potential coulometry [16], alpha spectrometry [16–19], gamma spectrometry [16,17,19], neutron activation analysis [17,19], Inductively Coupled Plasma-Atomic Emission Spectroscopy [20,21] or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [16,22–24]. Among these techniques, ICP-MS is commonly used as it is a quick analytical technique with simple sample preparation. A relative mass fraction uncertainty below 5 % can be obtained using the ID methodology (using a ^{242}Pu spike) or the gravimetric standard addition method [22,25]. Combining TIMS and ICP-MS helps to accurately measure Th and Np at the same time.

This paper presents the analytical protocol combining dissolution, TIMS and ICP-MS measurements to analyze (Th,Np) O_2 powder. ICP-MS and TIMS measurement methodologies will be highlighted. Uncertainty estimation computation will be detailed.

II. Experimental

2.1. Materials, reagents and certified reference materials

Nitric acid ($w = 67\text{-}70\%$, J.T. Baker) was of Ultrex II reagent grade. Hydrofluoric acid ($w = 40\%$, Merck) was of Suprapur grade. Deionized water was provided by a MilliQ system (resistivity: $18.2\text{ M}\Omega\text{ cm}$, Millipore, Milford). ($9.5\text{ mol L}^{-1}/0.005\text{ mol L}^{-1}$) HNO_3/HF , $1\text{ mol L}^{-1}\text{ HNO}_3$ and $0.5\text{ mol L}^{-1}\text{ HNO}_3$ solutions were prepared by volumetric dilution in deionized water.

The Th spike solution used in the ID methodology was the IRMM 060 certified reference material (CRM) provided by the Joint Research Centre of the European Commission. This CRM contains high amounts of ^{230}Th and its mass fraction and isotope ratio are certified.

Its Th mass fraction was $40.43(30) \mu\text{g g}^{-1}$ ($k = 2$) at the certification date (1998/02/01). This mass fraction was updated at the date of use to correct the ^{230}Th radioactive decay using a $75380(60)$ years ($k = 2$) half-life [26].

The Np (^{237}Np 100 at. %) in nitric solution was purchased from the Analytical Methods Committee (CETAMA) of the CEA. This solution is certified for a neptunium mass fraction of $980.8(90) \mu\text{g g}^{-1}$ ($k = 2$) at the certification date (2006/02/02). This mass fraction was updated at the date of use to correct the ^{237}Np radioactive decay using a $2155000(14)$ years ($k = 2$) half-life [26].

The TIMS filaments were in metal rhenium with a purity of 99.99 % and were provided by ATES.

2.2. Analytical protocol

A scheme of the analytical protocol is presented in Figure 1. The (Th,Np) O_2 powder (initial sample) was divided in two aliquots containing about 120 mg each (hereafter referred to as aliquot 1 and 2). Both TIMS and ICP-MS techniques require using solutions. Thus, the first step was the dissolution of aliquot 1 and 2. About 10 mL of a ($9.5 \text{ mol L}^{-1} / 0.005 \text{ mol L}^{-1}$) HNO_3/HF mixture was added to each aliquot. These solutions (aliquot powder + nitric and hydrofluoric acid) were heated at 135 C for about 70 hours in a sealed PFA vial until total dissolution. The obtained solutions (hereafter the dissolution solutions of the aliquot 1 and 2 are referred to as solution 1 and 2, respectively) had a Th and Np mass fraction of about 5 mg g^{-1} . Two independent gravimetric dilutions of solution 1 were performed with $1 \text{ mol.L}^{-1} \text{ HNO}_3$ solution to obtain a mass fraction close to the IRMM 060 CRM (about $40 \mu\text{g g}^{-1}$). Hereafter, the two diluted solutions 1 are referred to as sample (1-1) and sample (1-2). Likewise, two independent gravimetric dilutions of solution 2 were performed with $1 \text{ mol L}^{-1} \text{ HNO}_3$ solution. The two diluted solutions 2 are referred to as sample (2-1) and sample (2-2).

2.3. Instrumentation

2.3.1. Thermal Ionization Mass Spectrometry

The Th mass fraction ($[Th]$) was determined using ID-TIMS according to Eq. (1).

$$[Th] = f \cdot [Th]_T \cdot \frac{m_T}{m_S} \cdot \frac{M_S}{M_T} \cdot \frac{(230)_T}{(232)_S} \cdot \frac{\left(\frac{^{232}Th}{^{230}Th}\right)_{Mix} - \left(\frac{^{232}Th}{^{230}Th}\right)_T}{1 - \left(\frac{^{232}Th}{^{230}Th}\right)_{Mix} \cdot \left(\frac{^{230}Th}{^{232}Th}\right)_S} \quad (1)$$

Where f is the dilution factor used to compute the Th mass fraction in the aliquot 1 or 2, T refers to the spike (or tracer), Mix refers to the sample - spike mixture and S refers to the sample, m are the masses involved in the mixture, M are the atomic weights, (230) and (232) are the isotope abundances. The $[Th]_T$, M_T , $(230)_T$ and $(^{232}Th/^{230}Th)_T$ parameters are directly obtained from the CRM certificate. From the measured $(^{230}Th/^{232}Th)_S$ ratio, the M_T and $(230)_T$ parameters are computed. The $(^{230}Th/^{232}Th)_{mix}$ ratio was measured by TIMS. Only the f , m_T , m_S and $(^{230}Th/^{232}Th)_{mix}$ ratio parameters are modified from a sample – spike mixture to another. The others parameters ($[Th]_T$, M_T , M_S , $(230)_T$, $(232)_S$, $(^{230}Th/^{232}Th)_S$ and $(^{230}Th/^{232}Th)_S$) are the same from a sample – spike mixture to another.

