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Direct determination of the $^{237}\text{Np}/^{238}\text{U}$ ratio in nuclear fuel samples by multicollection inductively coupled plasma mass spectrometry (MC-ICP-MS)

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Abstract

A new method for the direct measurement of $^{237}\text{Np}/^{238}\text{U}$ ratio in irradiated UO_2 pellets by multicollection inductively coupled plasma mass spectrometry (MC-ICP-MS) is proposed. It allows the determination of ratios down to $10 \times 10^{-6} \text{ mol} \cdot \text{mol}^{-1}$ using ion counter and Faraday cup. This approach was validated by intercomparison with the usual two-step-method (Quadrupole ICP-MS for ^{237}Np determination and isotope dilution mass spectrometry (IDMS) for ^{238}U). For ratios between 10×10^{-6} and $100 \times 10^{-6} \text{ mol} \cdot \text{mol}^{-1}$, expanded uncertainties ($k=2$) varied from 2.75% to 0.81%, twice lower than the uncertainties determined by the usual method.

Keywords MC-ICP-MS · Neptunium · Mass spectrometry · Elemental analysis · Atomic ratio

Introduction

Neptunium is commonly measured in the nuclear field for various applications such as radioactive waste management, environmental samples or nuclear fuel characterization [1–6]. In the field of nuclear fuel characterization, it is of great importance to obtain experimental data after irradiation in order to qualify nuclear database and neutronic calculation codes. ^{237}Np has three main ways of production [1, 7, 8] in the nuclear reactor:

1. a (n, 2n) reaction inducing the production of ^{237}Np from ^{238}U .
2. a ^{236}U atom, produced by the reaction of ^{235}U with a neutron, generating ^{237}U by neutron capture which then becomes ^{237}Np by β -decay.
3. ^{237}Np can be produced by α -decay of ^{241}Am , produced into the reactor.

Insufficient knowledge about the ^{236}U neutron capture cross section can therefore lead to uncertainties in the

back-end of spent nuclear fuel or reprocessed uranium-recycling studies due to the underestimation of the amount of ^{237}Np and by consequence of ^{238}Pu in the spent fuel which is produced by neutron capture of ^{237}Np [9, 10].

In order to gain better knowledge of nuclear data of radionuclides, some specific irradiation campaigns have been realized in dedicated experimental nuclear reactors. One of them was performed in the 1980's: UO_2 pellets doped with the ^{236}U isotope were irradiated in the experimental pressurized water reactor Melusine in Grenoble (France) [11–14] and stored after irradiation during more than 30 years. After irradiation, the measurements of the $^{237}\text{Np}/^{238}\text{U}$ ratio could help to understand the underestimation of ^{237}Np in the spent fuel. In these experimental samples, the predicted $^{237}\text{Np}/^{238}\text{U}$ ratio varied between $10 \times 10^{-6} \text{ mol} \cdot \text{mol}^{-1}$ and $100 \times 10^{-6} \text{ mol} \cdot \text{mol}^{-1}$.

Numerous techniques make it possible to measure ^{237}Np in different matrices as referenced and reviewed in [1, 15]. ^{237}Np can be determined by either alpha spectrometry [16–18], alpha liquid scintillation with rejection of β - γ emitters [19, 20], neutron activation analysis [18], high-resolution gamma spectroscopy (HRGS) [18, 21, 22] or mass spectrometry techniques such as glow discharge mass spectrometry (GDMS) [8], accelerator mass spectrometry [23, 24] or inductively coupled plasma mass spectrometry (ICP-MS) [6, 16, 17, 21, 25–28]. The latter technique has in the last 20 years become more and more

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utilized due to its rapidity, high sample throughput, and low limit of detection ($< \text{fg/g}$) [20, 29] compared to the other techniques. ICP-MS can be also hyphenated with separative techniques to measure ^{237}Np [30, 31]. Another major advantage of the ICP-MS technique, as the other mass spectrometric techniques, comes from the absence of isobaric interference at the m/z ratio = 237 amu [21].

If in the environmental samples, the main difficulty is the chemical separation to eliminate the matrix from the ^{237}Np fraction [18, 27], in the case of nuclear samples, the most challenging point is the presence of high amounts of uranium relative to Np. In addition to this, the studied UO_2 pellets contain an unusual amount of ^{236}U . Therefore, in the ICP-MS technique, the peak tail coming from the ^{238}U isotope or molecular interferences (i.e., $^{236}\text{UH}^+$) can lead to inaccuracies if these phenomena are not properly corrected [16]. In quadrupole ICP-MS (Q-ICP-MS) techniques, ^{237}Np as well as other elements present in nuclear samples can be measured using the external calibration curve method or the gravimetric standard addition method [6]. The literature has also described the use of multi collection ICP-MS (MC-ICP-MS) without performing measurements in the multi-collection mode [32].

In the Nuclear Isotopic and Elemental Analytical development Laboratory (LANIE) of the French Atomic and Alternative Energies Commission (CEA) Paris-Saclay, the $^{237}\text{Np}/^{238}\text{U}$ ratio is precisely determined with a two-step method: the first step consists in measuring the ^{237}Np concentration using Q-ICP-MS; the second is to establish the ^{238}U concentration using single isotope dilution mass spectrometry (IDMS). The latter step requires the additional determination of the uranium isotope composition. This conventional approach was limited for some samples analyzed in the present study in relation to the significant abundance sensitivity of the Q-ICP-MS technique: some of the samples had an estimated $^{237}\text{Np}/^{238}\text{U}$ around $10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ with as a direct consequence the potential difficulties of precisely measuring the ^{237}Np in such samples. To overcome this issue, a new method was developed on a multi-collection inductively coupled plasma mass spectrometer (MC-ICP-MS). This approach, based on a calibration curve, uses a Faraday cup to determine ^{238}U and a secondary electron multiplier (SEM) equipped with a retarding potential quadrupole filter (RPQ) to measure ^{237}Np . In this configuration, the SEM allows the measurement of a low signal of ^{237}Np and the RPQ filter improves the abundance sensitivity of the instrument. This novel method makes it possible to analyze relatively low elemental $^{237}\text{Np}/^{238}\text{U}$ ratios from $10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ to $100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ without a prior chemical separation step and without the need for uranium isotope composition determination as is required for the IDMS approach.

