International Journal of Mass Spectrometry 291 (2010) 101–107

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Review

Accurate determination of Curium and Californium isotopic ratios by inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) in ^{248}Cm samples for transmutation studies

A. Gourgiotis[a,*], H. Isnard[a], M. Aubert[a], E. Dupont[b], I. AlMahamid[c,d], G. Tiang[g], L. Rao[g], W. Lukens[g], P. Cassette[e], S. Panebianco[b], A. Letourneau[b], F. Chartier[f]

[a] Commissariat à l'Energie Atomique, DEN/DPC/SECR/LANIE, 91191 Gif-sur-Yvette Cedex, Bâtiment 391, France
[b] Commissariat à l'Energie Atomique, DSM/IRFU/SPhN, 91191 Gif-sur-Yvette Cedex, France
[c] New York State Department of Health, Wadsworth Center, Albany, NY 12201, USA
[d] School of Public Health, New York State University at Albany, USA
[e] Commissariat à l'Energie Atomique, LIST, Laboratoire National Henri Becquerel (LNE-LNHB), F-91191 Gif sur Yvette, France
[f] Commissariat à l'Energie Atomique, DEN/DPC, 91191 Gif-sur-Yvette Cedex, France
[g] Lawrence Berkeley National Laboratory, Division of Chemical Sciences, Berkeley, CA 94720, USA

ARTICLE INFO

Article history:
Received 11 December 2009
Received in revised form 18 January 2010
Accepted 2 February 2010
Available online 6 February 2010

Keywords:
Quadrupole ICP-MS
Californium
Curium
Isotope ratio measurements
Transmutation

ABSTRACT

The French Atomic Energy Commission has carried out several experiments including the mini-INCA (INcineration of Actinides) project for the study of minor-actinide transmutation processes in high intensity thermal neutron fluxes, in view of proposing solutions to reduce the radiotoxicity of long-lived nuclear wastes. In this context, a Cm sample enriched in ^{248}Cm (~97%) was irradiated in thermal neutron flux at the High Flux Reactor (HFR) of the Laue-Langevin Institute (ILL). This work describes a quadrupole ICP-MS (ICP-QMS) analytical procedure for precise and accurate isotopic composition determination of Cm before sample irradiation and of Cm and Cf after sample irradiation. The factors that affect the accuracy and reproducibility of isotopic ratio measurements by ICP-QMS, such as peak centre correction, detector dead time, mass bias, abundance sensitivity and hydrides formation, instrumental background, and memory blank were carefully evaluated and corrected. Uncertainties of the isotopic ratios, taking into account internal precision of isotope ratio measurements, peak tailing, and hydrides' formations ranged from 0.3% to 1.3%. This uncertainties' range is quite acceptable for the nuclear data to be used in transmutation studies.

Contents

---

[*] Corresponding author. Tel.: +33 169081848; fax: +33 169085411.
E-mail address: alkiviadis.gourgiotis@cea.fr (A. Gourgiotis).

1387-3806/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2010.02.002

1. Introduction

Management of nuclear waste produced during the burn-up of nuclear fuel is one of the crucial challenges in this century. A very promising way under investigation for the management of radioactive waste is the transmutation of long-lived radionuclides in a fast neutron nuclear reactor into shorter lived or stable ones [1–3]. Therefore, transmutation of long-lived nuclides has been investigated in various systems for characterisation of their nuclear data. Due to their limited role in conventional fuel cycles, minor-actinides (MA) have not been extensively studied and their nuclear parameters are not always known with the precision required for transmutation dedicated system [4,5]. In this context, the French Atomic Energy Commission has carried out several experiments including the mini-INCA (INcineration of Actinides) project. The objective of this project is to extend the field of investigation of minor-actinides (1), which play an important role in the nuclear waste inventories for future nuclear energy scenarios, and (2) for which nuclear parameters are determined with significant discrepancies between different nuclear data libraries. Several radionuclides have been previously examined [6,7].

Part of these studies is based on experimental results obtained after irradiation of pure isotopes in the High Flux Reactor (HFR) of the Laue-Langevin Institut (ILL). The isotopic composition measurements of the studied isotopes before and after irradiation by mass spectrometric techniques are used to improve or complete nuclear data libraries. As a part of this program, a Cm sample enriched in ^{248}Cm (~97%) was irradiated in thermal neutron flux in the HFR of the ILL. The main objective of the program is to determine ^{248}Cm neutron capture cross-sections and to study part of the isotopic chains of Cm, Bk, and Cf. The simplified evolution chain of ^{248}Cm under neutron irradiation is presented in Fig. 1. Fig. 1 shows that the short-lived ^{249}Cm (64.15 min) generated by neutron capture of ^{248}Cm, decays into ^{249}Bk (330 d), which in turn decays to ^{249}Cf (351 y). Isotopes of ^{250}Cf (13 y), ^{251}Cf (898 y), and ^{252}Cf (2.6 y) are generated by neutron capture of ^{249}Cf, ^{250}Cf, and ^{251}Cf, respectively.

