



**HAL**  
open science

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

A. Gourgiotis, Hélène Isnard, Anthony Nonell, M. Aubert, G. Stadelmann, E. Dupont, I. Almahamid, G. Tiang, L. Rao, W. Lukens, et al.

## ► To cite this version:

A. Gourgiotis, Hélène Isnard, Anthony Nonell, M. Aubert, G. Stadelmann, et al.. Bk and Cf chromatographic separation and  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  elemental ratios determination by inductively coupled plasma quadrupole mass spectrometry. *Talanta*, 2013, 106, pp.39 - 44. 10.1016/j.talanta.2012.11.056 . cea-01792079

**HAL Id: cea-01792079**

**<https://cea.hal.science/cea-01792079>**

Submitted on 19 Mar 2020

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

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

1 **Bk and Cf chromatographic separation and  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  ratios**  
2 **determination by inductively coupled plasma quadrupole mass spectrometry**  
3  
4

5 A. Gourgiotis<sup>1,7</sup>, H. Isnard<sup>1</sup>, A. Nonell<sup>1</sup>, M. Aubert<sup>1</sup>, G. Stadelmann<sup>1</sup>, E. Dupont<sup>2,8</sup>, I.  
6 AlMahamid<sup>3</sup>, G. Tiang<sup>6</sup>, L. Rao<sup>6</sup>, W. Lukens<sup>6</sup>, P. Cassette<sup>4</sup>, S. Panebianco<sup>2</sup>, A. Letourneau<sup>2</sup>,  
7 F. Chartier<sup>5</sup>  
8

9 1. Commissariat à l'Energie Atomique (CEA), DEN/DPC/SEARS/LANIE, 91191 Gif-sur-  
10 Yvette Cedex, France.

11 2. Commissariat à l'Energie Atomique (CEA), DSM/IRFU/SPhN, 91191 Gif-sur-Yvette  
12 Cedex, France.

13 3. New York State Department of Health, Wadsworth Center, Albany, NY 12201, and School  
14 of Public Health, New York State University at Albany, USA

15 4. Commissariat à l'Energie Atomique (CEA), LIST, Laboratoire National Henri Becquerel  
16 (LNE-LNHB), F-91191 Gif sur Yvette, France

17 5. Commissariat à l'Energie Atomique (CEA), DEN/DPC, 91191 Gif-sur-Yvette Cedex,  
18 France.

19 6. Lawrence Berkeley National Laboratory, Division of Chemical Sciences, Berkeley, CA  
20 94720, USA

21 7. Centre National de la Recherche Scientifique (CNRS), Institut de Physique du Globe de  
22 Paris, Equipe de Géochimie et de Cosmochimie, 1 rue Jussieu - 75238 Paris cedex 05, France

23 8. OECD Nuclear Energy Agency, 92130 Issy-les-Moulineaux, France  
24  
25

26 Correspondence to: Hélène ISNARD, [helene.isnard@cea.fr](mailto:helene.isnard@cea.fr)  
27

28 **Highlights**  
29

- 30 • Bk, Cf and Cm separation by liquid chromatography in a  $^{248}\text{Cm}$  irradiated sample  
31 • This separation was performed by ICP-QMS/HPLC coupling  
32 • Isotope ratio composition of the purified fractions by ICP-QMS  
33 • With work we contribute more precise data for actinide neutron capture cross-  
34 sections

35  
36  
37  
38 **Keywords**

39 Liquid chromatography, HPLC, ICP-QMS, Berkelium, Californium, Curium  
40  
41  
42

43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68

## 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  $^{248}\text{Cm}$  (~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  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  elemental ratios in the  $^{248}\text{Cm}$  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, 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 liquid chromatography with an ICP-QMS. All conditions of element separation by liquid chromatography and the different steps of the analytical protocol in order to obtain the isotopic and elemental ratios are presented. Uncertainties of Cf isotopic ratios range from 0.3% to 0.5% and the uncertainty of the  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  elemental ratios are respectively 6.1% and 3.2%. This level of uncertainty for both isotopic and elemental ratios is rather acceptable for transmutation studies.