The aim of the present article was to present the methodology used for developing and validating the direct measurement of the $^{237}\text{Np}/^{238}\text{U}$ ratio using MC-ICP-MS. After a detailed description of the method, also including the instrumentation, the analytical condition and the mathematical equations, the validation realized in two steps is presented. Firstly, a simulated sample gravimetrically prepared with certified reference solutions was measured using the new approach on MC-ICP-MS and compared to the value derived from the certificates. Secondly, a comparison was made with the conventional approach (IDMS for ^{238}U measurement + Q-ICP-MS for ^{237}Np measurement) on two samples. The results obtained on six UO_2 dissolved pellets and a simplified uncertainty assessment model was established and discussed.

Experimental

Reagents and reference material solutions

High purity 67–70% nitric acid (PlasmaPURE, from SCP Science, Baie d'Urfé, Canada) and ultrapure water (resistivity of 18.2 M Ω cm, Milli-Q system, Millipore, Milford, USA) were used to prepare the reagents and clean all the materials.

A natural uranium solution produced by the CEA Commission for the Establishment of Analytical Methods (CEA-Marcoule/ISEC/DMRC/CETAMA) was selected as the reference solution. The concentration of this solution was $196.21 \pm 0.20 \text{ g}\cdot\text{kg}^{-1}$ as a result of the Eqrain 15 interlaboratory comparison circuit organized by CETAMA [33]. A fraction of this stock solution was gravimetrically diluted in HNO_3 3 M to reach a concentration of $1149.6 \pm 1.8 \text{ }\mu\text{g}\cdot\text{g}^{-1}$. A certified reference solution for ^{237}Np ($[\text{Np}] = 1.008 \pm 0.006 \text{ g}\cdot\text{L}^{-1}$) obtained from the CEA Marcoule/ISEC/DMRC/CETAMA was gravimetrically diluted in HNO_3 1 M in order to reach a concentration of $316.2 \pm 2.0 \text{ ng}\cdot\text{g}^{-1}$. These two diluted solutions, kept under weight control, were used at each analytical session to prepare standard solutions for the calibration curve by Q-ICP-MS and MC-ICP-MS or for the preparation of simulated samples.

From those solutions, a “simulated sample” containing a $100 \text{ }\mu\text{g}\cdot\text{g}^{-1}$ solution of uranium with a $^{237}\text{Np}/^{238}\text{U}$ ratio of $(28.40 \pm 0.19) \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ was gravimetrically prepared. This ratio was in the range of the $^{237}\text{Np}/^{238}\text{U}$ ratios to be determined in the irradiated UO_2 pellet samples (see next paragraph). The given uncertainty was the expanded uncertainty ($k=2$) obtained by combining uncertainties from the reference solutions and the weights.

For the Q-ICP-MS analysis, a bismuth solution ($1000 \text{ mg}\cdot\text{L}^{-1}$) in HNO_3 2% from (SPEX CertiPrep,

Metuchen, USA), certified in content, was used to prepare an internal standard solution to correct the signal drift.

For isotopic dilution measurements (IDMS) of ^{238}U concentration, a ^{233}U spike, called IRMM-040 and certified by the European Commission—Joint Research Centre—Geel, formerly Institute of Reference Materials and Measurements, was used. This certified reference material was gravimetrically diluted at a concentration of $96.50 \pm 0.17 \mu\text{g}\cdot\text{g}^{-1}$ and its isotopic composition was also certified at $^{233}\text{U}/\text{U} = 98.0430 \pm 0.0057\%$.

UO₂-irradiated pellet samples

The analyzed samples described in this article were ^{236}U isotope-doped UO_2 pellets. They had been irradiated in the 1980's in the Melusine reactor in CEA Grenoble for experimental purposes. After their irradiation cycle, the pellets have been stored in the COMIR facility (CEA Marcoule) for more than 30 years. Recently, they have been dissolved in hot cells in the Atalante Facility (CEA Marcoule) in 9 M boiling nitric acid for several hours [34] and aliquots of the dissolution solutions were shipped to the LANIE. According to the neutron calculation code, in 2018, the ratio of interest $^{237}\text{Np}/^{238}\text{U}$ varied between 10×10^{-6} and $100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ and the ratio $^{238}\text{Pu}/^{238}\text{U}$ was $< 2 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$, allowing the direct measurement of ^{238}U by MC-ICP-MS without any chemical separation. The neutron calculation indicated also that the $^{236}\text{U}/^{238}\text{U}$

ratios varied between 0.001 and 0.015 depending on the studied sample.

Instrumentation and methods

Direct measurement of the $^{237}\text{Np}/^{238}\text{U}$ ratio by MC-ICP-MS

From the U and Np diluted reference solutions described above, Np/U standard solutions were gravimetrically prepared before each experimental session in HNO_3 2%. The aimed concentration in ^{238}U was around $200 \text{ ng}\cdot\text{g}^{-1}$. For each standard solution, the appropriate amount of neptunium solution was added in order to frame the expected $^{237}\text{Np}/^{238}\text{U}$ atomic ratio in the analyzed samples (Table 1).