The precise determination of the isotopic compositions of actinides in nuclear samples has been almost the exclusive domain of the Thermal Ionization Mass Spectrometry (TIMS) over the last three decades [8–10]. This method advanced analytical capacities with per-mil-level precision (RSD-Relative Standard Deviation) [11–13] and the latest generation of these instruments allows isotope measurements with precision of several ppm levels [14–16]. This situation has changed with the introduction of Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), providing precisions on isotope ratio measurements equivalent to TIMS (RSD $\leq$ 0.01%) [17–21]. The recent development of inductively coupled plasma mass spectrometry fitted with a quadrupole mass analyzer (ICP-QMS) has also been used for isotope ratio measurements [22–28]. Even if accuracy and precision attained with this instrument (RSD ~ 0.1–1%) remain inferior compared to TIMS and MC-ICP-MS, simple and low cost instrumentation, and simplified measurement process make ICP-QMS more practical to use than TIMS or MC-ICP-MS. Two basic reasons for the inferior accuracy and precision of ICP-QMS compared to TIMS and MC-ICP-MS are the sequential rather than simultaneous isotope measurement and the Gaussian peaks' shape characteristic of these instruments [29]. Some recent studies have been conducted in order to improve ICP-QMS performance when measuring isotope ratios [23,25,30]. Compared with radiation measurement methods, ICP-QMS offers a number of advantages for isotope ratio measurements due to easier sample preparation steps, excellent detection limits, shorter measurement time and the capability to carry out precise isotope ratio measurements [31]. For nuclear data relevant to this case study, the accuracy and the precision attained with ICP-QMS are quite sufficient. Indeed, depending on the final objective of the measurement, the ICP-QMS accuracy and precision might remain significantly below other sources of uncertainty (e.g., neutron fluence during irradiation).

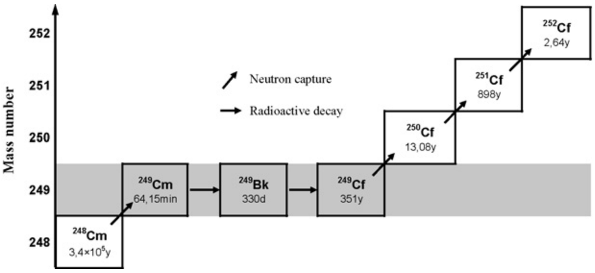

Fig. 1. Simplified evolution chain of ^{248}Cm under neutron irradiation. After 1-year cooling period, ^{249}Cm has totally decayed.

In this work, a methodology for a precise and accurate determination of isotopic composition of Cm sample enriched in ^{248}Cm (~97%), before and after irradiation in the HFR of the ILL by ICP-QMS has been developed.

The factors that affect the accuracy and precision of isotopic ratios by ICP-QMS, such as the peak centre correction, detector dead time, mass bias, abundance sensitivity and hydrides formation, instrumental background, and memory blank were carefully evaluated and corrected. Isotopic results for Cm before sample irradiation and Cm, Bk, and Cf after sample irradiation are presented with the full experimental and analysis procedures that were followed to obtain these data.

2. Experimental

2.1. Instrumentation settings

An ICP-QMS X series mass spectrometer (Thermo Electron, Winsford, UK) housed at the Isotopic Elementary and Nuclear Analysis Laboratory (LANIE) of the French Atomic Energy Commission (CEA Saclay) was used in this study. The ICP-QMS, the first X series modified with ion source and placed in a glove box to work with radioactive samples, was previously described [32]. Sample introduction into the plasma was made via a quartz peltier-cooled impact bead spray chamber and a quartz concentric nebulizer (1.0 mL/min). Self-aspiration mode was used for the sample introduction in order to minimize discrete noise components caused by rotation of the peristaltic pump.

All of the experimental parameters were daily optimized with a multi-elements test solution in order to obtain the maximum counting rates on ^{115}In$^+$ and ^{238}U$^+$ for this tuning. After a verification test of key parameters (sensitivity, stability, and oxide level test), the instrument is ready to perform measurements. The typical sensitivity and stability (relative standard deviation) values measured in 10 min for both ^{115}In$^+$ and ^{238}U$^+$ are $\sim 4 \times 10^5$ cps/ppb and <3‰, respectively. Oxide level test is performed by measuring the ^{140}CeO$^+$/^{140}Ce$^+$ ratio with typical values varying between 3% and 4%. The ICP-QMS operating and measurement conditions are summarized in Table 1.

2.2. Sample preparation

Two powder samples, 11 μg and 37 μg of ^{248}Cm in the form of Cm-nitrate were provided by the Lawrence Berkeley National Laboratory. The samples were canned into quartz tubes sealed under low pressure atmosphere. The first sample was sent directly to the LANIE laboratory to determine Cm isotopic composition before irradiation. The second sample was placed inside an aluminium

Table 1
Instrument settings for the ICP-QMS.

	Value/description
Sample introduction system	
Impact bead spray chamber	
Concentric nebulizer	1.0 mL/min
Self-aspiration mode	
Spray chamber temperature	3 °C
ICP-QMS X conditions	
RF power	1400 W
Nebulizer gas flow	0.8–0.9 L/min
Auxiliary gas flow	0.9 L/min
Cool gas flow	15 L/min
Data acquisition	
Peak width (10%)	0.82 a.m.u.
Detection mode	Pulse counting
Scan mode	Peak jumping

container and was irradiated for 16 days (December 3–19, 2007) inside the V4 irradiation channel [33] of the HFR of ILL in Grenoble-France. After irradiation and a cooling period of about 1 year the capsule was sent to the LANIE laboratory. The powders of both samples were dissolved with 4M HNO_3 (Normatom Prolabo) and after complete dissolution were diluted for isotopic analysis. All dilutions were performed in 0.5 M nitric sub-boiling acid. This acid was obtained by dilution of sub-boiling 14 M nitric acid, using an EVAPOCLEAN system (Analab, France), in deionized water (resistivity 18.2 MΩ cm) obtained from a Milli Q system (Millipore, Milford, MA, USA). All samples' preparation was performed in a glove box.

Non-irradiated and irradiated samples' survey runs were performed in a mass range between $m/z = 229$ and 236, in order to identify impurities that can create oxides isobaric interferences within the mass range of interest. For both samples, no impurities were detected.