$(^{230}Th/^{232}Th)_S$ and $(^{232}Th/^{230}Th)_{mix}$ isotope ratios were measured with TIMS. The Thermo Fisher Triton TIMS used for the experiments were previously described in details [27]. As there are no isobaric interferences between Np (237 mass) and Th isotopes (230 and 232 masses), no chemical separation was needed. All the experiments were performed with about 500 ng of Th deposited on to the filament. A double Re-filament configuration was used to control independently the evaporation and the ionization filament temperature. For the deposit procedure, 1 μ L of solution was deposited onto the filament previously outgassed for 20 min at 4.5 A (before reaching 4.5 A, the current increased at 2.0 A min⁻¹) in a high vacuum chamber ($< 5 \times 10^{-6}$ mbar). After deposition, the sample preparation was dried with a 0.4 A current. Then the current was increased progressively to 2 A in 10 s.

The measurements were performed with the total evaporation method (hereafter referred to as TE method) to overcome the isotope fractionation, main cause of the measurement bias by TIMS [28]. The TE method is a reference method to measure

actinides isotope ratio [6,27,29]. The TE method, based on the evaporation and ionization of the entire sample, is composed of three steps. The first step is the adjustment phase where the ionization filament is heated to a filament current of 5.6 A in 10 min. Then, the evaporation filament is heated to obtain a $^{232}\text{Th}^+$ ion beam of 1 mV. This ion beam intensity is obtained for an evaporation filament current of about 1.9 A. A “peak center” (mass calibration and ions beam centering in the detector) and the lens optimization of the ion source are performed on the $^{232}\text{Th}^+$ ion beams. In the second step (acquisition step), the data acquisition is started. The evaporation filament current starts to increase until the Th isotopes ion beam intensity reaches the target intensity (here 0.4 V). The evaporation filament is then controlled to keep the ions beam intensity constant, by increasing the evaporation current when necessary. The integration time was set at 0.131 s. When the evaporation filament current reaches a maximum value of 6 A and the ion beam decreases down to a 10 mV signal, the data acquisition is then finished (shutdown phase). The Th isotope cumulated signal was about 1200 V. From the Th quantity deposited on to the filament and the obtained cumulated signal, the ionization efficiency can be computed. An ionization efficiency about 0.001 % was observed. This low ionization efficiency is expected as Th is one of the most difficult element to ionize in TIMS [7].

For the $(^{232}\text{Th}/^{230}\text{Th})_{\text{mix}}$ isotope ratios measurement, the ^{230}Th and ^{232}Th isotopes were measured on Faraday cups coupled to $10^{11} \Omega$ current amplifier (hereafter referred to as FC 11). For the $(^{230}\text{Th}/^{232}\text{Th})_{\text{S}}$ isotope ratio measurement the ^{232}Th isotope was collected using a FC 11. The ^{230}Th isotope was detected using a Secondary Electron Multiplier (SEM) equipped with a Retarding Potential Quadrupole Lenses, decreasing the abundance sensitivity by 1 order of magnitude. The SEM calibration was performed using the method previously described [27].

The Th in the $(\text{Th},\text{Np})\text{O}_2$ powder (required to compute the $[\text{Th}]_{\text{S}}$) is natural – *i.e.* $^{232}\text{Th} = 99.98(2)$ at.% [30]. Nevertheless, the Th isotopic composition of the sample was verified. Three deposits of about 500 ng were analyzed using the TE method.

For the ID methodology, three (sample – spike) mixtures were prepared gravimetrically for each sample (1-1), (1-2), (2-1) and (2-2): 250 μL of the IRMM 060 CRM and 250 μL of sample were mixed for each preparation. Each mixture was evaporated after preparation, and then dissolved again in 40 μL of 1 mol L^{-1} nitric acid. This step provided the complete homogenization of the (sample – spike) mixture [12]. 1 μL (about 500 ng of Th) of this final solution was deposited onto a filament for each individual measurement.

The Th mass fraction in the aliquot 1 ($[Th]_1$) is the average of Th mass fraction obtained with the three (sample (1-1) – spike) mixtures measurements and with the three (sample (1-2) – spike) mixture measurements (Figure 1). Likewise, the Th mass fraction in the aliquot 2 ($[Th]_2$) is the average of the Th mass fractions obtained from samples (2-1) and (2-2) measurements. Finally, the Th mass fraction of the (Th,Np) O_2 powder ($[Th]$) is the average of the Th mass fractions obtained from both aliquots (Figure 1).

2.3.2. Inductively Coupled Plasma Mass Spectrometry

The ICP-MS measurements were performed using a PerkinElmer Elan DRCE equipped with a glove box. The ICP-MS was dedicated to the Np analysis. The plasma power was set at 1300 W. The plasma, auxiliary and nebulizer gas flow rates were set at 15, 1.025 and 1.01 $\text{L}\cdot\text{min}^{-1}$, respectively. A Meinhard concentric nebulizer was used with a low volume baffled cyclonic spray chamber. Samples were analyzed using peak hopping and a dwell time was set to 50 ms amu^{-1} . The number of sweeps was set at 10. The reading per replicate was set at 1. The total number of replicates was set at 60 [31]. The measured isotopes were ^{232}Th and ^{237}Np .

The Np mass fraction was quantified using the gravimetric standard addition method combined with internal standard (hereafter referred to as GSA method) [25,32]. The Th present with in the sample was used as the analytical internal standard.

First, a 10-fold dilution was obtained gravimetrically for the Np CRM. The final mass fraction of the diluted Np CRM ($[Np]_{CRM}$) was about 100 $\mu\text{g g}^{-1}$. Three different blends and a no addition sample (hereafter referred to as addition 0) were prepared gravimetrically for the sample (1-1). For the addition 0, 200 μL of sample (1-1) and 4800 μL of 0.5 mol L^{-1}

HNO₃ were mixed. The three different blends (hereafter referred to as addition 1, 2 and 3) were prepared by mixing:

- 200 µL of sample (1-1)
- + 100 µL for addition 1, 200 µL for addition 2 and 300 µL for addition 3 of the diluted Np CRM
- + 4700 µL for addition 1, 4600 µL for addition 2 and 4500 µL for addition 3 of 0.5 mol L⁻¹ HNO₃

Addition 0 and blends for the samples (1-2), (2-1) and (2-2) were prepared in the same way as for the sample (1-1). Then, an approximate 250-fold dilution for each of the sixteen solutions (addition 0, 1, 2 and 3 for the samples (1-1), (1-2), (2-1) and (2-2)) was obtained volumetrically to be suitable for ICP-MS measurements. The Np mass fractions were about 9, 17, 26 and 34 ng g⁻¹ for addition 0, 1, 2 and 3, respectively. The Th mass fraction, used as the internal standard, was about 9 ng g⁻¹ in each ICP-MS solution.