Aliquots of the UO_2 samples were diluted in HNO_3 2% to reach a uranium concentration of $200 \text{ ng}\cdot\text{g}^{-1}$.

Direct $^{237}\text{Np}/^{238}\text{U}$ ratio measurements were carried out on a NEPTUNE Plus MC-ICP-MS (Thermo Scientific, Bremen, Germany). The source of this instrument has been modified to be surrounded by a glovebox in order to handle radioactive samples. The introduction system was composed of a $100 \mu\text{L}\cdot\text{min}^{-1}$ PFA micronebulizer (Elemental scientific, ESI, USA) and a dual quartz spray chamber arrangement (cyclonic + scott) connected to a PC3 Peltier chiller (Elemental Scientific, ESI, USA). Operating parameters are given in Table 2.

The sensitivity and the signal stability were optimized daily on a tune solution containing uranium and were

Table 1 Experimental setup of each analytical session

	Session 1	Session 2	Session 3	Session 4
	$^{237}\text{Np}/^{238}\text{U}$ ratio in $\times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$			
Etalon 0	0.00	0.00	0.00	0.00
Etalon 1	9.65 ± 0.06	9.65 ± 0.06	9.22 ± 0.06	9.40 ± 0.06
Etalon 2	48.12 ± 0.31	48.12 ± 0.31	23.16 ± 0.15	23.50 ± 0.15
Etalon 3	97.07 ± 0.62	97.07 ± 0.62	45.24 ± 0.29	47.07 ± 0.30
Etalon 4	200.31 ± 1.3		69.73 ± 0.45	70.31 ± 0.45
Etalon 5			92.45 ± 0.60	93.71 ± 0.60
Etalon 6				117.28 ± 0.75
Samples analyzed during the session				
	Session 1	Session 2	Session 3	Session 4
$10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$		X	X	X
$25 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$			X	X
Simulated Sample	X	X		
$40 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$			X	X
$70 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1*}$				X
$90 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1*}$				X
$100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$	X			

The upper part of this table gives the concentration of the standard solution used during the analytical session and their associated expanded uncertainties ($k=2$). The lower part gives the studied samples identified with the estimated $^{237}\text{Np}/^{238}\text{U}$ ratio analyzed during the session. The asterisk indicates the samples that were also analyzed with the Q-ICP-MS + IDMS approach. "Simulated Sample" stands for simulated sample with a concentration of $28.4 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$.

Table 2 ICP-MS parameters during $^{237}\text{Np}/^{238}\text{U}$ determinations

<i>Neptune plus MC-ICP-MS parameters</i>	
RF Power	1100 W
Plasma gas flow rate	15 L·min ⁻¹
Auxiliary gas flow rate	1.0 L·min ⁻¹
Nebulizer gas flow rate	0.95 L·min ⁻¹
Sample uptake rate	0.1 mL·min ⁻¹
Nebulizer type	100 μL·min ⁻¹ PFA micronebulizer (ESI)
Spray chamber type	Quartz dual cyclonic and Scott chambers equipped with a PC3 Peltier chiller (ESI)
<i>X series Q-ICP-MS parameters</i>	
RF Power	1100 W
Plasma gas flow rate	15 L·min ⁻¹
Auxiliary gas flow rate	1.0 L·min ⁻¹
Nebulizer gas flow rate	0.90 L·min ⁻¹
Sample uptake rate	0.4 mL·min ⁻¹
Nebulizer type	400 μL·min ⁻¹ quartz concentric nebulizer
Spray chamber type	Quartz cyclonic spray chamber connected to a PC3 Peltier chiller (ESI)

greater or equal to 0.1 V/ppb during all analytical sessions which represent a ^{238}U signal greater or equal to 20 V (for 200 ppb).

Analyses were performed at low mass resolution in static mode. Faraday cups and the central secondary electron multiplier (SEM) equipped with a retarding potential quadrupole (RPQ) were used (Table 3), and such filter reduces the abundance sensitivity by a factor around 100. If needed (i.e., if the SEM had not been used for several months), a cleanup of the SEM was realized by detecting 5 mV of ^{238}U for at least 2 h. Intercalibration gains and baselines for the Faraday cups were electronically determined before each analytical session. The reproducibility of the electronic gains was better than 20 ppm·day⁻¹. The SEM/Faraday cup yield was also determined by measuring a 5 mV ^{238}U signal on the central cup and SEM at the beginning and the end of a session. Even if this yield was not used for calculation, its value should be greater than 80% to ensure that the detector was working in good operating conditions. SEM dark noise was also measured

before the analytical sessions and was always found below 0.2 cps.

Detector configurations for each analytical step are given in Table 3. As shown in this table, uranium isotopes were determined on Faraday cups and ^{237}Np on the SEM. The cups measuring ^{234}U , ^{235}U and ^{238}U were connected to 10¹¹ Ω and ^{236}U to 10¹² Ω amplifiers.

The analytical sequences were composed of consecutive quantifications of blank (HNO₃ 2%), standard and sample measurements. The blank method contained 1 block of 10 cycles with an integration time of 8 s. The sample (or standard) method was divided into 2 blocks of 10 cycles, each cycle being analyzed with an integration time of 8 s (Table 3).