For mass bias correction, an in-house $^{248}Cm/^{246}Cm = 8.937 \pm 0.018$ standard solution was used. The in-house standard nitric solution was certified using TIMS by 6 independent measurements and by the total evaporation method [34,35]. This method, takes into account the integration of all ions formed during analysis and is considered accurate because the effects of isotope fractionation that occur during the evaporation process are virtually eliminated in the final results. The isotope ratio precision obtained by the total evaporation method is given by the external RSD_{ext} for a number n of measurements, and no test for the rejection of anomalous data is used [35]. Therefore, RSD_{ext} obtained by the total evaporation method is generally inferior to the precision obtained of the conventional dynamic MC-TIMS method.

2.3. Analytical method

Mass spectra of non-irradiated and irradiated Cm samples present obviously a very high isotopic abundance of ^{248}Cm comparing to the other isotopes (Fig. 2). The electron multiplier detector employed in this study could use an analogue mode (ion intensity > 2×10^6 cps) or a pulse counting mode (ion intensity < 2×10^6 cps) for ion signal measurements.

In order to avoid high count rates on the electron multiplier and assure pulse counting as detection mode for more robust conditions, measurement of Cm samples isotopic composition was not performed in one single peak jumping routine. Thus $^{248}Cm^+/^{246}Cm^+$ isotopic ratio was measured first in a low concentrated solution (~4 ng/g of ^{248}Cm), and in a second run the $^{245}Cm^+/^{246}Cm^+$, $^{247}Cm^+/^{246}Cm^+$, $^{249}(Bk^+ + Cf^+)/^{251}Cf^+$, $^{250}Cf^+/^{251}Cf^+$, $^{252}Cf^+/^{251}Cf^+$ isotopic ratios were measured in a high concentrated solution (~100 ng/g of ^{248}Cm). Each measurement consisted of twenty-five consecutive integrations (cycles). Isotopes' dwell time ranged from 10 ms for the high abundance isotopes to 40 ms for the low abundance isotopes [26].

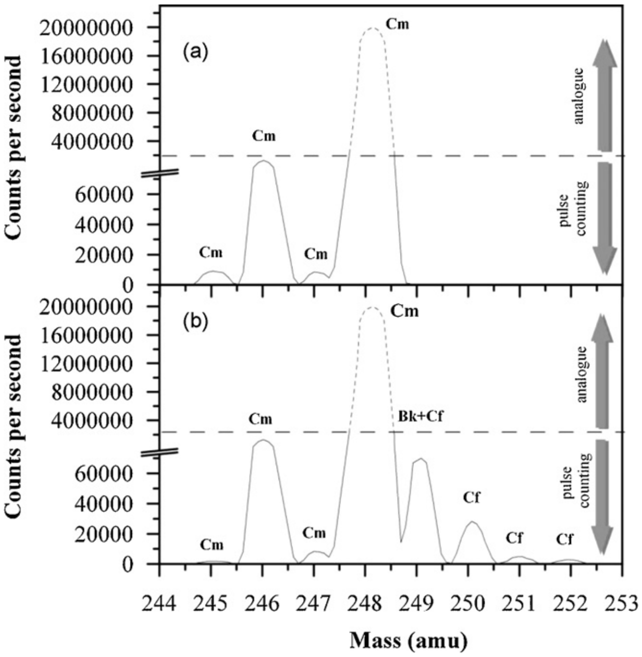

Fig. 2. Mass spectrum of non-irradiated (a), and irradiated (b) Cm samples.

For a number of 100 sweeps per cycle, the total measurement times were about 3 and 10 min for the low and high concentrated solutions, respectively. The isotopes of interest and their respective dwell times are listed in Table 2.

3. Results and discussion

3.1. Peak centre correction

As has been mentioned above the characteristics of Gaussian peaks obtained by mass spectrometers using a quadrupole mass filter limit the accuracy and precision of isotopic ratio measurements. For instance, the measured isotopic ratio could vary gradually over time. For this reason, all isotope ratio measurements were performed with three channels per peak centred symmetrically around the maximum point (peak centre) (Fig. 3). The peak centre of each isotope was identified visually by performing a scan through the mass range of interest before each measurement. The value of the mass corresponding to the peak centre of each isotope was defined as new mass analyte in the database of the instrument software (PlasmaLab).

As can be seen in Fig. 3, accurate peak centre correction for ^{246}Cm and ^{248}Cm isotopes improves the accuracy of the non-bias corrected $^{246}Cm^+/^{248}Cm^+$ isotopic ratio of the in-house $^{248}Cm/^{246}Cm = 8.937 \pm 0.018$ certified solution.

3.2. Dead time correction

For highly accurate measurements, detector dead time was appropriately corrected according to the method proposed by Russ [36] using an isotope ratio of an element differing from unity. To minimize possible dependence between detector dead time and element mass, an isotope ratio of an element with a mass number close to that of the analyte element was selected [37].

For this reason, the isotopic ratio $^{235}U^+/^{238}U^+ = 0.01014 \pm 0.00001$ of uranium (CRM U010) certified

Table 2
Isotopes, dwell time and channels per peak used in this work.

m/z	Dwell time/ms	Channels/peak	Analyte	Comments
228	10	1		Background
235	20	3	^{235}U	Dead time/hydrides/tailing
237	30	1		Tailing
238	10	3	^{235}U	Dead time
239	30	3	^{238}UH$^+$	Hydrides
245	40	3	^{245}Cm	Non-irradiated and irradiated Cm
246	10	3	^{246}Cm	Non-irradiated and irradiated Cm
247	40	3	^{247}Cm	Non-irradiated and irradiated Cm
248	10	3	^{248}Cm	Non-irradiated and irradiated Cm
249	20	3	^{249}(Cf + Bk)	Irradiated Cm
250	40	3	^{250}Cf	Irradiated Cm
251	40	3	^{251}Cf	Irradiated Cm
252	40	3	^{252}Cf	Irradiated Cm

solutions with different concentration levels were determined with the automatic detector dead time correction disabled (set to zero *via* the software). For each concentration level, the 'normalized' isotope ratios (isotope ratio corrected for the dead time divided by the true value) were plotted as a function of the values used for the dead time correction leading to curves with a point of intersection (Fig. 4). All dead time corrections were carried out according to Eq. (1).

$$C_{\mathrm{corr}} = \frac{C_{\mathrm{meas}}}{1 - \tau C_{\mathrm{meas}}} \qquad (1)$$

where C_{corr} is the corrected intensity (cps), C_{meas} is the measured intensity and τ is the detector dead time, typically τ = 10–50 ns [38,39]. The intersection of the curves corresponding to different concentration levels provides the correct value for the detector dead time.