A $(y(x) = a \cdot x + b)$ linear relation was plotted for each of the samples: $y = {}^{237}\text{Np}/{}^{232}\text{Th} \cdot m(\text{internal standard})/m(\text{sample})$, as the sample and internal standard masses are the same the relation can be simplified to $y = {}^{237}\text{Np}/{}^{232}\text{Th}$ intensity ratio and $x = m(\text{diluted Np CRM})/m(\text{sample})$. The calibration curve obtained for sample (1-1) is shown in Figure 1.

The Np mass fraction ($[Np]_{S(1-1)}$) obtained in aliquot 1 with sample (1-1) calibration curve was computed using Eq. (2).

$$[Np]_{S(1-1)} = f_{S(1-1)} \cdot \frac{b}{a} \cdot [Np]_{CRM} \quad (2)$$

Where $f_{S(1-1)}$ is the sample (1-1) dilution factor to compute the Np mass fraction in aliquot 1. The same computation can be performed to obtain the Np mass fraction in aliquot 1 with

sample (1-2) calibration curve ($[Np]_{S(1-2)}$) and in aliquot 2 with sample (2-1) and (2-2) calibration curves ($[Np]_{S(2-1)}$) and ($[Np]_{S(2-2)}$), respectively).

As for Th measurement, Np mass fraction in aliquot 1 ($[Np]_1$) was the average of the Np mass fraction obtained with the samples (1-1) and (1-2) measurements (Figure 1). Similarly, the Np mass fraction in aliquot 2 ($[Np]_2$) was the average of the Np mass fractions obtained with the samples (2-1) and (2-2) measurements. Finally, the Np mass fraction of the (Th,Np)O₂ powder ($[Np]$) was the average of the Np mass fractions obtained with both aliquots (Figure 1).

2.4. Uncertainties estimation and results evaluation

2.4.1. Uncertainty on thorium mass fraction

The uncertainty calculation of Th mass fraction, determined by ID-TIMS, was detailed previously for uranium [10] and used here for Th. It was estimated by combining the uncertainties from each term of the isotope dilution equation (Eq. (1)) and was showed in Eq. (3).

$$\begin{aligned}
u^2([Th]) = & \left(\frac{m_T}{m_S} \cdot \frac{(230)_T}{(232)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{Mix} - R_T}{1 - R_{Mix} \cdot R_S} \right)^2 \cdot u^2([Th]_T) \\
& + \left([Th]_T \cdot \frac{1}{m_S} \cdot \frac{(230)_T}{(232)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{Mix} - R_T}{1 - R_{Mix} \cdot R_S} \right)^2 \cdot u^2(m_T) \\
& + \left(-[Th]_T \cdot \frac{m_T}{m_S^2} \cdot \frac{(230)_T}{(232)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{Mix} - R_T}{1 - R_{Mix} \cdot R_S} \right)^2 \cdot u^2(m_S) \\
& + \left([Th]_T \cdot \frac{m_T}{m_S} \cdot \frac{1}{(232)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{Mix} - R_T}{1 - R_{Mix} \cdot R_S} \right)^2 \cdot u^2((230)_T) \\
& + \left(-[Th]_T \cdot \frac{m_T}{m_S} \cdot \frac{(230)_T}{(232)_S^2} \cdot \frac{M_S}{M_T} \cdot \frac{R_{Mix} - R_T}{1 - R_{Mix} \cdot R_S} \right)^2 \cdot u^2((238)_S) \\
& + \left([Th]_T \cdot \frac{m_T}{m_S} \times \frac{(230)_T}{(232)_S} \cdot \frac{M_S}{M_T} \cdot \frac{(R_{Mix} - R_T) \cdot R_{Mix}}{(1 - R_{Mix} \cdot R_S)^2} \right)^2 \cdot u^2(R_S) \\
& + \left(-[Th]_T \cdot \frac{m_T}{m_S} \cdot \frac{(230)_T}{(232)_S} \cdot \frac{M_S}{M_T} \cdot \frac{1}{1 - R_{Mix} \cdot R_S} \right)^2 \cdot u^2(R_T) \\
& + \left([Th]_T \cdot \frac{m_T}{m_S} \cdot \frac{(230)_T}{(232)_S} \cdot \frac{M_S}{M_T} \cdot \frac{1 - R_T \cdot R_S}{(1 - R_S \cdot R_{Mix})^2} \right)^2 \cdot u^2(R_{Mix}) \\
& + u^2(\text{dilution}) + u^2(\text{precision})
\end{aligned} \tag{3}$$

Where R_{mix} is the $(^{230}\text{Th}/^{232}\text{Th})_{mix}$ ratio, R_T is the $(^{230}\text{Th}/^{232}\text{Th})_T$ ratio and R_S is the $(^{232}\text{Th}/^{230}\text{Th})_S$ ratio. In Eq. (3), the molar masses uncertainties were considered negligible and were not taken into account for the final uncertainty computation. The term $u(\textit{precision})$ is the method precision. The term $u(\textit{dilution})$ is the sample dilution uncertainty.