In order to correct the $^{237}\text{Np}/^{238}\text{U}$ raw data, abundance sensitivity measurements were performed at the beginning and the end of the day by establishing the $^{237}/^{238}\text{U}$ ratio in a 200-ppb natural uranium solution. The ion beam at mass 237 was measured on the SEM and the $^{238}\text{U}^+$ ion beam on H1 Faraday cup. The hydride rate was also determined twice

Table 3 Detector configuration on the MC-ICP-MS

		L3	L2	L1	C (SEM)	H1	Integration time (s)	Cycles	Block
Np Method/blank	Isotopes	^{234}U	^{235}U	^{236}U	^{237}Np	^{238}U	8 s	10	2/1
	Amplifiers	10 ¹¹ Ω	10 ¹¹ Ω	10 ¹² Ω		10 ¹¹ Ω			
Abundance sensitivity method	Measured masses/ Isotopes				237.05	^{238}U	16 s	10	1
	Amplifiers					10 ¹¹ Ω			
Hydride method	Measured species			^{238}U	$^{238}\text{UH}^+$		16 s	10	1
	Amplifiers			10 ¹¹ Ω					

in an analytical session by measuring—in the same natural uranium solution—the $^{238}\text{U}^+$ signal on the L1 Faraday cup and the $^{238}\text{UH}^+$ species on the SEM.

For the hydride determination, the amplifier connected to L1 had to be a $10^{11} \Omega$ amplifier to avoid saturation. The methods contained 10 cycles of measurements with an integration time of 16 s. The cup configurations for abundance sensitivity and hydride methods are given in Table 3. Except for one analytical session where the value is around 1.3 ppm, the abundance sensitivity was established as being below 1 ppm. The abundance sensitivity was systematically higher at the end of the analytical session as the pressure in the analyzer increased during the day but remained quite close to the specifications of the manufacturer (< 1 ppm on the SEM). The hydride rate (ie. Ratio $^{238}\text{UH}^+ / ^{238}\text{U}^+$) was around 1×10^{-5} — 3×10^{-5} (depending on the analytical session) and stayed relatively stable throughout the day. These values were in agreement with the manufacturer's recommendation ($\sim 1 \times 10^{-5}$).

$^{237}\text{Np}^+$ raw data were corrected for the blank, the abundance sensitivity (average of the measurements) and the mean hydride rate according the following Eq. (1):

$$\begin{aligned} {}^{237}\text{Np}_{\text{corr.}}^+ &= {}^{237}\text{Np}_{\text{raw}}^+ - \text{blk}_{237} - \left(\frac{{}^{238}\text{UH}^+}{{}^{238}\text{U}^+} \right) \\ &\times ({}^{236}\text{U}_{\text{raw}}^+ - \text{blk}_{236}) - \left(\frac{237}{238} \frac{\text{U}^+}{\text{U}^+} \right) \\ &\times ({}^{238}\text{U}_{\text{raw}}^+ - \text{blk}_{238}) \end{aligned} \quad (1)$$

Here:

${}^{237}\text{Np}_{\text{corr.}}^+$ is the intensity of $^{237}\text{Np}^+$ corrected in cps,

${}^{237}\text{Np}_{\text{raw}}^+$ is the intensity of $^{237}\text{Np}^+$ without correction in cps,

blk_{236} , blk_{237} and blk_{238} are respectively the intensities at masses 236, 237, and 238 in the HNO_3 2% solution in cps, the $\left(\frac{{}^{238}\text{UH}^+}{{}^{238}\text{U}^+} \right)$ and the $\left(\frac{237}{238} \frac{\text{U}^+}{\text{U}^+} \right)$ ratios are respectively the mean hydride rate and mean abundance sensitivity measured with the 200 ppb U solution at the beginning and at the end of the session,

${}^{236}\text{U}_{\text{raw}}^+$ and ${}^{238}\text{U}_{\text{raw}}^+$ are respectively the measured intensity of ${}^{236}\text{U}^+$ and ${}^{238}\text{U}^+$ converted into cps.

The measured atomic ratio $^{237}\text{Np}/^{238}\text{U}$ is given as Eq. (2):

$$\left(\frac{{}^{237}\text{Np}}{{}^{238}\text{U}} \right)_{\text{measured}} = \left(\frac{{}^{237}\text{Np}_{\text{corr.}}^+}{{}^{238}\text{U}^+ - \text{blk}_{238}} \right) \quad (2)$$

$^{237}\text{Np}/^{238}\text{U}$ determination by Q-ICP-MS and IDMS measurements

In order to validate the new approach proposed in this study, the $^{237}\text{Np}/^{238}\text{U}$ ratio of several dissolved spent nuclear fuel

samples was quantified by a two-step approach involving the ^{237}Np determination by Q-ICP-MS and the ^{238}U determination by IDMS for cross-comparison. This is the reference method used in the laboratory to characterize the $^{237}\text{Np}/^{238}\text{U}$ ratio and it consists in determining the U concentration in the spent fuel using isotopic dilution mass spectrometry associated with thermal ionization mass spectrometry (TIMS) measurements, and in establishing the content of ^{237}Np using an external calibration curve by Q-ICP-MS.

In the present research work, this method was only used on two of the dissolved pellets (with $^{237}\text{Np}/^{238}\text{U}$ around 70×10^{-6} and $90 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$), and these two samples were indeed analyzed before the direct measurement method was developed. The results obtained at that time were then used to validate the MC-ICP-MS method.