In addition the y-position of the intersection point permits an estimation of the amount of mass discrimination. In Fig. 4a, it can be seen that the intersection of the curves gives a detector dead time equal to 34 ns. The same result can be better visualized by plotting the standard deviation of the dead time corrected isotope ratios for the different concentration levels as a function of the applied dead time correction. The dead time is obtained for the minimum value of the standard deviation (Fig. 4b).

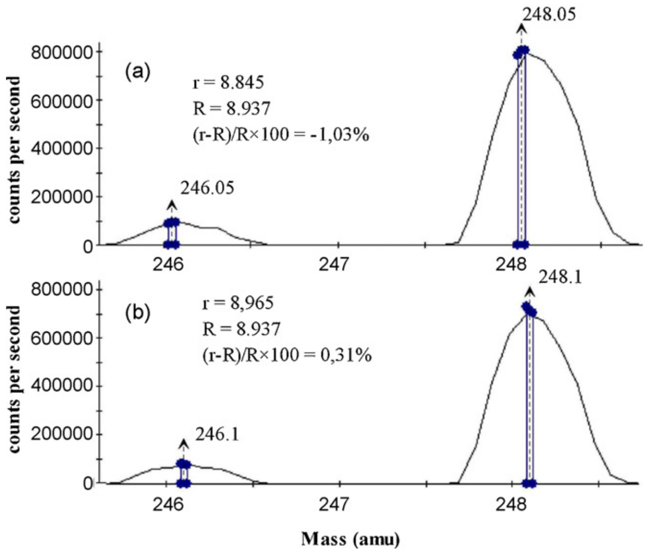

Fig. 3. Peak centre correction for ^{246}Cm$^+$ and ^{248}Cm$^+$ isotopes. Three channels per peak were used with a separation of ±0.02 a.m.u. from the central channel. (a) Poor symmetrical centring of the channels around the peaks centre. (b) Symmetrical centring of the channels around the peaks improves the relative difference between the measured non-bias corrected ^{246}Cm$^+$/^{248}Cm$^+$ isotopic ratio (r) and the ^{248}Cm$^+$/^{246}Cm$^+$ isotopic ratio reference value (R).

3.3. Mass bias correction

A sample-standard bracketing procedure was adopted to correct for mass bias. Instrumental mass bias is significant in ICP-MS analyses and must therefore be carefully determined and corrected.

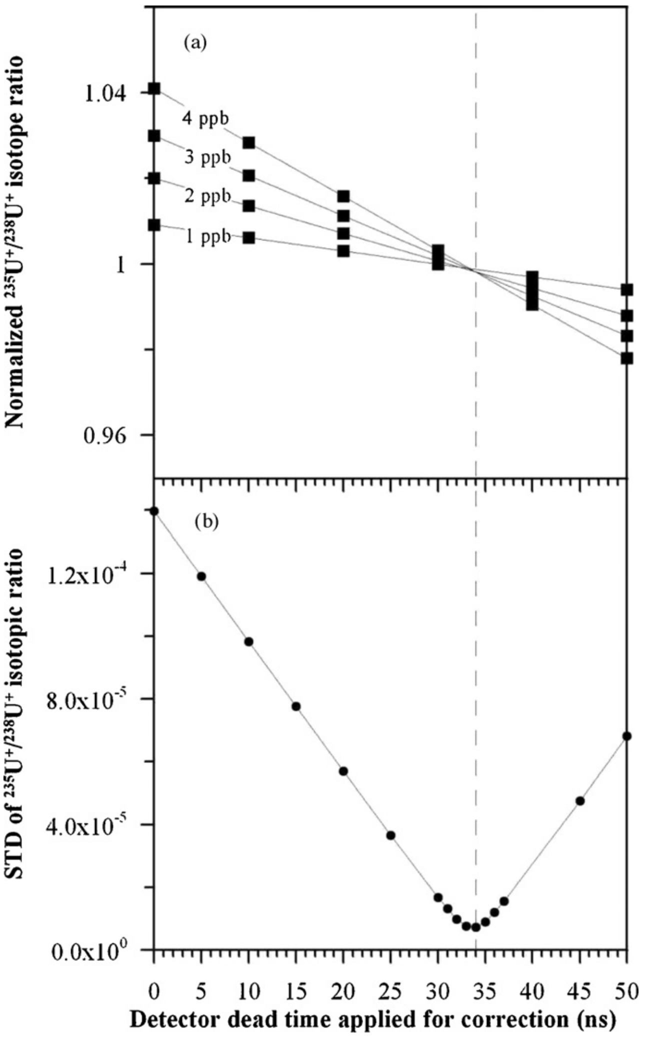

Fig. 4. Normalized ^{235}U$^+$/^{238}U$^+$ isotope ratio (a) and its standard deviation (b) as a function of the applied values for dead time correction, obtained for U010 certified reference solutions with a uranium concentration ranging from 1 to 4 ppb.