2.4.2. Uncertainty on neptunium mass fraction

The relative uncertainty on Np mass fraction for aliquot 1 using sample (1-1) and (1-2) calibration curves ($u([Np]_i)/[Np]_i$, $k = 1$), computed using the variance propagation method, is presented in Eq. (4). The same equation can be used for aliquot 2 using sample (2-1) and (2-2) calibration curves.

$$\begin{aligned} \left(\frac{u([Np]_1)}{[Np]_1}\right)^2 &= \left(\frac{u([Np]_{CRM})}{[Np]_{CRM}}\right)^2 + \frac{\sqrt{C_{S(1-1)}^2 + C_{S(1-2)}^2}}{2} + \left(\frac{u(x_i)}{x_i}\right)^2 \\ &+ \left(\frac{u(\textit{dilution})}{\textit{dilution}}\right)^2 + \left(\frac{u(\textit{precision})}{\textit{precision}}\right)^2 \end{aligned} \quad (4)$$

With

$$C_{S(1-1)} = \frac{\sum_{i=1}^n [y_i - (b + a \cdot x_i)]^2}{2 \cdot b^2} \cdot \left[\frac{1}{4} + \frac{\left(\frac{b}{a} + \bar{x}\right)^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right]$$

With a the slope of the linear fit function, b the y-intercept of the linear fit function, x_i the $m(\textit{Np CRM})/m(\textit{sample})$ ratio for additions with $i = 0, 1, 2$ and 3 , \bar{x} the x_i average, and y_i the $^{237}\text{Np}/^{232}\text{Th}$ intensity ratio for additions with $i = 0, 1, 2$ and 3 . The first term of Eq. (4) ($u([Np]_{CRM})/[Np]_{CRM}$) is the CRM relative uncertainty. The second term (C_S) is the regression line uncertainty. The regression lines of sample (1-1) and (1-2) are obtained independently. Thereby, the term linked to the regression line uncertainty in Eq. (4) is given by the quadratic sum of the sample (1-1) and (1-2) regression line uncertainty divided by the measurement number (here 2). The third term ($u(x_i)/x_i$) is the $m(\textit{Np CRM})/m(\textit{sample})$ ratio relative uncertainty. The fourth term ($u(\textit{dilution})/\textit{dilution}$) is the weighing relative

uncertainty due to the dissolution and gravimetric dilutions. The $(u(\textit{precision})/\textit{precision})$ term is given by the relative standard deviation of the Np mass fraction obtained using the samples (1-1) and (1-2) results divided by the square root of the number of dissolutions (here 1). The terms, other than the regression line uncertainty, are not independent (and so not divided by the square root of the number of measurement): the same dissolution, the same Np CRM solution and the same balance were used for all calibration curves.

The calculation of the relative uncertainty of the Np mass fraction in the (Th,Np)O₂ powder ($u([Np])/[Np]$, $k = 1$) is presented in Eq. (5).

$$\begin{aligned} \left(\frac{u([Np])}{[Np]}\right)^2 &= \left(\frac{u([Np]_{CRM})}{[Np]_{CRM}}\right)^2 + \frac{\sqrt{C_{S(1-1)}^2 + C_{S(1-2)}^2 + C_{S(2-1)}^2 + C_{S(2-2)}^2}}{4} \\ &+ \left(\frac{u(x_i)}{x_i}\right)^2 + \left(\frac{u(\textit{dilution})}{\textit{dilution}}\right)^2 + \left(\frac{u(\textit{precision})}{\textit{precision}}\right)^2 \end{aligned} \quad (5)$$

As for Eq. (4), the regression lines term is divided by the number of measurements (here 4) as the regression lines were determined independently. The $(u(\textit{precision})/\textit{precision})$ term is given by the relative standard deviation of the Np mass fraction obtained in the aliquots 1 and 2 divided by the square root of the number of dissolution (here 2) as the two dissolution are performed independently.

2.4.3. Thorium and neptunium amount fractions and stoichiometry

The Th/metal ($\%Th$) and Np/metal ($\%Np$) amount ratios in the (Th,Np)O₂ powder were obtained with Eq. (6).

$$\%Th = \frac{n(Th)}{n(Th) + n(Np)}$$

and

$$\%Np = \frac{n(Np)}{n(Th) + n(Np)}$$

(6)

With $n(Th)$ and $n(Np)$ the amount fraction calculated from the Th and Np mass fraction in the powder, respectively: $n(Th)=[Th]/M(Th)$ and $n(Np)=[Np]/M(Np)$. Using Eq. (6), the powder stoichiometry was found to be $Th_{\%Th}Np_{\%Np}O_2$.

The Th/metal ($u(\%Th)$, $k = 1$) and Np/metal ($u(\%Np)$, $k = 1$) amount ratio uncertainty (Eq. (7)) was estimated by combining the uncertainties from each term of Eq. (6).

$$u^2(\%Th) = \left(\frac{n(Np)}{(n(Th) + n(Np))^2} \right)^2 \cdot u^2(n(Th)) + \left(-\frac{n(Th)}{(n(Th) + n(Np))^2} \right)^2 \cdot u^2(n(Np))$$

and

$$u^2(\%Np) = \left(\frac{n(Th)}{(n(Th) + n(Np))^2} \right)^2 \cdot u^2(n(Np)) + \left(-\frac{n(Np)}{(n(Th) + n(Np))^2} \right)^2 \cdot u^2(n(Th)) \quad (7)$$

The uncertainties on $u(n(Th))$ and $u(n(Np))$ ($k = 1$) amount fractions were estimated by considering equal the relative uncertainties on the mass and on the amount fractions. The uncertainties on the molar mass are considered negligible.