Determining the ^{238}U concentration by isotope dilution mass spectrometry (IDMS)

According to the simplified isotopic dilution Eq. (3) [35], the ^{238}U concentration in the sample $C_{238\text{U-Sa}}$ can be established with knowledge of:

1. The molar mass (M_{Sa}) of each sample. They were quantified beforehand by Thermal Ionization Mass Spectrometry (TIMS). As those experiments are beyond the scope of this article, they are not described here but similar experiments can be found in [36] in the case of cerium samples.
2. The ratio $(^{238}\text{U}/^{233}\text{U})_{\text{sp}}$, the molar mass (M_{sp}), the isotope abundance in ^{233}U ($^{233}\text{U})_{\text{sp}}$, given in the reference material certificate.
3. The concentration of uranium $C_{\text{U-sp}}$ in the spike, calculated with the certificate and the dilution data.
4. The data coming from Spike-sample mixtures as described below.

$$C_{238\text{U-Sa}} = C_{\text{U-sp}} \times \frac{m_{\text{sp}}}{m_{\text{sa}}} \times \frac{M_{\text{sa}}}{M_{\text{sp}}} \times ({}^{233}\text{U})_{\text{sp}} \times \left[\left(\frac{{}^{238}\text{U}}{{}^{233}\text{U}} \right)_{\text{Blend}} - \left(\frac{{}^{238}\text{U}}{{}^{233}\text{U}} \right)_{\text{sp}} \right] \quad (3)$$

For each sample, two IRMM-040 spike-sample mixtures were prepared in a glovebox through weighing (m_{sp} weight of the spike and m_{sa} weight of the sample). The mixtures were then dried on a hot plate.

Chemical separation using a 100–200 mesh AG 1-X4 resin (Biorad, Hercules, CA, USA) was realized on the mixtures in a nitric acid medium in order to separate the uranium from the matrix and interfering elements (protocol described in [37]).

The separated uranium fraction was then diluted in order to reach a concentration of $50 \text{ ng}\cdot\mu\text{L}^{-1}$ in HNO_3 2% to be analyzed by Thermal Ionization Mass Spectrometry

(TIMS) using the total evaporation technique [38–41] in order to determine the $(^{238}\text{U}/^{233}\text{U})_{\text{blend}}$ ratio. A 1 μL -droplet of each mixture was then deposited with a pipet on a 99.99% degassed side Re-filament, and the droplet is dried by applying a current through the filament. Filaments were loaded in a nuclearized thermal ionization mass spectrometer Sector 54 from GV Instruments (Manchester, UK) suitable for handling radioactive samples, as described previously [42, 43].

Determining the ^{237}Np concentration by a Q-ICP-MS external calibration curve

This method consists in measuring the ^{237}Np content by an external calibration curve.

From the diluted reference material solutions, 6 standard solutions were freshly prepared for each experimental session in HNO_3 2%, and each one contained about 2 $\text{ng}\cdot\text{g}^{-1}$ of bismuth (internal standard) and a variable concentration of neptunium (from $[^{237}\text{Np}] = 0$ to 2 $\text{ng}\cdot\text{g}^{-1}$). Additionally, a CETAMA natural uranium solution of 10 $\mu\text{g}\cdot\text{g}^{-1}$ uranium and 2 $\text{ng}\cdot\text{g}^{-1}$ bismuth was prepared (matrix solution) to determine the abundance sensitivity and hydride rate.

Aliquots of each sample were gravimetrically diluted into HNO_3 2% and mixed with bismuth solution in order to reach a uranium concentration of 10 $\mu\text{g}\cdot\text{g}^{-1}$ and a bismuth concentration of 2 $\text{ng}\cdot\text{g}^{-1}$. The ^{237}Np concentration was then established on those dilutions.

A quadrupole Inductively Coupled Plasma Mass spectrometer (ICP-MS) ‘‘X series’’ from Thermo Electron (Winsford, UK) was used for these measurements. The source of this instrument had been modified and was surrounded by a glovebox to handle radioactive samples as previously described in [44, 45]. Sample introduction in the plasma was realized via a quartz cyclonic spray chamber connected to a PC3 Peltier chiller (Elemental Scientific, ESI, USA) and a quartz concentric nebulizer (400 $\mu\text{L}\cdot\text{min}^{-1}$). Operating parameters are given in Table 2. Tuning and calibration of the instrument were performed before each analytical session using a multi-elemental solution containing indium and uranium at concentrations of about 1 ppb in order to obtain a stability better than 2% on the ion beams and a sensitivity in the range of 300,000 cps and 500,000 cps. Oxides and the doubly-charged species rate were kept as low as possible (respectively $^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+ < 3\%$ and $^{138}\text{Ba}^{2+} / ^{138}\text{Ba}^+ < 3\%$).

Q-ICP-MS makes it possible to determine of ^{209}Bi , ^{237}Np , ^{234}U , ^{235}U and ^{236}U in each standard solution. Due to the high concentration of the ^{238}U isotope in the solutions, it was not measured to avoid any risk of detector saturation. A dwell time of 40 ms/analyte was selected and 200 sweeps were realized in each run. For the standards and samples, 10 runs per analysis were performed. As less precision was

required for the blank (HNO_3 2%) and for the matrix solution, only 3 and 5 runs were performed, respectively.

The analytical sequence consisted in analyzing HNO_3 2% (blank), standard solutions and samples. The natural uranium solution with a concentration of 10 $\mu\text{g}\cdot\text{g}^{-1}$ was also examined at the beginning, in the middle and at the end of the analytical session in order to establish the hydride rate measured at masses 239 ($^{238}\text{UH}^+$) and the calculated $^{238}\text{U}^+$ ion beam intensity derived from the $^{234}\text{U}^+$ ion beam intensity and isotopic composition. This estimation of the $^{238}\text{U}^+$ ion beam was necessary, as the $^{238}\text{U}^+$ ion beam was too high to be directly measured. The abundance sensitivity of the instrument was quantified with masses 237 and estimated $^{238}\text{U}^+$ ion beam intensity. During the various analytical sessions, the abundance sensitivity was between 1.9 and 3 ppm and the hydride rate between 8×10^{-5} and 1.2×10^{-4} .