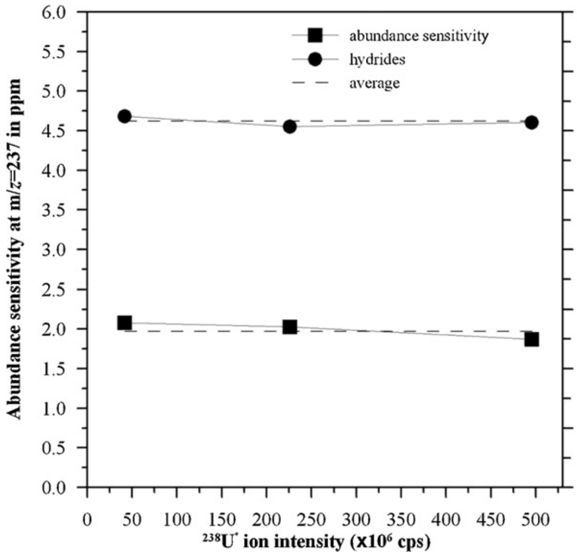

Fig. 5. Abundance sensitivity and hydrides formation as a function of $^{238}U^+$ ion intensity. Errors bars are expressed at 95% confidence level (2σ) and are within the symbols.

For mass bias correction, the exponential law was used [40,41]:

$$R = r\left(\frac{m_2}{m_1}\right)^{\beta} \tag{2}$$

where r and R are the measured and true ratios of isotope2/isotope1; m_2, and m_1 are atomic masses of isotope2 and isotope1, and β is the mass fractionation factor.

Measurements of both non-irradiated and irradiated Cm samples were bracketed with the in-house $^{248}Cm/^{246}Cm = 8.937 \pm 0.018$ standard solution. Mass bias corrections were performed in all isotope ratios assuming identical Cm, Bk, and Cf mass bias factors.

3.4. Corrections for abundance sensitivity and hydrides formation

The high ion intensity of $^{246,248}Cm^+$ isotopes during measurement of the concentrated sample solutions (~100 ppb of ^{248}Cm) creates interferences on the $^{245,247}Cm^+$ and $^{249}(Bk^+ + Cf^+)$ isotopes including hydrides formation and peak tailing.

Peak tailing and hydrides formation for Cm were derived experimentally by using U010 uranium standard solution assuming similar U and Cm peak tailing and hydrides formation. Measurements of U peak tailing and hydrides formation were performed on different U010 concentrations in order to assure a constant peak tailing and hydrides formation in different ion beam intensities of the major isotope.

The value of $^{237/238}U^+$ ratio was used to derive tail contribution of $^{248}Cm^+$ on $^{247}Cm^+$ and of $^{246}Cm^+$ on $^{245}Cm^+$ to correct the measurement ratios of $^{245}Cm^+/^{246}Cm^+$ and $^{247}Cm^+/^{246}Cm^+$, respectively. Vacuum conditions in the analyzer influence the degree of tailing effect [41]. For the analyzer vacuum value of our ICP-QMS (~10^{-7} mbar), the average abundance sensitivity during all the analytical session of $^{238}U^+$ at $m/z = 237$ was about 1.97 ± 0.02 ppm (Fig. 5).

In order to quantify hydrides contribution of $^{238}U^+$ on $m/z = 239$ the $^{238}UH^+/^{238}U^+$ ratio was measured. This ratio was used to correct $^{247}Cm^+$ and $^{249}(Bk^+ + Cf^+)$ from isobaric interferences of $^{246}CmH^+$ and $^{248}CmH^+$ respectively; $^{247}Cm^+$ combines the effect of tailing and hydride formation. The average $^{238}UH^+/^{238}U^+$ ratio was found to be $(35.7 \pm 0.1) \times 10^{-6}$ (Fig. 5). The most important factors affecting hydride generation are the mode and rate of sample introduction into the plasma [42–45]. Crain and Alvarado [42] reported that $^{238}UH^+/^{238}U^+$ ratio was 32×10^{-6} and 18×10^{-6} using a V-groove pneumatic (Fisons Elemental) and a U5000-AT (Cetac) ultrasonic nebulisation respectively. Membrane desolvation and the small sample uptake rates minimize significantly the generation of $^{238}UH^+$. For instance, using a MCN-6000 (Cetac) Shen et al. [25] found that $^{238}UH^+/^{238}U^+$ ratio during U analysis was 2×10^{-6}.

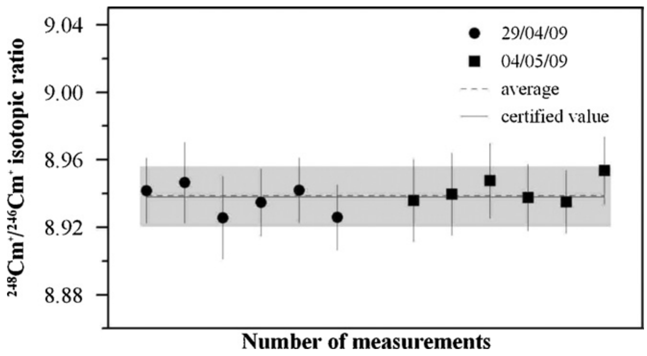

Fig. 6. Reproducibility of $^{248}Cm^+/^{246}Cm^+$ standard solution ratio at two different days of measurements using ICP-QMS. Dashed and plain lines represent the average value of the 12 measurements and the $^{248}Cm^+/^{246}Cm^+$ ratio reference value (8.937), respectively. Shaded area corresponds to the TIMS reference value error (±0.018) expressed at 95% confidence level (2σ).

Note that for more precise and accurate results for peak tailing and hydride formation only $^{237/235}U^+$ and $^{238}UH^+/^{235}U^+$ ratios were measured and converted to $^{237/238}U^+$ and $^{238}UH^+/^{238}U^+$ using the isotopic ratio $^{235}U/^{238}U = 0.01014 \pm 0.00001$.