2.4.4. (Th,Np)O₂ purity

The purity of the (Th,Np)O₂ powder (expressed as Eq. (8)).can be estimated using amount fractions determined by ID-TIMS and ICP-MS ($n(Th)$ and $n(Np)$) and the found stoichiometry considering a pure $Th_{\%Th}Np_{\%Np}O_2$ oxide

$$purity = \frac{n(Th) + n(Np)}{n_{sto}(Th) + n_{sto}(Np)} \quad (8)$$

$n_{sto}(Th)$ and $n_{sto}(Np)$ are the Th and Np theoretical amount fractions obtained with the powder stoichiometry ($\%Th$ and $\%Np$) and considering oxygen/metal ratio equal to 2.00

(confirmed by X-ray powder diffraction [5]). Switching theoretical amount fraction according to Eq. (9), leads to Eq. (10).

$$n_{sto}(Th) + n_{sto}(Np) = \frac{1}{\%Th \cdot M(Th) + \%Np \cdot M(Np) + 2 \cdot M(O)} \quad (9)$$

$$purity = (n(Th) + n(Np)) \cdot (\%Th \cdot M(Th) + \%Np \cdot M(Np) + 2 \cdot M(O)) \quad (10)$$

The uncertainty on purity ($u(purity)$, $k = 1$) (expressed as Eq. (11)) was estimated by combining the uncertainties from each term of Eq. (10). The molar mass uncertainties are considered negligible.

$$\begin{aligned} u^2(purity) = & [\%Th \cdot M(Th) + \%Np \cdot M(Np) + 2 \cdot M(O)]^2 \\ & \cdot [u^2(n(Th)) + u^2(n(Np))] + [M(Th)(n(Th) + n(Np))]^2 \\ & \cdot u^2(\%Th) + [M(Np)(n(Th) + n(Np))]^2 \cdot u^2(\%Np) \end{aligned} \quad (11)$$

III. Results and discussion

3.1. Thorium mass fraction using ID-TIMS

The isotopic composition of the Th constituting the (Th,Np)O₂ powder was verified. The results obtained for the ²³⁰Th/²³²Th isotope ratio was 1.73(18)×10⁻⁵. The Residual Standard deviation (RSD) of the three measurements was 2.7 %, which is close to the RSD observed for similar isotope measurement using TE method with SEM analysis [33]. The ²³²Th isotopic abundance was computed to 99.998(10) %, corresponding to the natural Th isotopic composition [30].

To the best of our knowledge, no CRM with a certified ²³⁰Th/²³²Th isotope ratio closed to 1 (isotope ratio mainly measured in this study with the ID methodology) is commercially available. It is difficult to evaluate the ²³⁰Th/²³²Th ratio measurement. Isotope ratio measurement using the TE method helps overcoming the lack of CRM as no CRM is

required for the analysis and for the isotope fractionation correction. The results evaluation was performed by controlling the isotope fractionation law for each TIMS measurement. The $^{230}\text{Th}/^{232}\text{Th}$ ratio decrease during a measurement using the TE method: lighter isotopes evaporate faster than heavier isotopes. The obtained RSD for the Th mass fraction measured for each group of 3 (sample – spike) mixtures prepared for each sample was 0.10 %, 0.02 %, 0.05 % and 0.07 % for the sample (1-1), (1-2), (2-1) and (2-2), respectively. This low RSD seems to confirm the good accuracy of the results. Moreover, measurements on uranium and americium CRM with isotope ratio close to 1 were previously measured with a maximum bias below 0.05 % [27], confirming the good accuracy of the TE method for actinides isotope ratios analysis.

The Th mass fraction results are presented in Table 1. The Th mass fractions determined are $0.4168(39) \text{ g g}^{-1}$ for aliquot 1 and $0.4189(39) \text{ g g}^{-1}$ for aliquot 2. The results RSD obtained with the individual aliquot 1 and 2 measurements are below 0.02 %. The final Th mass fraction in the $(\text{Th,Np})\text{O}_2$ powder is $0.4179(39) \text{ g g}^{-1}$ with an RSD of 0.36 %. The relative uncertainty is estimated at 0.92 % ($k = 2$). The relative contributions, expressed in percent, of the main uncertainty sources for the Th mass fraction in the sample are given in Figure 3. The main uncertainty sources are the uncertainty on the spike mass fraction (66 % of the total budget) and the precision (30 % of the total budget). The Th CRM has a relative mass fraction uncertainty of about 0.74 % ($k = 2$). The uncertainty on the $^{232}\text{Th}/^{230}\text{Th}$ ratio of the sample spike mixture is a low uncertainty source (1 % of the total budget).

3.2. Neptunium mass fraction using the gravimetric standard addition method combined with internal standard

The first analyses for Np quantification were performed using the ID methodology with a ^{242}Pu spike solution [22]. The $^{237}\text{Np}/^{242}\text{Pu}$ ratio was then determined by ICP–MS. However, this methodology was not selected because the $(\text{Th,Np})\text{O}_2$ powder was slightly contaminated by plutonium which deteriorated and complicated the analysis.

The Np mass fraction results, measured using the GSA method, are presented in Table 1. The coefficients of determination (R^2) were between 0.99994 and 0.99999 for all the

calibration curves (Figure 2). The Np mass fraction for the aliquots 1 and 2 are $0.456(10) \text{ g g}^{-1}$. The RSD obtained for the aliquots 1 and 2 are 0.25 % and 0.28 %, respectively. The final Np mass fraction in the (Th,Np)O₂ powder was found to be $0.4558(80) \text{ g g}^{-1}$ with a relative uncertainty estimated at 1.8 % ($k = 2$). The RSD between the values of aliquots 1 and 2 are below 0.1 %. The main uncertainty sources, presented in Figure 3, are the uncertainty due to the regression line (72 % of the total budget) and the CRM Np mass fraction (26 % of the total budget).

Using the Th present within the sample as internal standard presented different advantages. First, internal standard addition is not necessary: the number of experiments in glove boxes is reduced. The cross contamination risk, very present when experiments are performed in glove boxes, is reduced to minimum. Equations are also simplified as the sample and internal standard masses are the same. Moreover, ²³²Th and ²³⁷Np masses and ionization potentials ($608.5 \text{ kJ mol}^{-1}$ for Th and $604.5 \text{ kJ mol}^{-1}$ for Np) are similar. Finally, Th is a good enough internal standard for Np analysis.