69

## 70 **1. Introduction**

71

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

85 During the irradiation, radiative neutron capture on  $^{248}\text{Cm}$  ( $T_{1/2}=3.48 \times 10^5$  y) generates  $^{249}\text{Cm}$   
86 ( $T_{1/2}=64.15$  m), which decays to  $^{249}\text{Bk}$  ( $T_{1/2}=330$  d) and then to  $^{249}\text{Cf}$  ( $T_{1/2}=352$  y). Successive  
87 neutron captures on  $^{249}\text{Cf}$ , lead to the formation of  $^{250}\text{Cf}$  ( $T_{1/2}=13.1$  y),  $^{251}\text{Cf}$  ( $T_{1/2}=898$  y) and  
88  $^{252}\text{Cf}$  ( $T_{1/2}=2.6$  y). The scheme of the  $^{248}\text{Cm}$  chain under neutron irradiation for one year  
89 cooling period of the  $^{248}\text{Cm}$  sample is presented in Figure 1. The first part of the analytical  
90 developments performed for this sample can be found in Gourgiotis et al. [5], where the  
91 procedures for accurate determination of non-interfered Cm, Cf and  $^{249}(\text{Bk}+\text{Cf})/^{251}\text{Cf}$  atomic  
92 ratios before and after irradiation are presented. These developments, based on the use of an  
93 inductively coupled plasma quadrupole mass spectrometer (ICP-QMS, X series, Thermo

94 Electron, Winsford, UK) with control and correction of all instrumental parameters such as  
95 blank, background, peak center, tailing, hydrides level, mass bias and detector dead time, have  
96 led to isotopic ratio uncertainties (from 0.3% to 1.3%) compatible with nuclear data  
97 requirements for primary standards. However, the  $m/z=249$  interference resolution between  
98  $^{249}\text{Bk}$  and  $^{249}\text{Cf}$  for  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  elemental ratio measurements, was not  
99 performed in this previous work. It is well known that the chemical properties of these  
100 elements are similar: they form trivalent cations in solution as their most stable oxidation  
101 states, and they have similar ionic radii. Nevertheless separation of Cm, Cf and Bk could be  
102 performed using separative techniques. These separations can be based on extraction  
103 chromatography using e.g. di(2ethylhexyl)phosphoric acid (HDEHP) [6-8], or by ion  
104 exchange chromatography using a tertiary pyridine resin[9] or diethylenetriaminepentaacetate  
105 (DTPA) as eluent[10]. The most frequently used method is cation exchange separation with  
106  $\alpha$ -hydroxy acid as eluent [11]. This separation is used in the case of lanthanides and minor  
107 actinides separation in nuclear fuel samples [12,13] and is performed using High Performance  
108 Liquid Chromatography (HPLC). Due to high selectivity obtained, a complete separation can  
109 be achieved. Furthermore the chromatographic column could be directly coupled to the ICP-  
110 QMS [14,15] in the case of very small amounts of elements (several nanograms).

111 In this work we present the chromatographic separation of Bk, Cf and Cm in the irradiated  
112 sample of  $^{248}\text{Cm}$  by HPLC/ICP-QMS coupling and the precise and accurate determination of  
113 the isotopic composition of Cf after Bk-Cf separation as well as the determination of  
114  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  ratios. The analytical development performed here, takes into  
115 account the low mass of available samples and the relatively small amounts of Bk and Cf  
116 versus Cm in the irradiated sample.

