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Bk and Cf chromatographic separation and $^{249}Bk/^{248}Cm$ and $^{249}Cf/^{248}Cm$ elemental ratios determination by inductively coupled plasma quadrupole mass spectrometry

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ABSTRACT

The French Atomic Energy Commission has carried out several experiments for the study of minor-actinide transmutation processes in high intensity thermal neutron flux. In this context a Cm sample enriched in ^{248}Cm (~97%) was irradiated in a thermal neutron flux at the High Flux Reactor (HFR) of the Laue–Langevin Institute (ILL). The precise and accurate determination of Cf isotope ratios and of $^{249}Bk/^{248}Cm$ and $^{249}Cf/^{248}Cm$ elemental ratios in the ^{248}Cm irradiated sample is crucial for the calculation of actinide neutron capture cross-sections. This work describes an analytical procedure for the separation and the isotope ratio measurement of Bk and Cf in the irradiated sample. The Bk and Cf separation is based on a lanthanides separation protocol previously developed by the laboratory. Well-defined retention times for Bk and Cf were obtained by coupling the Ionic Chromatography (IC) with an ICP-QMS. All conditions of element separation by IC and the different steps of the analytical protocol in order to obtain the isotopic and elemental ratios are presented. Relative uncertainties of Cf isotopic ratios range from 0.3% to 0.5% and the uncertainty of the $^{249}Bk/^{248}Cm$ and $^{249}Cf/^{248}Cm$ elemental ratios are respectively 6.1% and 3.2%. This level of uncertainty for both isotopic and elemental ratios is in perfect agreement with the requirement for transmutation studies.

1. Introduction

The Nuclear Energy Division of the French Atomic Energy Commission (CEA) is conducting several research programs concerning the transmutation of high-activity long-lived radionuclides. The main objective of these studies is to reduce waste radiotoxicity and heat production for a safer and more efficient repository space exploitation, as part of the partitioning and transmutation strategies [1–3]. Transmutation processes are studied for various types of reactors such as thermal, fast, and dedicated transmuters, leading to the necessity of high quality nuclear data (neutron capture and fission cross-sections). Within this framework, a highly enriched ^{248}Cm sample (~97%) has been irradiated in the High Flux Reactor (HFR) of the Laue–Langevin Institut (ILL) in order to improve uncertainties on ^{248}Cm irradiation evolution chain, for instance on neutron capture and fission cross-sections and on the half-lives of the produced isotopes. Such improvements require the development of adapted analytical techniques for the high precision determination of the quantity of each isotope of the evolution chain at a given time.

During the irradiation, radiative neutron capture on ^{248}Cm ($T_{1/2}$ = 3.48×10^5 y) generates ^{249}Cm ($T_{1/2}$ = 64.15 m), which decays to ^{249}Bk ($T_{1/2}$ = 330 d) and then to ^{249}Cf ($T_{1/2}$ = 352 y). Successive neutron captures on ^{249}Cf, lead to the formation of ^{250}Cf ($T_{1/2}$ = 13.1 y), ^{251}Cf ($T_{1/2}$ = 898 y) and ^{252}Cf ($T_{1/2}$ = 2.6 y). The scheme of the ^{248}Cm chain under neutron irradiation for one year cooling period of the ^{248}Cm sample is presented in Fig. 1. The first part of the analytical developments performed for this sample can be found in Gourgiotis

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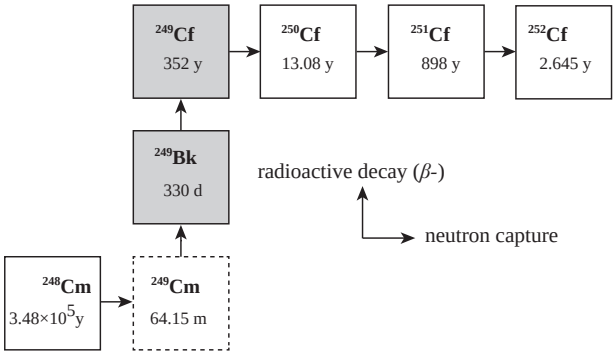

Fig. 1. Evolution chain of the ^{248}Cm under neutron irradiation. One of the major drawbacks in this work was the occurrence of ^{249}Bk–^{249}Cf isobaric interference (shaded area). At the time of sample analysis the ^{249}Cm (dashed line) has totally decayed.