3.3.(Th,Np)O₂ stoichiometry and purity

Th and Np mass fraction determined with TIMS and ICP-MS measurements helped to find the Th_{0.4836(50)}Np_{0.5164(50)}O₂ stoichiometry (computation details can be found in Eq. (6)). Considering the ThO₂ and NpO₂ masses involved during the powder metallurgy process of the mixed dioxide, the theoretical stoichiometry should be Th_{0.507}Np_{0.493}O₂. The obtained stoichiometry is close to the one using the masses involved during the process but remains significantly different. Different reason can explain this difference of about 5 %. The work in a shielded line, where the powder was synthesized, is delicate: powder loss can occur during the process. The impurities proportion in the ThO₂ and NpO₂ powders was not taken into account: the weighing was performed considering a pure ThO₂ and NpO₂ powder. Finally, the scale used in shielded line have a higher uncertainty than scales used in glove boxes or on benchtops. The weighing process is delicate in a hot cell which can lead to significant uncertainty.

Combining the obtained stoichiometry and an oxygen/metal ratio equal to 2.00 [5] a purity of 0.993(16) is calculated (computation details can be found in Eq. (10)). The purity

relative uncertainty is estimated at 1.6 % ($k = 2$). This purity, very close to 1, confirmed the stoichiometry obtained from ID-TIMS and ICP-MS measurements. The contamination of the material was very limited as the hot cell, where the $(\text{Th,Np})\text{O}_2$ was manufactured, was completely cleaned before the ceramic processing.

IV. Conclusions

The accurate elemental composition of the $(\text{Th,Np})\text{O}_2$ mixed oxide was determined by combining TIMS and ICP-MS measurements. After dissolution, the Th mass fraction was quantified by ID-TIMS with an expected uncertainty below 1 %. The Np mass fraction was measured using the gravimetric standard addition method combined with an internal standard. The expected uncertainty was about 1.8 %. As Th was initially present in the sample, this element was used as the internal standard. The strategy consisting in using an element already present within the sample had some advantages: reduction of manipulations in glove boxes, reduction in the cross-contamination risk reduction and simplification of the equation used.

A $\text{Th}_{0.4836(50)}\text{Np}_{0.5164(50)}\text{O}_2$ stoichiometry was obtained and was close to the target value estimated from the initial mixture of ThO_2 and NpO_2 raw powders. Finally, a purity close to 1 was computed.

In the future, this combined ID-TIMS and GSA method with ICP-MS methodology will be used for other elements when using ID is difficult due to spike lack. For instance, uranium cerium oxide can be analyzed with this methodology: uranium with ID-TIMS measurement and cerium with ICP-MS measurement.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to Dr. S. Baghdadi for her precious advice on the present paper. We are grateful to C. Rivier (CEA/DES/ISEC/DMRC/SASP/L2AT) for uncertainties discussions, and to A. Boyer, J.-L. Dautheribes and P.-E. Kalpakdjian for their helps on ICP-MS.

Table

Table 1: Th mass fraction determined by ID-TIMS and Np mass fraction obtained with the GSA method. U corresponds to the total relative uncertainty ($k = 2$)

	Th		Np	
	<u>Aliquot 1</u>	<u>Aliquot 2</u>	<u>Aliquot 1</u>	<u>Aliquot 2</u>
Results (g g^{-1})	0.4168(39)	0.4189(39)	0.456(10)	0.456(10)
RSD (%)	0.02	0.01	0.25	0.28
	<u>(Th,Np)O₂ powder</u>			
Results (g g^{-1})	0.4179(39)		0.4558(80)	
RSD (%)	0.36		0.05	
U (% , $k = 2$)	0.92		1.8	

Figure

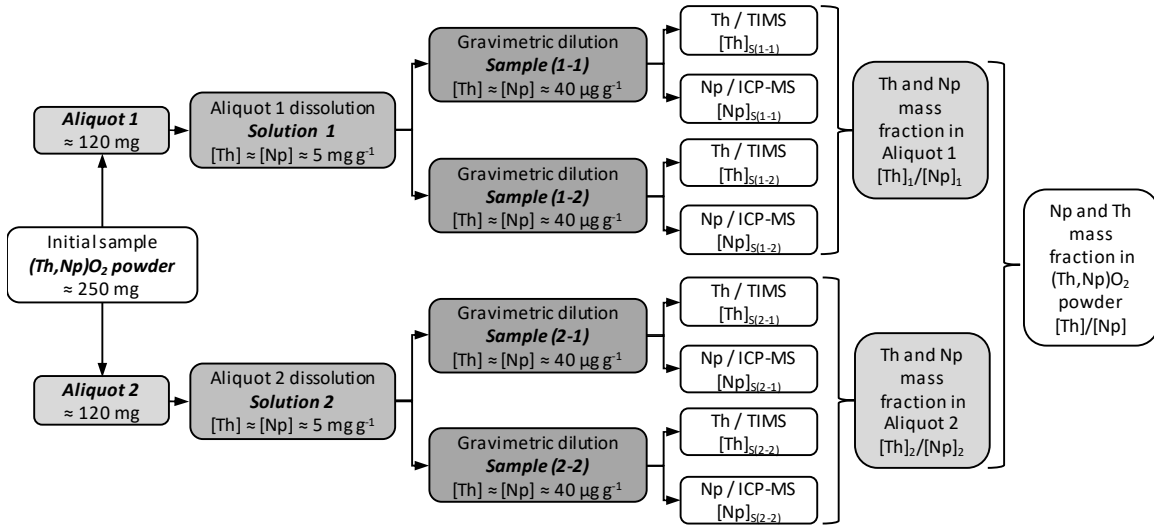


Figure 1: Schematic of the analytical protocol

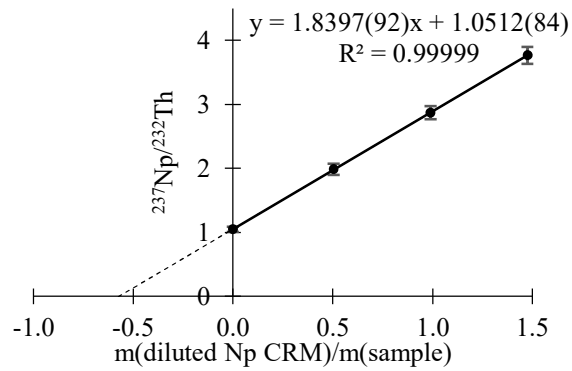


Figure 2: Calibration curve obtained for sample (1-1)