3.5. Instrumental background and memory blank

Instrumental background was monitored during samples measurement at $m/z = 228$ (Table 2) and a typical level was <5 cps.

For memory blank, a washing procedure was applied after every sample or standard, including a short pre-wash of 2 min 2% HNO_3 + 2% HCl and a 2% sub-boiling HNO_3 wash for 10 min to reduce isotopes' intensities. After washing, the intensities of all the relevant isotopes were measured. These values were then used as the blank solution background correction for subsequent sample or standard measurements. Typical values of such solution blanks were $^{235}U^+ < 20$ cps, $237 < 10$ cps, $^{238}U^+ < 200$ cps, $^{245}Cm^+ < 10$ cps, $^{246}Cm^+ < 15$ cps, $^{247}Cm^+ < 10$ cps, $^{248}Cm^+ < 50$ cps, $^{249}(Bk^+ + Cf^+) < 10$ cps, $^{250}Cf^+ < 10$ cps, $^{251}Cf^+ < 20$ cps, $^{252}Cf^+ < 10$ cps. The wash procedure effectively reduces the intensities to less than 0.01% of the original ion intensities.

3.6. Accuracy and reproducibility of $^{248}Cm^+/^{246}Cm^+$ isotope ratio measurements

The reproducibility and accuracy of $^{248}Cm^+/^{246}Cm^+$ isotopic ratio in our certified in-house Cm solution were evaluated using a 4-ppb solution. The results, corrected for dead time and mass bias, for two different days of measurements are presented in Fig. 6. The relative standard error (RSE = RSD/$\sqrt{n}$, where n is the number of cycles per analysis, $n = 25$), with 95% of confidence level was between 0.2% and 0.3%. The reproducibility or external precision, expressed as the relative standard deviation (RSD_{ext}), obtained for measurements on two different days and for 12 measurements was ~0.1%. The accuracy of the 12 measurements mean value compared to the certified value of 8.937 ± 0.018 was within ~0.9‰ as calculated using Eq. (3)

$$\text{Accuracy} = \frac{r - R}{R} \times 1000 \tag{3}$$

Table 3
Average isotopic composition values of non-irradiated and irradiated Cm samples.

Concentration of ^{248}Cm in ppb	Isotope ratio	Method	Number of replicates	Non-irradiated	% Error	Irradiated	% Error
~100	$^{245}Cm^+/^{246}Cm^+$	ICP-QMS	3	0.010821 (85)	0.78	0.001918 (15)	0.92
~100	$^{247}Cm^+/^{246}Cm^+$	ICP-QMS	3	0.004687 (61)	1.29	0.005389 (61)	1.13
~4	$^{248}Cm^+/^{246}Cm^+$	ICP-QMS	5	38.55 (13)	0.33	38.30 (11)	0.29
		TIMS	3	38.54 (11)	0.28	38.23 (9)	0.24
~100	$^{249}(Bk^+ + Cf^+)/^{251}Cf^+$	ICP-QMS	3			16.55 (11)	0.68
~100	$^{250}Cf^+/^{251}Cf^+$	ICP-QMS	3			6.387 (34)	0.54
~100	$^{252}Cf^+/^{251}Cf^+$	ICP-QMS	3			0.3778 (33)	0.87

where r and R are the measured and reference values of the $^{248}Cm^+/^{246}Cm^+$ isotopic ratio, respectively.

3.7. Isotopic composition for non-irradiated and irradiated Cm samples

The developed analytical procedure described above was applied for measuring isotopic composition of non-irradiated and irradiated Cm samples. All values obtained were corrected for dead time, mass bias, background, and memory blank. Peak tailing and hydrides corrections were performed for the appropriate isotopes as described in Section 3.4, only for the concentrated solutions (~100 ng/g of ^{248}Cm).

Measurements of Cm isotopic ratios before and after sample irradiation are presented in Fig. 7. In order to validate the efficiency of the peak centre, mass bias, and dead time corrections, the $^{248}Cm^+/^{246}Cm^+$ isotopic ratio of non-irradiated and irradiated Cm samples was also determined by TIMS using the total evaporation method. As can be seen in Fig. 7c, a good agreement between ICP-QMS and TIMS methods was obtained. The relative difference of the average values between the two methods is 0.03% and 0.2% for non-irradiated and irradiated Cm samples, respectively. Isotopic composition measurements of Cf and Bk created after Cm irradiation are presented in Fig. 8. In the present work, isobaric interference at $m/z = 249$ of $^{249}Cf^+$ and $^{249}Bk^+$ was not resolved.

The $^{249}(Cf^+ + Bk^+)/^{251}Cf^+$ isotopic ratio (Fig. 8a) was measured assuming identical Cf and Bk sensitivities. The assumption is realistic considering their first ionization potential [46]. Cf and Bk separation by chromatographic techniques or eventually with the collision reaction cell of the ICP-MS could be attractive methods to resolve this interference over the time scale of the present work. Another method plan for this analysis is the use of liquid scintillation counting for measuring the β-deacy of ^{249}Bk. The average values of isotopic composition for both non-irradiated and irradiated Cm samples are summarized in Table 3.