Results and discussion

The results for the samples (UO_2 pellets solution and simulated sample) were obtained during four different analytical sessions. The $^{237}\text{Np}/^{238}\text{U}$ ratio of each standard solution and the analyzed samples during those analytical runs are given in Table 1. As already mentioned above, standards had been prepared in order to bracket the samples to be analyzed in the session. Generally, except for the first session where a higher range of standards was analyzed, standards with a $^{237}\text{Np}/^{238}\text{U}$ ratio between 0 and $100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ were used. For each measurement (standards and samples), the ^{237}Np signal intensity was corrected according to Eq. (1) and the $(^{237}\text{Np}/^{238}\text{U})_{\text{measured}}$ was determined using Eq. (2). The corrections due to hydride rate ($^{236}\text{UH}^+$) and the abundance sensitivity represent respectively a number of counts per second < 350 cps and between 600 and 2300 cps depending on the analytical conditions. The hydride rate contribution is at least twice lower than the abundance sensitivity contribution, this latest being the most important correction. The contribution of the hydride correction to the total signal on mass 237 amu is $< 0.5\%$; the contribution of the abundance sensitivity is $< 5\%$ depending on the conditions.

In each analytical session, for the standards, a calibration curve of the ‘‘reference’’ $^{237}\text{Np}/^{238}\text{U}$ ratios (calculated with weight and certificates) versus the experimentally obtained ratios was plotted. An example of such a calibration curve is given in Fig. 1. A linear regression model was used and the slope (a) and intercept (b) of the regression line were determined for each analytical session according to the model. Table 4 gives the values obtained for each parameter (a) and (b). As shown in the table, in each analytical session, the coefficient of determination was $R^2 > 0.9999$ demonstrating a good correlation between the measured and reference values using a linear model.

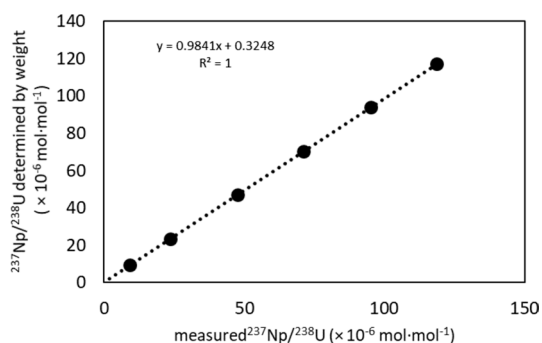


Fig. 1 Plot representing an example of a calibration curve used during this study. The $^{237}\text{Np}/^{238}\text{U}$ calculated using the dilution weight and the certificates is plotted versus the measured $^{237}\text{Np}/^{238}\text{U}$ ratio. The dots are the results of the standard measurements, and the dashed line is the linear regression model used to determine the $^{237}\text{Np}/^{238}\text{U}$ ratio in the sample

Table 4 Parameters of each linear regression for the four calibration curves determined during the study

	a	b	R ²
session 1	0.99874	0.06956	1.00000
session 2	0.97968	0.02139	1.00000
session 3	0.89584	-0.15127	0.99998
session 4	0.98410	0.32480	0.99999

(a) is the parameter representing the slope, (b) is the intercept according to the model $y = ax + b$, and R^2 is the coefficient of determination

Validation of direct measurements by MC-ICP-MS

The validation of the method was done in two steps, by measuring:

1. the gravimetrically prepared “simulated sample” on the Neptune Plus and comparing it with the $^{237}\text{Np}/^{238}\text{U}$ ratio derived from certificates and weight (Fig. 2),
2. two samples ($^{237}\text{Np}/^{238}\text{U} \approx 70 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ and $^{237}\text{Np}/^{238}\text{U} \approx 90 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$), with both the new MC-ICP-MS direct method and the classical “IDMS + Q-ICP-MS” approach (Fig. 3)

Concerning the simulated sample, as observed in Fig. 2, the relative difference between the value measured with the MC-ICP-MS and the reference value obtained by weighing was around 0.2% for the 1st analytical session and 0.4% for the second. The experimental values were within the expanded uncertainties of the reference value (0.64%), and the method could therefore be validated for the $30 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ reference solution. It should be noted that the represented expanded measurement uncertainties

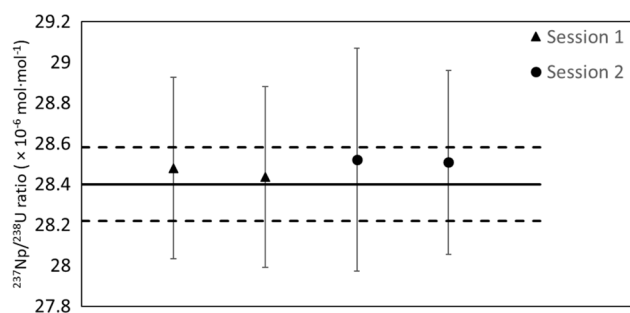


Fig. 2 Results obtained by MC-ICP-MS of the $^{237}\text{Np}/^{238}\text{U}$ ratio for a “simulated solution”: the black line represents the reference value derived from certificates and weight. The dashed line corresponds to the uncertainties ($k=2$) of the reference value. The triangles are the results obtained during the 1st analytical session and the circles are the results from the 2nd session. The error bars represent the expanded uncertainties ($k=2$) of the measurements using the model given in Eq. 4

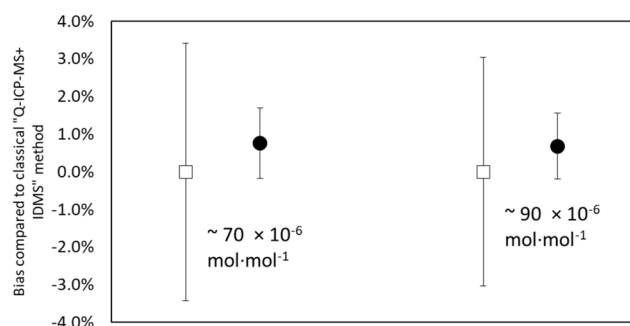


Fig. 3 Comparison between the classical “Q-ICP-MS + IDMS” method (squares) and the new method by MC-ICP-MS (black dots) for two samples (around 70×10^{-6} and $90 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$). The indicated values are the bias compared to the classical method. The represented expanded uncertainties are given with a coverage factor of 2

($k=2$) were those found when following the model that will be discussed in the next paragraph.