117

118

119

## 120 **2. Analytical strategy**

121

122 In order to calculate the  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  elemental ratios, a well-defined  
123 analytical procedure was developed. This procedure consists in five steps (Figure 2): Step 1)  
124 chromatographic separation of Cf and Bk, Step 2)  $^{249}\text{Cf}$  -  $^{249}\text{Bk}$  sensitivity control in ICP-  
125 QMS, Step 3)  $^{249}(\text{Bk}+\text{Cf})$  concentration measurement using a  $^{249}\text{Cf}$  standard, Step 4)  
126 measurement of the  $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$  atomic ratio in the initial sample and Cf isotope ratios  
127 measurement in the purified fraction, and Step 5)  $^{248}\text{Cm}$  concentration measurement by  
128 Thermal Ionisation Mass Spectrometry (TIMS) associated with Isotope Dilution (ID). During  
129 the first step the ICP-QMS was coupled with the ionic chromatography for monitoring the  
130 target elements, Cf and Bk. After optimization of the chromatographic separation conditions  
131 for Cf, Bk and Cm, two independent injections of irradiated  $^{248}\text{Cm}$  were performed for the  
132 recuperation of  $^{249}\text{Bk}$  and Cf pure fractions. The objective of the second step was to  
133 investigate  $^{249}\text{Cf}$  and  $^{249}\text{Bk}$  respective sensitivities in the ICP-QMS. The pure  $^{249}\text{Bk}$  fraction  
134 was weighted and aliquoted in two different solutions. The  $^{249}\text{Bk}$  concentration in the first  
135 solution was calculated through its activity measured by Triple to Double Coincidence Ratio  
136 (TDCR) method. The concentration of the second solution was measured by ICP-QMS using  
137 a  $^{249}\text{Cf}$  calibration curve for comparative purposes. As detailed below, the two concentrations  
138 were found to be in good agreement within analytical uncertainties which confirms that  $^{249}\text{Cf}$   
139 and  $^{249}\text{Bk}$  display similar sensitivities in the ICP-QMS. This demonstration allowed the  
140 measurement of  $^{249}(\text{Bk}+\text{Cf})$  concentration and  $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$  isotope ratio by ICP-QMS in  
141 the third and fourth step, respectively. In addition, the Cf pure fraction recovered during the  
142 first step was analysed to determine its isotopic composition by ICP-QMS during the fourth

143 step. The absolute  $^{248}\text{Cm}$  concentration was determined in the fifth step by isotope dilution  
144 (ID) in TIMS using a certified  $^{244}\text{Cm}$  spike.

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

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

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

151  
152 Where  $a$ ,  $b$ ,  $c$ , and  $d$ , are the  $^{249}(\text{Bk}+\text{Cf})$  concentration,  $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$  and  $^{249}\text{Cf}/^{250}\text{Cf}$   
153 atomic ratios and the  $^{248}\text{Cm}$  concentration, respectively (Figure 2).  $M_{249\text{Bk}}$ ,  $M_{249\text{Cf}}$  and  $M_{248\text{Cm}}$   
154 are the atomic masses of  $^{249}\text{Bk}$ ,  $^{249}\text{Cf}$  and  $^{248}\text{Cm}$ .  $M_{249\text{Mean}}$  is the mean atomic mass of  $M_{249\text{Bk}}$   
155 and  $M_{249\text{Cf}}$  used for the isobaric interference  $^{249}(\text{Bk}+\text{Cf})$ .

156

### 157 3. Experimental setup

158

#### 159 3.1 Instrumentation

160

##### 161 3.1.1. Ion chromatographic instrumentation

162

163 To perform the Cf-Bk-Cm separation, a DIONEX (Sunnyvale, CA, USA) ICS 3000 IC pump  
164 was used with a LUNA SCX (Strong Cation Exchange) analytical column ( $250 \times 4.6$  mm)  
165 and a guard column (Phenomenex, Torrance, CA, USA). The stationary phase was silica-  
166 based and bonded with benzene sulfonic acid, with a particle size of  $5 \mu\text{m}$ . The eluent flow  
167 rate was  $1 \text{ mL}\cdot\text{min}^{-1}$  and the injection valve was equipped with a  $20 \mu\text{L}$  sample loop. To

168 perform the recuperation of the Bk and Cf fractions, a four-ways selection valve has been  
169 added between the column and the nebulizer. An illustration of the implantation of ion  
170 chromatography in glove box environment was presented in a previous study [14].

171

### 172 3.1.2. ICP-MS instrumentation

173

174 The experiments were carried out on a quadrupole ICP-MS “X series” mass spectrometer  
175 from Thermo Electron (Winsford, UK) equipped with a hexapole collision / reaction cell (not  
176 used in this study). This ICP-MS is the first X series modified, with the ICP source in a glove  
177 box, in order to handle radioactive samples as previously described [5,16]. Sample  
178 introduction in the plasma was performed with a quartz bead impact spray chamber and a  
179 quartz concentric nebulizer (1.0 mL.min<sup>-1</sup>). Experimental parameters were daily optimized  
180 with a 1ppb U standard solution in order to obtain the maximum count rates and stability on  
181 <sup>238</sup>U signal. Typical sensitivity and stability (Relative Standard Deviation) values are 4.10<sup>5</sup> cps  
182 and 0.3-0.4%, respectively. Instrumental background at 228 u was typically 0-5 cps. The  
183 operating conditions of the instrument are listed in Table 1. The isotope ratio measurements  
184 were performed using previously described methodologies [5,17-19] which involves control  
185 and correction of all instrumental parameters (blank, background, peak center, hydride level,  
186 mass bias and detector dead time).