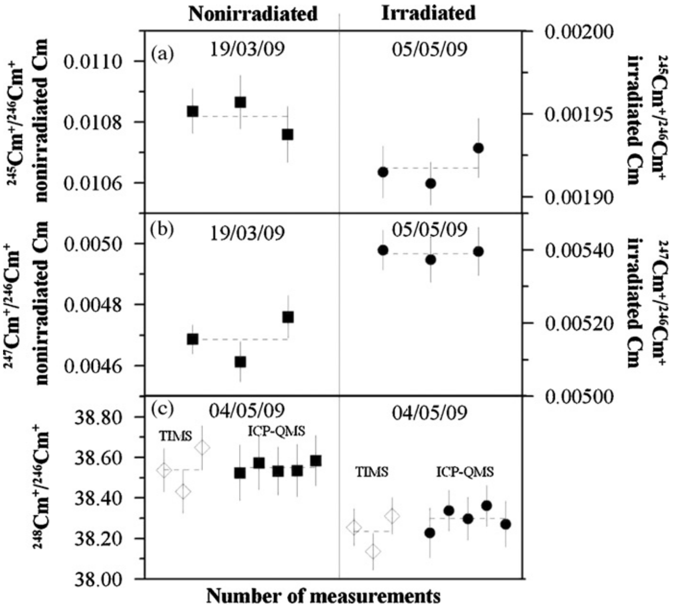

Fig. 7. Measurements of Cm isotopic composition for non-irradiated (left) and irradiated (right) by ICP-QMS (squares, circles) and TIMS (diamonds). Dashed lines represent the average value of the measurements. All errors are expressed at the 95% confidence level (2σ).

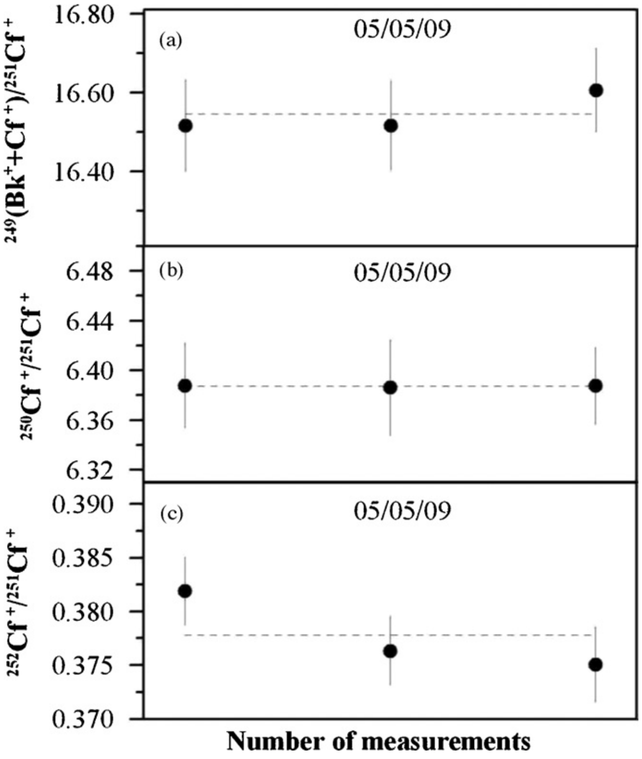

Fig. 8. Measurements of Cf and Cf + Bk, isotopic composition. Dashed lines represent the average value of the measurements. All errors are expressed at the 95% confidence level (2σ).

Uncertainties of all variables including certified solution $^{248}Cm/^{246}Cm$ isotopic ratio, standard error of measured isotopic ratios, peak tailing, and hydrides formation, were propagated using the general equation for error propagation [47] to determine the total error on the isotope ratios. All errors quoted in this study are at the 95% confidence level (2σ). Isotopic ratio errors ranged from 0.3% to 1.3% (Table 3). Important factors that affect isotopic ratio error are: background corrections for peak tailing and hydrides formation, and low isotopic abundance (ion intensity <2000 cps).

4. Conclusion

In this work, an analytical procedure for the isotopic measurement of transuranium isotopes (Cm, Cf) based on quadrupole ICP-MS was developed. The accurate and precise isotopic composition determination of Cm sample before and after irradiation was achieved by controlling and correcting factors that affect isotopic accuracy and precision, such as peak centre correction, detector dead time, mass bias, peak tailing, hydrides formation, instrumental background, and memory blank. Isotopic ratio uncertainties of all variables ranged from 0.3% to 1.3%. The precision attained on these measurements with ICP-QMS is sufficient to deduce the actinide capture cross-sections with the precision required for nuclear data libraries.

References

[1] M. Salvatores, A. Zaetta, C. Girard, M. Delpech, I. Slessarev, J. Tommasi, Appl. Radiat. Isot. 46 (1995) 681.

[2] D.E. Beller, G.J. Van Tuyle, D. Bennett, G. Lawrence, K. Thomas, K. Pasamehmetoglu, N. Li, D. Hill, J. Laidler, P. Fink, Nucl. Instrum. Methods A 463 (2001) 468.

[3] A. Takibayev, M. Saito, V. Artisyuk, H. Sagara, Prog. Nucl. Energy 47 (2005) 354.

[4] G. Aliberti, G. Palmiotti, M. Salvatores, T.K. Kim, T.A. Taiwo, M. Anitescu, I. Kodeli, E. Sartori, J.C. Bosq, J. Tommasi, Ann. Nucl. Energy 33 (2006) 700.

[5] O. Bringer, A. Letourneau, E. Dupont, Ann. Nucl. Energy 35 (2008) 1535.

[6] O. Bringer, H. Isnard, I. Aimahamid, F. Chartier, A. Letourneau, Nucl. Instrum. Methods A 591 (2008) 510.

[7] F. Marie, A. Letourneau, G. Fioni, O. Deruelle, C. Veyssiere, H. Faust, P. Mutti, I. AlMahamid, B. Muhammad, Nucl. Instrum. Methods A 556 (2006) 547.

[8] F. Chartier, M. Aubert, M. Pilier, Fresenius J. Anal. Chem. 364 (1999) 320.

[9] S. Richter, S.A. Goldberg, Int. J. Mass Spectrom. 229 (2003) 181.