et al. [4], where the procedures for accurate determination of non-interfered Cm, Cf and ^{249}(Bk+Cf)/^{251}Cf atomic ratios before and after irradiation are presented. These developments, based on the use of an inductively coupled plasma quadrupole mass spectrometer (ICP-QMS, X series, Thermo Electron, Winsford, UK) with control and correction of all instrumental parameters such as blank, background, peak center, tailing, hydrides level, mass bias and detector dead time, have led to isotopic ratio uncertainties (from 0.3% to 1.3%, $k=2$) compatible with nuclear data requirements for primary standards [5,6]. However, the $m/z=249$ interference resolution between ^{249}Bk and ^{249}Cf for ^{249}Bk/^{248}Cm and ^{249}Cf/^{248}Cm elemental ratio measurements, was not performed in this previous work. It is well known that the chemical properties of these elements are similar: they form trivalent cations in solution as their most stable oxidation states, and they have similar ionic radii. Nevertheless separation of Cm, Cf and Bk could be performed using separative techniques. These separations can be based on extraction chromatography using e.g. di(2-ethylhexyl)phosphoric acid (HDEHP) [7–9], or by Ion Exchange Chromatography using a tertiary pyridine resin [10] or diethylenetriaminepentaacetate (DTPA) as eluent [11]. The most frequently used method is cation exchange separation with α-hydoxy acid as eluent [12]. This separation is used in the case of lanthanides and minor actinides separation in nuclear fuel samples [13,14] and is performed using High Performance Liquid Chromatography (HPLC). Due to high selectivity obtained, a complete separation can be achieved. Furthermore the chromatographic column could be directly coupled to the ICP-QMS [15,16] in the case of very small amounts of elements (several nanograms).

In this work we present the chromatographic separation of Bk and Cf in the irradiated sample of ^{248}Cm by coupling the Ionic Chromatography (IC) with the ICP-QMS and the precise and accurate determination of the isotopic composition of Cf after Bk–Cf separation as well as the determination of ^{249}Bk/^{248}Cm and ^{249}Cf/^{248}Cm elemental ratios. The analytical development performed here, takes into account the low mass of available samples and the relatively small amounts of Bk and Cf versus Cm in the irradiated sample.

2. Analytical strategy

In order to calculate the ^{249}Bk/^{248}Cm and ^{249}Cf/^{248}Cm elemental ratios, a well-defined analytical procedure was developed. This procedure consists in five steps (Fig. 2): Step (1) chromatographic separation of Cf and Bk, Step (2) ^{249}Cf–^{249}Bk sensitivity control in ICP-QMS, Step (3) ^{249}(Bk+Cf) concentration measurement using a ^{249}Cf standard, Step (4) measurement of the ^{249}(Bk+Cf)/^{250}Cf atomic ratio in the initial sample and Cf isotope

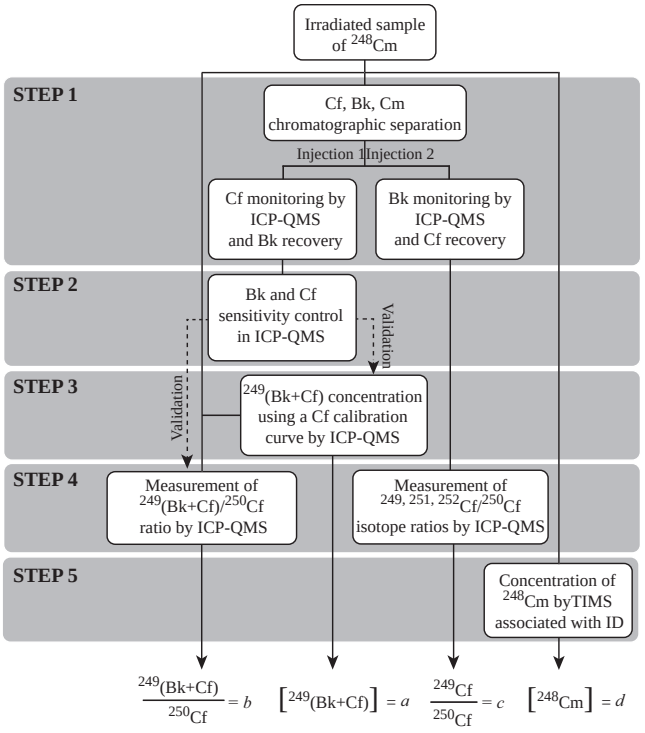

Fig. 2. Experimental procedure for Cf, Bk and Cm analysis in the irradiated ^{248}Cm sample.