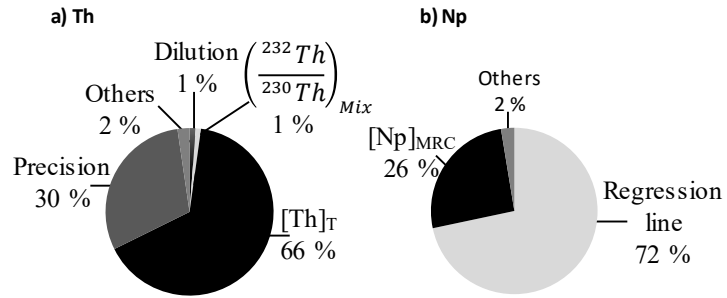


Figure 3: Relative contribution (%) of the main uncertainty sources for the Th mass fraction determined by ID TIMS (a) and for the Np mass fraction determined by the GSA method (b)

References

- [1] M. Beauvy, G. Berthoud, M. Defranceschi, G. Ducros, Y. Guérin, Y. Limoge, C. Madic, G. Santarani, J.-M. Seiler, P. Sollogoub, E. Vernaz, Nuclear fuels, LeMoniteur, Paris, France, 2009.
- [2] P. Damien, J. Aurélien, D. Thibaud, H. Nathalie, D. Philippe, B. Philippe, Fabrication and characterisation of $U_{0.85}Am_{0.15}O_{2-x}$ discs for MARIOS irradiation program, *J. Nucl. Mater.* 414 (2011) 503–507.
<https://doi.org/10.1016/j.jnucmat.2011.05.036>.
- [3] S. Pillon, Actinide-Bearing Fuels and Transmutation Targets, Elsevier Inc., 2012.
<https://doi.org/10.1016/B978-0-08-056033-5.00053-7>.
- [4] R. Vauchy, R.C. Belin, J.C. Richaud, P.J. Valenza, F. Adenot, C. Valot, Studying radiotoxic materials by high temperature X-ray diffraction, *Appl. Mater. Today.* 3 (2016) 87–95. <https://doi.org/10.1016/j.apmt.2016.03.005>.
- [5] R. Vauchy, P. Fouquet-Métivier, L. Medyka, J.-R. Sévilla, L. Marchetti, F. Lebreton, R. Lauwerier, A. Quemet, P. Coste, P.M. Martin, Manufacturing and characterization of $Th_{0.5}Np_{0.5}O_2$ thorium neptunium mixed oxide, To Be Submitt. (2020).
- [6] S.K. Aggarwal, Thermal ionisation mass spectrometry (TIMS) in nuclear science and technology – a review, *Anal. Methods.* 8 (2016) 942–957.
<https://doi.org/10.1039/c5ay02816g>.
- [7] S.K. Aggarwal, A review on the mass spectrometric analysis of thorium, *Radiochim. Acta.* 0 (2016) 1–11. <https://doi.org/10.1515/ract-2015-2559>.
- [8] S. Carter, R. Clough, A. Fisher, B. Gibson, B. Russell, J. Waack, Atomic spectrometry update: review of advances in the analysis of metals, chemicals and materials, *J. Anal. At. Spectrom.* 34 (2015) 2159–2216.
<https://doi.org/10.1039/C5JA90045J>.

- [9] S. Boulyga, S. Konegger-Kappel, S. Richter, L. Sangély, Mass spectrometric analysis for nuclear safeguards, *J. Anal. At. Spectrom.* 30 (2015) 1469–1489. <https://doi.org/10.1039/c4ja00491d>.
- [10] A. Quemet, A. Ruas, E. Esbelin, V. Dalier, C. Rivier, 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 (2019) 997–1004. <https://doi.org/10.1007/s10967-019-06670-y>.
- [11] J. Vogl, Characterisation of reference materials by isotope dilution mass spectrometry, *J. Anal. At. Spectrom.* 22 (2007) 475–492. <https://doi.org/10.1039/b614612k>.
- [12] J. Irrgeher, J. Vogl, J. Santner, T. Prohaska, Chapter 8 Measurement Strategies, in: *Sect. F. Mass Spectrom. Elem. Isot. Anal.*, The Royal Society of Chemistry, 2015: pp. 126–151. <https://doi.org/10.1039/9781849735407-00126>.
- [13] J.D. Fassett, P.J. Paulsen, Isotope Dilution Mass Spectrometry for Accurate Elemental Analysis, *Anal. Chem.* 61 (1989) 643A-649A. <https://doi.org/10.1021/ac00185a715>.
- [14] R.M. Essex, J.L. Mann, R.W. Williams, W.S. Kinman, A. Hubert, M.E. Bennett, A. Gourgiotis, A new thorium-229 reference material, *Appl. Radiat. Isot.* 134 (2018) 23–31. <https://doi.org/10.1016/j.apradiso.2017.07.050>.
- [15] S.M. Jerome, K. Carney, R. Essex, M.E. Fassbender, S. Goldberg, M. Kinlaw, S.P. LaMont, D. Mackney, J.J. Morrison, F.M. Nortier, Reference materials for neptunium determination, *Appl. Radiat. Isot.* 126 (2017) 44–48. <https://doi.org/10.1016/j.apradiso.2016.12.050>.
- [16] N. Xu, L. Tandon, D. Gallimore, E. Lujan, D.R. Porterfield, L. Colletti, K. Kuhn, Dissolution and assay of neptunium oxide, *J. Radioanal. Nucl. Chem.* 296 (2013) 245–249. <https://doi.org/10.1007/s10967-012-1947-z>.
- [17] L. Benedik, M. Trdin, Determination of low level Np-237 by various techniques,