[10] S. Richter, A. Alonso, J. Truyens, H. Kuhn, A. Verbruggen, R. Wellum, Int. J. Mass Spectrom. 264 (2007) 184.

[11] H. Chen, G.J. Wasserburg, Anal. Chem. 53 (1981) 2060.

[12] R. Jakopic, S. Richter, H. Kühn, L. Benedik, B. Pihlar, Y. Aregbe, Int. J. Mass Spectrom. 279 (2009) 87.

[13] J.L. Birck, Geostandard Newslett. 25 (2001) 253.

[14] G. Caro, B. Bourdon, J.-L. Birck, S. Moorbath, Geochim. Cosmochim. Acta 70 (2006) 164.

[15] D. Upadhyay, E.E. Scherer, K. Mezger, J. Anal. Atom. Spectrom. 23 (2008) 561.

[16] M.F. Thirlwall, Chem. Geol. 94 (1991) 13.

[17] A.J. Walder, P.A. Freedman, J. Anal. Atom. Spectrom. 8 (1992) 19.

[18] C.N. Maréchal, P. Télouk, F. Albarède, Chem. Geol. 156 (1999) 251.

[19] F. Vanhaecke, L. Balcaen, D. Malinovsky, J. Anal. Atom. Spectrom. 24 (2009) 863.

[20] J.P. Toutain, J. Sonke, M. Munoz, A. Nonell, M. Polve, J. Viers, R. Freydier, F. Sortino, J.L. Joron, S. Sumarti, Chem. Geol. 253 (2008) 74.

[21] W.M. White, F. Albarede, P. Telouk, Chem. Geol. 167 (2000) 257.

[22] L. Halicz, I. Segal, I. Gavrieli, A. Lorber, Z. Karpas, Anal. Chim. Acta 422 (2000) 203.

[23] A.S. Al-Ammar, R.M. Barnes, J. Anal. Atom. Spectrom. 16 (2001) 327.

[24] S. Aries, M. Motelica-Heino, R. Freydier, T. Grezes, M. Polve, Geostandard Newslett. 25 (2001) 387.

[25] C.C. Shen, H.T. Lin, M.F. Chu, E.F. Yu, X.F. Wang, J.A. Dorale, Geochem. Geophys. Geosyst. 7 (2006).

[26] J. Zheng, M. Yamada, Talanta 68 (2006) 932.

[27] E. Margui, M. Iglesias, I. Queralt, M. Hidalgo, Talanta 73 (2007) 700.

[28] K. Tagami, S. Uchida, Appl. Radiat. Isot. 61 (2004) 255.

[29] K. Blaum, C. Geppert, P. Müller, W. Nörtershäuser, K. Wendt, B.A. Bushaw, Int. J. Mass Spectrom. 202 (2000) 81.

[30] C.R. Quételet, B. Thomas, O.F.X. Donard, F.E. Grousset, Spectrochim. Acta Part B 52 (1997) 177.

[31] M.R. Smith, E.J. Wyse, D.W. Koppenaal, J. Radioanal. Nucl. Chem. Art. 160 (1992) 341.

[32] G. Favre, R. Brennetot, F. Chartier, P. Vitorge, Int. J. Mass Spectrom. 265 (2007) 15.

[33] A. Letourneau, O. Bringer, S. Chabod, E. Dupont, S. Panebianco, Proceedings of the International Conference on Nuclear Data for Science & Technology, April 22–27, EDP Sciences, Nice, France, 2007, p. 619.

[34] E.L. Callis, R.M. Abernathey, Int. J. Mass Spectrom. Ion Process. 103 (1991) 93.

[35] J.C. Dubois, G. Retali, J. Cesario, Int. J. Mass Spectrom. Ion Process. 120 (1992) 163.

[36] G. Russ III, in: A.R. Date, A.L. Gray (Eds.), Applications of inductively Coupled Plasma Mass Spectrometry, Blackie, Glasgow and London, 1989, pp. 90–114.

[37] F. Vanhaecke, G. de Wannemacker, L. Moens, R. Dams, C. Latkoczy, T. Prohaska, G. Stingeder, J. Anal. Atom. Spectrom. 13 (1998) 567.

[38] H. Cheng, R.L. Edwards, J. Hoff, C.D. Gallup, D.A. Richards, Y. Asmerom, Chem. Geol. 169 (2000) 17.

[39] S. Richter, S.A. Goldberg, P.B. Mason, A.J. Traina, J.B. Schwieters, Int. J. Mass Spectrom. 206 (2001) 105.

[40] W.A. Russell, D.A. Papanastassiou, T.A. Tombrello, Geochim. Cosmochim. Acta 42 (1978) 1075.

[41] C.C. Shen, R.L. Edwards, H. Cheng, J.A. Dorale, R.B. Thomas, S.B. Moran, S.E. Weinstein, H.N. Edmonds, Chem. Geol. 185 (2002) 165.

[42] J.S. Crain, J. Alvarado, J. Anal. Atom. Spectrom. 9 (1994) 1223.

[43] M. Hallenbach, J. Grohs, S. Mamich, M. Kroft, J. Anal. Atom. Spectrom. 9 (1994) 927.

[44] M.G. Minnich, R.S. Houk, J. Anal. Atom. Spectrom. 13 (1998) 167.

[45] J.S. Becker, R.S. Soman, K.L. Sutton, J.A. Caruso, H.J. Dietze, J. Anal. Atom. Spectrom. 14 (1999) 933.

[46] N. Erdmann, M. Nunnemann, K. Eberhardt, G. Herrmann, G. Huber, S. Kohler, J.V. Kratz, G. Passler, J.R. Peterson, N. Trautmann, A. Waldek, J. Alloys Compd. 271 (1998) 837.

[47] J. Kragten, Chemometr. Intell. Lab 28 (1995) 89.