ratios measurement in the purified fraction, and Step (5) ^{248}Cm concentration measurement by Thermal Ionisation Mass Spectrometry (TIMS) associated with Isotope Dilution (ID). During the first step the ICP-QMS was coupled with the IC for monitoring the target elements, Cf and Bk. After optimization of the chromatographic separation conditions for Cf, Bk and Cm, two independent injections of irradiated ^{248}Cm were performed for the recuperation of ^{249}Bk and Cf pure fractions. The objective of the second step was to investigate ^{249}Cf and ^{249}Bk respective sensitivities in the ICP-QMS. The pure ^{249}Bk fraction was weighted and aliquoted in two different solutions. The ^{249}Bk concentration in the first solution was calculated through its activity measured by Triple to Double Coincidence Ratio (TDCR) method. The concentration of the second solution was measured by ICP-QMS using a ^{249}Cf calibration curve for comparative purposes. As detailed below, the two concentrations were found to be in good agreement within analytical uncertainties which confirms that ^{249}Cf and ^{249}Bk display similar sensitivities in the ICP-QMS. This demonstration allowed the measurement of ^{249}(Bk+Cf) concentration and ^{249}(Bk+Cf)/^{250}Cf isotope ratio by ICP-QMS in the third and fourth step, respectively. In addition, the Cf pure fraction recovered during the first step was analysed to determine its isotopic composition by ICP-QMS during the fourth step. The absolute ^{248}Cm concentration was determined in the fifth step by isotope dilution (ID) in TIMS using a certified ^{244}Cm spike.

Finally the ^{249}Bk/^{248}Cm and ^{249}Cf/^{248}Cm elemental ratios were calculated by using the following equations:

$$\frac{^{249}\mathrm{Bk}}{^{248}\mathrm{Cm}} = \frac{M_{248Cm}}{M_{249Bk}}\left[\frac{a}{d}\left(1-\frac{c}{b}\frac{M_{249Cf}}{M_{249Mean}}\right)\right] \quad (1)$$

$$\frac{^{249}\mathrm{Cf}}{^{248}\mathrm{Cm}} = \frac{M_{248Cm}}{M_{249Mean}}\left(\frac{ac}{bd}\right) \quad (2)$$

where a, b, c, and d, are the ^{249}(Bk+Cf) concentration, ^{249}(Bk+Cf)/^{250}Cf and ^{249}Cf/^{250}Cf atomic ratios and the ^{248}Cm

concentration, respectively (Fig. 2). M_{249Bk}, M_{249Cf} and M_{248Cm} are the atomic masses of ^{249}Bk, ^{249}Cf and ^{248}Cm. $M_{249Mean}$ is the mean atomic mass of M_{249Bk} and M_{249Cf} that was used for the isobaric interference ^{249}(Bk+Cf).

3. Experimental setup

3.1. Instrumentation

3.1.1. Ion Chromatographic instrumentation

To perform the Cf–Bk–Cm separation, a DIONEX (Sunnyvale, CA, USA) ICS 3000 IC pump was used with a LUNA SCX (Strong Cation Exchange) analytical column (250 × 4.6 mm) and a guard column (Phenomenex, Torrance, CA, USA). The stationary phase was silica-based and bonded with benzene sulfonic acid, with a particle size of 5 μm. The eluent flow rate was 1 mL min^{-1} and the injection valve was equipped with a 20 μL sample loop. To perform the recuperation of the Bk and Cf fractions, a four-ways selection valve was added between the column and the nebulizer. An illustration of the implantation of the IC in a glove box environment was presented in a previous study [15].

3.1.2. ICP-MS instrumentation

The experiments were carried out on a quadrupole ICP-MS "X series" mass spectrometer from Thermo Electron (Winsford, UK) equipped with a hexapole collision/reaction cell (not used in this study). This ICP-MS is the first X series modified, with the ICP source in a glove box, in order to handle radioactive samples as previously described [4,17]. Sample introduction in the plasma was performed with a quartz bead impact spray chamber and a quartz concentric nebulizer (1.0 mL min^{-1}). Experimental parameters were optimized daily with a 1 ppb U standard solution in order to obtain the maximum count rates and stability on ^{238}U signal. Typical sensitivity and stability (Relative Standard Deviation) values are 4×10^5 cps and 0.3–0.4%, respectively. Instrumental background at 228 u was typically 0–5 cps. The operating conditions of the instrument are listed in Table 1. The isotope ratio measurements were performed using previously described methodologies [4,18–20] which involve control and correction of all instrumental parameters (blank, background, peak center, hydride level, mass bias and detector dead time).