Similarly, Fig. 3 represents a comparison of the results obtained with the classical method and direct measurements on MC-ICP-MS for two dissolved pellet samples with $^{237}\text{Np}/^{238}\text{U}$ ratios around 70×10^{-6} and $90 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$. As the “Q-ICP-MS + IDMS” approach was the reference method, results are indicated with a bias of 0% (square on the figure). For those two values, the expanded uncertainties ($k=2$) were the combination of the standard uncertainties originating from the IDMS method (around 0.2%) for ^{238}U determination and the reproducibility from several ^{237}Np determinations (around 1.5%–1.75%, $k=1$). For the direct measurements, differences of 0.8% and 0.65% were observed between the reference method (dot on the figure) and the new MC-ICP-MS direct approach. The expanded uncertainties of the MC-ICP-MS method calculated according

Table 5 Results obtained on dissolved UO₂ pellets

Samples	n	Value	U _{abs} (k=2)	Unit	U _{rel} (k=2)
10 × 10 ⁻⁶ mol·mol ⁻¹	5	18.53 × 10 ⁻⁶	0.51 × 10 ⁻⁶	mol·mol ⁻¹	2.75%
25 × 10 ⁻⁶ mol·mol ⁻¹	3	24.49 × 10 ⁻⁶	0.53 × 10 ⁻⁶	mol·mol ⁻¹	2.16%
40 × 10 ⁻⁶ mol·mol ⁻¹	3	40.71 × 10 ⁻⁶	0.59 × 10 ⁻⁶	mol·mol ⁻¹	1.45%
70 × 10 ⁻⁶ mol·mol ⁻¹	1	73.65 × 10 ⁻⁶	0.70 × 10 ⁻⁶	mol·mol ⁻¹	0.95%
90 × 10 ⁻⁶ mol·mol ⁻¹	1	92.73 × 10 ⁻⁶	0.81 × 10 ⁻⁶	mol·mol ⁻¹	0.87%
100 × 10 ⁻⁶ mol·mol ⁻¹	3	98.86 × 10 ⁻⁶	0.80 × 10 ⁻⁶	mol·mol ⁻¹	0.81%

to the model that will be described in the next paragraph were respectively 0.95% and 0.87% ($k=2$). At that point, an important advantage of the newly developed method could already be noticed: the uncertainties were three times below those determined by Q-ICP-MS + IDMS. The observed bias was insignificant within the uncertainties wherefore these two sets of experiments proved that the new method was validated.

Results and uncertainty assessment

Pellet samples were analyzed in different analytical sessions (see Table 1) and Table 5 gives the results for each sample. The indicated values are averages of several measurements. Absolute and relative combined expanded uncertainties are also listed with a coverage factor of 2 and the indicated relative expanded uncertainties are defined as the maximum of the individual uncertainties. For each measurement, the standard uncertainties were combined used the following model (Eq. 4):

$$u_{rel} = \sqrt{u_{rel,reg}^2 + u_{rel,MRC}^2 + u_{rel,meas}^2 + u_{rel,lt}^2} \quad (4)$$

Here:

$u_{rel, MRC}$ is the uncertainty of the reference U-Np mixtures ($u_{rel, MRC} = 0.32\%$).

$u_{rel, meas}$ is the relative standard deviation of the measured $^{237}\text{Np}/^{238}\text{U}$ ratio of the sample. This contribution varied between 0.1% and 0.3% depending on the day and the analytical conditions.

$u_{rel, reg}$ is the uncertainty of the linear regression. This uncertainty was determined via excel by calculating the impact of the slope and intercept uncertainties on the $^{237}\text{Np}/^{238}\text{U}$ ratio. It depended on the value of $^{237}\text{Np}/^{238}\text{U}$ and on the conditions of the analytical session. In Fig. 4, $u_{rel, reg}$ is plotted versus the $^{237}\text{Np}/^{238}\text{U}$ ratio, and as can be seen the relative uncertainty decreased when the ratio increased. Moreover, it was clear that this uncertainty was dependent on the analytical session. It varied between 0.04% and 0.72%.

$u_{rel, lt}$ is an uncertainty parameter linked to the reproducibility between different analytical sessions. Some measurements were performed on different dates, and the standard

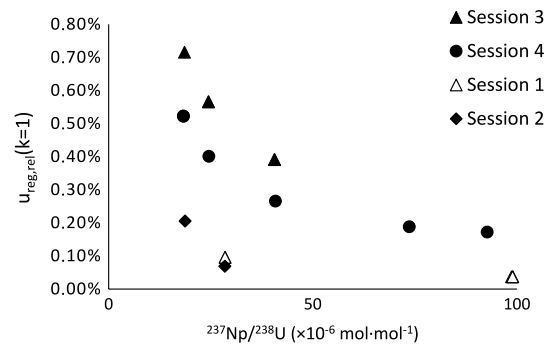


Fig. 4 The standard uncertainty ($k=1$) for the linear regression versus the $^{237}\text{Np}/^{238}\text{U}$ ratio for the different analytical sessions