- Appl. Radiat. Isot. 126 (2017) 208–213.
<https://doi.org/10.1016/j.apradiso.2017.02.005>.
- [18] J.M. Diodati, F.M. Sartori, ^{239}Np as a tracer of ^{237}Np in effluent samples and low level nuclear waste, *J. Radioanal. Nucl. Chem.* 272 (2007) 11–15.
<https://doi.org/10.1007/s10967-006-6834-z>.
- [19] N. Vajda, C.K. Kim, Determination of Transuranium Isotopes (Pu, Np, Am) by Radiometric Techniques: A Review of Analytical Methodology, *Anal. Chem.* 83 (2011) 4688–4719. <https://doi.org/10.1021/ac2008288>.
- [20] M. Krachler, R. Alvarez-Sarandes, P. Souček, P. Carbol, High resolution ICP-OES analysis of neptunium-237 in samples from pyrochemical treatment of spent nuclear fuel, *Microchem. J.* 117 (2014) 225–232.
<https://doi.org/10.1016/j.microc.2014.07.005>.
- [21] D.K. Pant, G.A. Chaugule, K.K. Gupta, P.G. Kulkarni, P.B. Gurba, P. Janardan, R.D. Changrani, P.K. Dey, P.N. Pathak, D.R. Prabhu, A.S. Kanekar, V.K. Manchanda, Neptunium estimation in the spent fuel dissolver solution by inductively coupled plasma-atomic emission spectroscopy, *J. Radioanal. Nucl. Chem.* 283 (2010) 513–518. <https://doi.org/10.1007/s10967-009-0367-1>.
- [22] B.S. Matteson, S.K. Hanson, J.L. Miller, W.J.J. Oldham, Concurrent determination of ^{237}Np and Pu isotopes using ICP-MS: Analysis of NIST environmental matrix standard reference materials 4357, 1646a, and 2702, *J. Environ. Radioact.* 142 (2015) 62–67. <https://doi.org/10.1016/j.jenvrad.2015.01.007>.
- [23] T.C. Kenna, Determination of plutonium isotopes and neptunium-237 in environmental samples by inductively coupled plasma mass spectrometry with total sample dissolution, *J. Anal. At. Spectrom.* 17 (2002) 1471–1479.
<https://doi.org/10.1039/b205001c>.
- [24] J.M. Barrero Moreno, M. Betti, J.I. Garcia Alonso, Determination of Neptunium and Plutonium in the Presence of High Concentrations of Uranium by Ion

- Chromatography–Inductively Coupled Plasma Mass Spectrometry, *J. Anal. At. Spectrom.* 12 (1997) 355–361. <https://doi.org/10.1039/a606359d>.
- [25] A.L. Hauswaldt, O. Rienitz, R. Jährling, N. Fischer, D. Schiel, G. Labarraque, B. Magnusson, Uncertainty of standard addition experiments: A novel approach to include the uncertainty associated with the standard in the model equation, *Accredit. Qual. Assur.* 17 (2012) 129–138. <https://doi.org/10.1007/s00769-011-0827-5>.
- [26] Henri Becquerel National Laboratory, Mini Table of radionuclides, First edition, EDP Sciences, 2015.
- [27] A. Quemet, A. Ruas, V. Dalier, C. Rivier, Americium isotope analysis by Thermal Ionization Mass Spectrometry using the Total Evaporation Method, *Int. J. Mass Spectrom.* 431 (2018) 8–14. <https://doi.org/10.1016/j.ijms.2018.05.017>.
- [28] E.L. Callis, R.M. Abernathy, High-precision isotopic analyses of uranium and plutonium by total sample volatilization and signal integration, *Int. J. Mass Spectrom. Ion Process.* 103 (1991) 93–105.
- [29] K.J. Mathew, A. Hasozbek, Comparison of mass spectrometric methods (TE, MTE and conventional) for uranium isotope ratio measurements, *J. Radioanal. Nucl. Chem.* 307 (2016) 1681–1687. <https://doi.org/10.1007/s10967-015-4484-8>.
- [30] J. Meija, T.B. Coplen, M. Berglund, W.A. Brand, P. De Bièvre, M. Gröning, N.E. Holden, J. Irrgeher, R.D. Loss, T. Walczyk, T. Prohaska, Isotopic compositions of the elements 2013 (IUPAC Technical Report), *Pure Appl. Chem.* 88 (2016) 293–306. <https://doi.org/10.1515/pac-2015-0503>.
- [31] S. Baghdadi, A. Quémét, E. Esbelin, Y. Manidren, S. Gracia, V. Dalier, R. Poinsignon-Jacquemin, L. Huyghe, E. Buravand, J.L. Dautheribes, C. Rivier, Zr precipitation kinetics in irradiated fuel dissolution solution by TIMS and ICP-MS: a combined study, *J. Radioanal. Nucl. Chem.* (2017) 1–6. <https://doi.org/10.1007/s10967-017-5602-6>.

- [32] O. Rienitz, K. Röhker, D. Schiel, J. Han, D. Oeter, New equation for the evaluation of standard addition experiments applied to ion chromatography, *Microchim. Acta.* 154 (2006) 21–25. <https://doi.org/10.1007/s00604-006-0494-0>.
- [33] A. Quemet, A. Ruas, V. Dalier, C. Rivier, Development and comparison of high accuracy thermal ionization methods for uranium isotope ratios determination in nuclear fuel, *Int. J. Mass Spectrom.* 438 (2019) 166–174. <https://doi.org/10.1016/j.ijms.2019.01.008>.