3.1.3. TIMS instrumentation

Curium isotope ratio measurements were performed on a Sector 54 mass spectrometer from GV Instruments (Manchester, UK). The source is placed inside a glove-box to handle radioactive samples. Removable rhenium triple filament arrangements were used. For Cm measurements, around 20 ng of Cm diluted in 0.25 M HNO_3 acid were deposited on the side rhenium filament. The instrument is equipped with seven faraday cups with 10^{11} Ω positive feedback resistors. The Faraday amplifier gains were calibrated daily before the analytical session. Reproducibility of the electric gains was better than 20 ppm/day.

The Cm data were acquired in static multicollection mode with Faraday cups, using the total evaporation method [21–23]. The reproducibility obtained for Cm isotopic measurement was evaluated with an in-house standard solution.

Table 1
ICP-QMS operating conditions.

Parameters	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 amu
Detection mode	Pulse counting
Scan mode	Peak jumping

3.1.4. Triple to Double Coincidence Ratio (TDCR) method

The measurement of the ^{249}Bk activity was performed using the Triple to Double Coincidence Ratio (TDCR) method in Liquid Scintillation (LS) Counting [24] at the Laboratoire National Henri Becquerel (LNHB). This is a primary measurement method, based on a statistical model of the light emission from the scintillator and a radiation-matter interaction model using a calculated beta spectrum. ^{249}Bk is mostly decaying through a beta transition to the fundamental level of ^{249}Cf, with global transition energy of 124.9 keV. For the uncertainty calculation parameters like the conservative Birks coefficient, counting statistics, blank counting, weighing process and maximum beta energy have been taken into account.

3.1.5. Alpha spectrometry

Alpha spectrometry was used for the correction of alpha emitter impurities like ^{245}Cm (radioactive daughter of ^{249}Cf) during the standardization of the ^{249}Cf sample at the LNHB laboratory. Before the sample measurement, the alpha source was prepared by deposition of a drop of the radioactive solution on a stainless steel disk coated with polystyrene latex microspheres, in order to improve the homogeneity of the crystallization. Then the source was measured in an alpha spectrometer equipped with an implanted silicon detector.

3.2. Reagents and materials

3.2.1. Reagents and solutions

All dilutions and dissolutions were performed in suprapure 0.5 M nitric acid. Nitric acid was obtained by dilution of sub-boiling nitric acid, using an EVAPOCLEAN system (Analab, France), in purified water obtained from a MilliQ system (Millipore, Milford, MA, USA). A multi-element Tuning Solution (SPEX) at 1000 μg mL^{-1} (diluted to 1 ng mL^{-1}) was used daily for ICP-QMS short-term stability and counting tests optimization. A U SPEX solution was used as an internal standard for ICP-MS measurements.

For the lanthanides separation, 2-hydroxy-2-methylbutyric acid (HMBA, Sigma–Aldrich) dissolved in purified water was used as complexing agent. The pH of the mobile phase was adjusted with a 25% ammonia solution (Merck, Darmstadt, Germany). Methanol (Merck) was used for column conditioning.

3.2.2. Samples

3.2.2.1. Irradiated ^{248}Cm sample. ^{248}Cm (37 μg) in the form of Cm-nitrate were provided by the Lawrence Berkeley National Laboratory. The sample is enriched in ^{248}Cm (~97%), but also contains ^{246}Cm (~2.5%), ^{245}Cm (~0.03%) and ^{247}Cm (~0.01%). The irradiation and preparation of the sample after irradiation were previously described [4]. Mass spectra of the sample after irradiation still present a very high abundance of ^{248}Cm and ^{246}Cm compared to other isotopes. After sample dissolution in HNO_3 4 N, ^{248}Cm concentration was ~1.7 μg g^{-1}.

3.2.2.2. ^{249}Cf sample. ^{249}Cf (10 μg) in the form of Cf nitrate were provided by the Lawrence Berkeley National Laboratory. The powder was dissolved with 4 M HNO_3 (Normatom Prolabo) and after complete dissolution the sample was sent to the (LNHB) for standardization. Liquid Scintillation Counting (LSC) and alpha spectrometry for alpha emitter impurities correction were used in order to standardize this sample. The activity concentration of ^{249}Cf sample was found equal to 9965 ± 13 Bq/g.