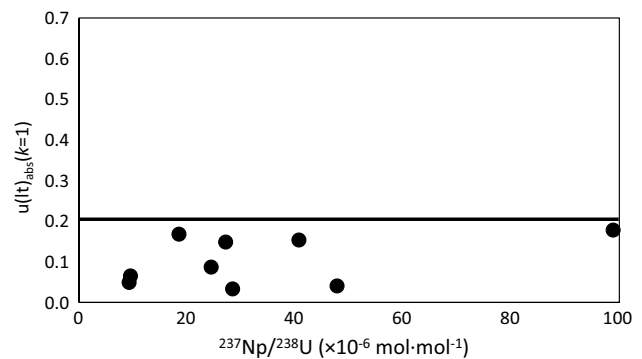


Fig. 5 Plot representing the $u(lt)_{abs}$ contribution ($k=1$) versus the $^{237}\text{Np}/^{238}\text{U}$ ratio. The black line represents the value 0.2

deviation between the various measurements is plotted in Fig. 5. As observed on this graph, the standard deviation did not exceed 0.2. This absolute value was converted into a relative contribution and added to the uncertainties.

By combining these contributions using Eq. 4, a relative expanded uncertainty ($k=2$) varying between 0.81% for the samples with the highest $^{237}\text{Np}/^{238}\text{U}$ ratio and 2.75% for the samples with the lowest $^{237}\text{Np}/^{238}\text{U}$ ratio was calculated (Table 5). These values were globally equivalent to or lower than the expanded uncertainties obtained with the usual method which were generally around 2–4%. Figure 6 presents two examples of uncertainty budgets: one with the budget of the lowest $^{237}\text{Np}/^{238}\text{U}$ ratio (around

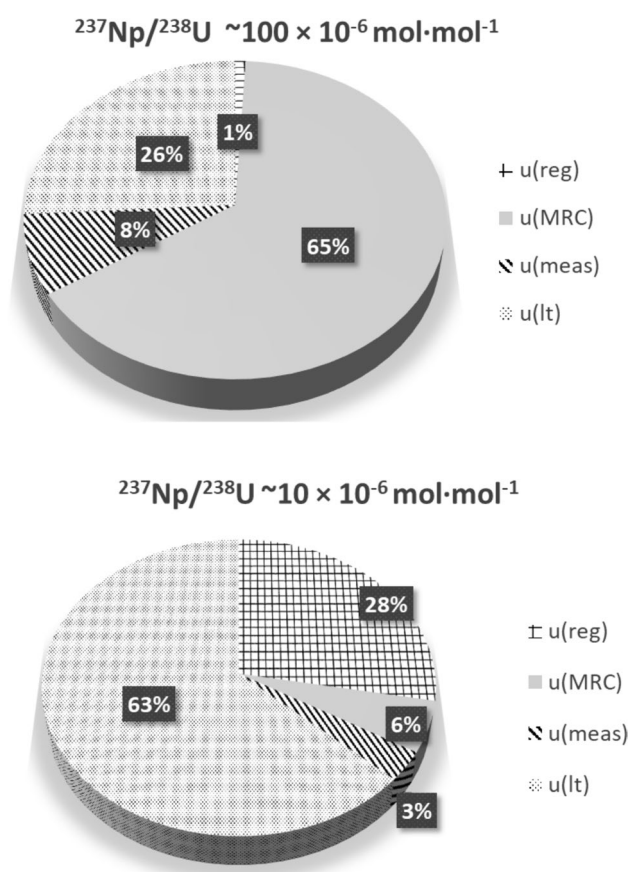


Fig. 6 Uncertainty budget on two samples: one with $^{237}\text{Np}/^{238}\text{U} = 10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ and one with $^{237}\text{Np}/^{238}\text{U} = 100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$

$10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$) and one with the highest (around $100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$). The uncertainty budget was quite different for the 2 examples. For the higher $^{237}\text{Np}/^{238}\text{U}$ -sample, the biggest contribution to the uncertainty (i.e., up to 65% to the final value) was that of the U-Np reference mixtures and the second main contributor was the parameter called u_{It} which represented around 25–30% of the contribution. This tendency changed for the lowest ratios, for which the main contribution became the parameter linked to measuring the external reproducibility (u_{It}) (more than 60%), followed by the uncertainty of linear regressions. Regardless of the $^{237}\text{Np}/^{238}\text{U}$, the uncertainty originating from the measurement itself brought the smallest contribution.

Conclusion

A new method to directly measure the $^{237}\text{Np}/^{238}\text{U}$ atomic ratio has been successfully developed and applied on real irradiated samples in which the amount of ^{238}Pu was negligible. The method made it possible to measure low

$^{237}\text{Np}/^{238}\text{U}$ ratios (around $10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$), which could not be quantified by the conventional laboratory approach. This described method did not require prior chemical separation steps and used a MC-ICP-MS equipped with Faraday cups and an ion counter detector. It was achievable to measure samples with a $^{237}\text{Np}/^{238}\text{U}$ ratio varying from $10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ to $100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$. The method was validated by carrying out measurements of a simulated solution and by comparing the obtained results on two real samples with the more commonly used technique “Q-ICP-MS + IDMS”.

The described approach displayed multiple advantages:

1. Analytically, since the RPQ improved the abundance sensitivity, this direct method allowed measurements of atomic ratios close to $10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ which would not be possible with the commonly used technique.
2. It suppresses the chemical separation step, reducing the number of steps in the glovebox and also the duration of radiation exposure for the analysts.
3. Knowledge of the isotope composition of uranium is not required for such measurements.
4. The relative expanded uncertainties obtained were between 2.75% and 0.81% for an elemental ratio varying between $10 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ and $100 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ which was lower than or equivalent to the uncertainties obtained by the commonly used technique.

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Data availability The authors declare that the data supporting the findings of this study are available within the paper. If needed, any additional data can be asked to the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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