3.2.3. Standard and spike solutions

3.2.3.1. Cm standard. An in-house $^{248}Cm/^{246}Cm = 8.937 \pm 0.018$ ($k=2$) standard solution was used. This solution was certified using TIMS by the total evaporation technique. Six independent measurements were performed in order to evaluate the isotope ratio uncertainty of Cm.

3.2.3.2. ^{244}Cm spike solution. The concentration of ^{244}Cm spike was qualified through its activity by alpha spectrometry at an uncertainty of 0.2% at $k=2$ (LMRI CEA laboratory). The isotopic composition of this spike was qualified at the LANIE laboratory by thermal ionization mass spectrometry using the procedures previously described [13,25]. It was enriched at around 93% in ^{244}Cm with a $^{248}Cm/^{244}Cm$ isotope ratio around $0.000127 \pm 3 \times 10^{-6}$ ($k=2$) at the date of the measurement. The concentration of this spike was recalculated at the date of mixing between spike and sample by considering the half-life of Cm isotopes presented in Table 2.

4. Results and discussion

4.1. STEP 1: Cf, Bk, Cm chromatographic separation and Bk, Cf pure fractions recovery

All analytical developments and optimisations for rare earth elements separation were performed using a protocol previously available in the laboratory[13]. LUNA SCX column which includes benzene sulfonic acid group and 2-hydroxy-2-methylbutyric acid as a complexing agent in eluent solution were used for the separation of rare earth elements [12,26,27]. The analytical conditions were chosen to reach the best selectivity between Cf and Bk. These conditions were obtained by using HMB eluent at 0.085 M with pH adjusted to 3.6. The monitoring of the element elution was performed by coupling the IC with the ICP-QMS as previously described [15]. The separation yield of Cf and Bk were about 80%. For the yield estimation, the injected concentrations of the two analytes of interest were calculated using the theoretical quantities predicted by the nuclear burn-up code CINDER'90 [28].

Table 2
Half-lives of the isotopes used in this work. Where y, d and m are respectively years, days and minutes.

Isotopes	Half-life
^{243}Cm	29.1 ± 0.1 y
^{244}Cm	18.11 ± 0.03 y
^{245}Cm	8480 ± 60 y
^{246}Cm	4760 ± 40 y
^{248}Cm	$3.48 \times 10^5 \pm 6.10^3$ y
^{249}Cm	64.15 ± 0.03 m
^{249}Bk	330 ± 4 d
^{249}Cf	351 ± 2 y
^{250}Cf	13.08 ± 0.09 y
^{251}Cf	898 ± 44 y
^{252}Cf	2.645 ± 0.008 y

Several injections of irradiated ^{248}Cm were performed and the retention times on the peaks for the Cf and the Bk were found to be reproducible (~1%) and equal to ~11.5 min and ~17 min respectively (Fig. 3). As seen in Fig. 3, delay between Cf and Bk elution (1 min) in association with the return to baseline between the two peaks guarantees the high purity of the fractions. These well-defined retention times allowed the recovery of Cf and Bk pure fractions on two independent injections of around 5 μg of irradiated ^{248}Cm. During the first injection of ^{248}Cm, the Cf was monitored by ICP-QMS. After the total Cf elution, the valve selector was turned towards a clean recipient for Bk recovery. For the second injection the valve selector was turned towards a second clean recipient for Cf recovery. Then, when full Cf recovery was achieved, the valve selector was turned towards the ICP-QMS in order to monitor the beginning of the Bk elution in order to prevent any Bk contamination of the Cf fraction. Pure Bk and Cf fractions were then dried before 0.5 N HNO_3 reconditioning.

4.2. STEP 2: Bk and Cf sensitivity control in the ICP-QMS

A total weight of 4.46 g of pure ^{249}Bk solution was obtained. An aliquot of this solution ($m_1=2.65$ g) was sent to the LNHB laboratory for the determination of the ^{249}Bk activity by TDCR. The ^{249}Bk concentration was then deduced using its half-life (Table 2). In the second aliquot ($m_2=1.81$ g), the ^{249}Bk concentration was measured using a ^{249}Cf calibration curve. ^{238}U was used as an internal standard. The two independently measured ^{249}Bk concentrations were found in good agreement ($^{249}Bk_{ICP-QMS} = 0.0304 \pm 0.0012$ ng/g; $k=2$ and $^{249}Bk_{TDCR} = 0.0299 \pm 0.0011$ ng/g; $k=2$). This means that the measured ^{249}Bk concentration using the ^{249}Cf calibration curve is correct and therefore we can consider that Bk and Cf have the same sensitivity in the ICP-QMS with an uncertainty of 4% ($k=2$). This observation is also consistent with the very close first ionization potentials of Bk and Cf [29]. The validation of this step allowed the measurement of the ^{249}(Bk+Cf) concentration and of the ^{249}(Bk+Cf)/^{250}Cf atomic ratio in the third and fourth steps respectively.

4.3. STEP 3: ^{249}(Bk+Cf) concentration measurement

The ^{249}(Bk+Cf) concentration was measured by using the same ^{249}Cf calibration curve based on the similar sensitivities observed between the two elements (within analytical uncertainties) as

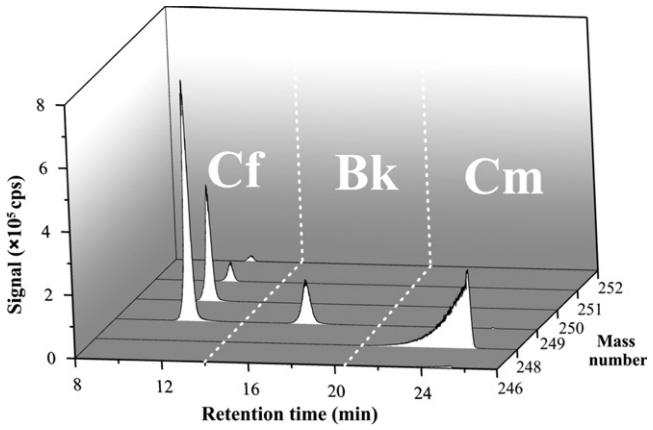

Fig. 3. Cf, Bk and Cm chromatographic separation of the irradiated ^{248}Cm sample. This chromatogram was performed by coupling the IC with the ICP-QMS. Due to the high abundance of ^{248}Cm, after the beginning of Cm elution the monitoring was interrupted in order to protect the Secondary Electron Multiplier of the ICP-QMS from high ion counting rates.

demonstrated in the previous step. This measurement allowed the determination of the "*a*" parameter (Fig. 2).

4.4. STEP 4: $^{249}(Bk+Cf)/^{250}Cf$ atomic ratio (initial ^{248}Cm sample) and Cf isotope ratios measurement (purified fraction)

In this step the measurements of $^{249}(Bk+Cf)/^{250}Cf$ and of $^{249,251,252}Cf/^{250}Cf$ were performed by ICP-QMS based on previously developed methodologies for isotope ratio measurements by ICP-QMS[4,18–20]. According to these methods, all ratios were corrected for memory blank, peak center, hydride level, instrumental mass bias and detector dead time. The results are presented in Table 3. These measurements led to the determination of the "*b*" and "*c*" parameters (Fig. 2). The good consistency of the analytical procedure for isotope ratio measurements by ICP-QMS was confirmed by comparing the $^{251}Cf/^{250}Cf$, $^{252}Cf/^{250}Cf$, $^{249}(Bk+Cf)/^{250}Cf$ ratios obtained in this work with previously obtained results [4] for the same sample of irradiated ^{248}Cm. As can be seen in Fig. 4, a good agreement within uncertainties was observed.

4.5. STEP 5: determination of ^{248}Cm concentration using ID technique

The Cm concentration in the ^{248}Cm irradiated sample was determined by isotope dilution from the following equation:

$$[Cm]_S = [Cm]_{Sp} \times \frac{m_{Sp}}{m_S} \times \frac{M_S}{M_{Sp}} \times \frac{(244)_{Sp}}{(248)_S} \times \left[\left(\frac{^{248}Cm}{^{244}Cm} \right)_{Mix} - \left(\frac{^{248}Cm}{^{244}Cm} \right)_{Sp} \right] \quad (3)$$

where *Mix*, *S* and *Sp* stands respectively for mixture, sample and spike; and *m* and *M* are the masses and atomic weights in the sample and the spike, "(244)" and "(248)" are the atomic abundance expressed in atoms. All the isotope ratios are expressed as atomic ratios.

Two mixtures of the spike and sample solutions were prepared by weight to determine the $(^{248}Cm/^{244}Cm)_{Mix}$ ratio in the sample by TIMS. Each solution was evaporated after mixing, and then redissolved in HNO_3 2% media. The relative difference obtained between the two mixtures is 0.13%. The uncertainty on the ^{248}Cm sample concentration was evaluated by calculating the combined uncertainties of each contributing term [30]. The value found for the Cm concentration in the sample was $1.729 \pm 0.008\ \mu g\ g^{-1}$ ($k=2$) corresponding to a ^{248}Cm concentration of $1.685 \pm 0.008\ \mu g\ g^{-1}$ ($k=2$). This measurement leads to the determination of the "*d*" parameter (Fig. 2).

4.6. Evaluation of uncertainties

All the results obtained in this work are presented in Table 3. The uncertainties were evaluated by the calculation of each contributing term of Eqs. (1) and (2) [30]. The uncertainty propagation on the $^{249}Bk/^{248}Cm$ and $^{249}Cf/^{248}Cm$ ratios was performed on the basis of the spreadsheet method for uncertainty propagation [31,32] and relative uncertainties were found to be 6.1% and 3.2% ($k=2$), respectively. Due to the low Bk amount compared to that of Cf in our sample (Bk/Cf∼1/6.6), the uncertainty on the Bk sensitivity (4%; $k=2$) in the ICP-QMS does not have an important contribution on the uncertainties of "*a*" and "*b*" parameters and for this reason has not been taken into account. As can be seen in the Fig. 5, the major uncertainty contribution regarding the $^{249}Bk/^{248}Cm$ elemental ratio uncertainty comes from the "*b*" parameter ($^{249}(Bk+Cf)/^{250}Cf$) whereas the "*a*" parameter ($^{249}(Bk+Cf)$ concentration) is dominant on the uncertainty budget of the $^{249}Cf/^{248}Cm$ elemental ratio. These results are of major importance for future experimental procedures design because the "key" parameters governing the uncertainties budget are highlighted. The isotope and elemental ratio uncertainties reached in this work are perfectly adapted for actinide neutron

Table 3
Average isotopic and elemental composition and isotope concentrations of the ^{248}Cm irradiated sample. (1), (2), (3) and (4) are the *a*, *b*, *c* and *d* values respectively. All ratios are expressed as atomic ratios.

Terms	Method	Replicates	Value	% (*k*=2)	Date of meas.
$^{249}(Bk+Cf)/^{250}Cf$	ICP-QMS	3	(2)2.787(20)	0.7	07/21/2010
$^{249}Cf/^{250}Cf$	ICP-QMS	2	(3)2.419(9)	0.4	07/22/2010
$^{251}Cf/^{250}Cf$	ICP-QMS	2	0.1680(8)	0.5	07/22/2010
$^{252}Cf/^{250}Cf$	ICP-QMS	2	0.04610(20)	0.4	07/22/2010
$^{249}(Bk+Cf)$	ICP-QMS	1	(1)3.62(11) ng/g	3	07/20/2010
^{248}Cm	TIMS (ID)	1	(4)1685(8) ng/g	0.5	07/26/2010
$^{249}Bk/^{248}Cm$			0.000283(17)	6.1	
$^{249}Cf/^{248}Cm$			0.00186(6)	3.2	

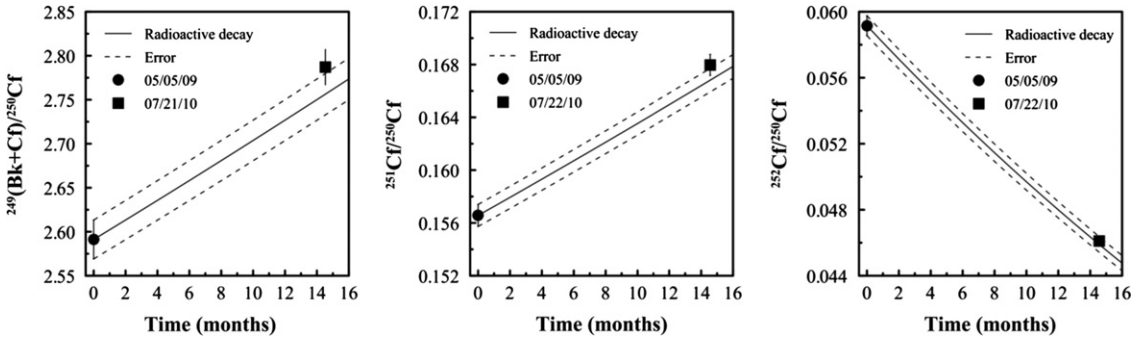

Fig. 4. Comparison between isotope ratios obtained in this work (07/21–22/10) and isotope ratios obtained by Gourgiotis et al. (05/05/10) for the same sample of irradiated ^{248}Cm. As can be seen in the figure, the time corrected ratios (solid line) measured on 05/05/09 are found to be consistent within uncertainties with the isotope ratios measured in this work. For the radioactive decay uncertainty (Error – dashed line) both isotope ratio uncertainties and radioactive decay constant uncertainties have been taken into account.

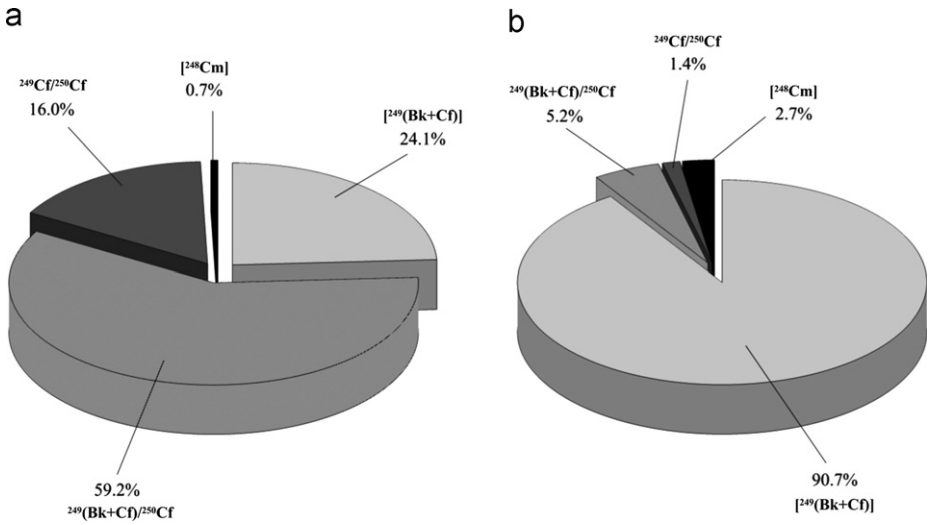

Fig. 5. Uncertainties contributions regarding the uncertainties of ^{249}Bk/^{248}Cm (a) and ^{249}Cf/^{248}Cm (b) elemental ratios.

capture cross-section calculation since they are significantly below other sources of uncertainty (e.g., neutron fluence during irradiation). These results will allow a significant reduction of ^{248}Cm and ^{249}Bk capture cross-section uncertainties, which are larger than 20% ($k=2$) with significant discrepancies between the available data. The comparison between theoretical and experimental data will be given in a further work.

However, if lower uncertainties are required in the future on ^{249}Bk/^{248}Cm and ^{249}Cf/^{248}Cm elemental ratios for nuclear applications, both high transmission MC-ICP-MS and isotope dilution approaches can be envisioned, together with a better definition of ^{249}Bk and ^{249}Cf respective sensitivities.

5. Conclusion

This work is the second part of the analytical development that was performed for the measurement of the elemental and isotope ratio composition of an irradiated ^{248}Cm sample. The major drawback for the determination of ^{249}Bk/^{248}Cm and ^{249}Cf/^{248}Cm elemental ratios was the isobaric interference of ^{249}Bk and ^{249}Cf in the irradiated sample. For this reason, the previously developed protocol in the laboratory for lanthanides separation by Ion Chromatography was adapted for Cf, Bk and Cm separation. The element elution was monitored by coupling the IC with the ICP-QMS. After several number of irradiated sample injections, well-defined retention times for Cf, Bk and Cm were obtained. A second critical point in this work was the measurement of ^{249}(Bk+Cf) concentration and of ^{249}(Bk+Cf)/^{250}Cf atomic ratio. In order to proceed in this measurement, Cf and Bk sensitivities were tested in the ICP-QMS and found to be similar with an uncertainty of 4%. All parameter uncertainties were propagated for the uncertainty calculation of ^{249}Bk/^{248}Cm and ^{249}Cf/^{248}Cm elemental ratios. Furthermore, the "key" parameters governing the uncertainties budget were identified for future experimental procedures improvement.

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