187

188

189

190

191

192

193

### 194 3.1.3. TIMS instrumentation

195

196 Curium isotope ratio measurements were performed on a Sector 54 mass spectrometer from  
197 GV Instruments (Manchester, UK). The source is placed inside a glove-box to handle  
198 radioactive samples. Removable rhenium triple filament arrangements were used. For Cm  
199 measurements, around 20 ng of Cm diluted in 0.25M HNO<sub>3</sub> acid were deposited on the side  
200 rhenium filament. The instrument is equipped with seven faraday cups with 10<sup>11</sup>Ω positive  
201 feedback resistors. The Faraday amplifier gains were calibrated daily before the analytical  
202 session. Reproducibility of the electric gains was better than 20 ppm/day.

203 The Cm data were acquired in static multicollection mode with Faraday cups, using the total  
204 evaporation method [20-22]. The reproducibility obtained for Cm isotopic measurement was  
205 evaluated with an in house standard solution.

206

### 207 3.1.4. Triple to Double Coincidence Ratio (TDCR) method

208

209 The measurement of the <sup>249</sup>Bk activity was performed using the Triple to Double Coincidence  
210 Ratio (TDCR) method in Liquid Scintillation (LS) Counting [23] at the Laboratoire National  
211 Henri Becquerel (LNHB). This is a primary measurement method, based on a statistical  
212 model of the light emission from the scintillator and a radiation-matter interaction model  
213 using a calculated beta spectrum. <sup>249</sup>Bk is mostly decaying through a beta transition to the  
214 fundamental level of <sup>249</sup>Cf, with global transition energy of 124.9 keV. For the uncertainty  
215 calculation parameters like the conservative Birks coefficient, counting statistics, blank  
216 counting, weighing process and maximum beta energy have been taken into account.

217

218

### 219 3.1.5. Alpha Spectrometry

220

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

227

## 228 **3.2 Reagents and materials**

229

### 230 3.2.1 Reagents and solutions

231

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

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

242

243  
244  
245  
246  
247  
248  
249  
250  
251  
252  
253  
254  
255  
256  
257  
258  
259  
260  
261  
262  
263  
264  
265  
266  
267

### 3.2.2. Samples

#### 3.2.2.a Irradiated $^{248}\text{Cm}$ sample

37  $\mu\text{g}$  of  $^{248}\text{Cm}$  in the form of Cm-nitrate were provided by the Lawrence Berkeley National Laboratory. The sample is enriched in  $^{248}\text{Cm}$  ( $\sim 97\%$ ), but also contains  $^{246}\text{Cm}$  ( $\sim 2.5\%$ ),  $^{245}\text{Cm}$  ( $\sim 0.03\%$ ) and  $^{247}\text{Cm}$  ( $\sim 0.01\%$ ). The irradiation and preparation of the sample after irradiation were previously described[5]. Mass spectra of the sample after irradiation still present a very high abundance of  $^{248}\text{Cm}$  and  $^{246}\text{Cm}$  comparing to other isotopes. After sample dissolution in  $\text{HNO}_3$  4N,  $^{248}\text{Cm}$  concentration was  $\sim 1.7 \mu\text{g}\cdot\text{g}^{-1}$ .

#### 3.2.2.b $^{249}\text{Cf}$ sample

10  $\mu\text{g}$  of  $^{249}\text{Cf}$  in the form of Cf nitrate were provided by the Lawrence Berkeley National Laboratory. The powder was dissolved with 4M  $\text{HNO}_3$  (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  $^{249}\text{Cf}$  sample was found equal to  $9965 \pm 13 \text{ Bq/g}$ .

268

### 269 3.2.3 Standard and spike solutions

270

#### 271 3.2.3.a Cm standard

272

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

276

#### 277 3.2.3.b $^{244}\text{Cm}$ spike solution

278

279 The concentration of  $^{244}\text{Cm}$  spike was qualified through its activity by alpha spectrometry at  
280 an uncertainty of 0.2% at  $k=2$  (LMRI CEA laboratory). The isotopic composition of this spike  
281 was qualified at the LANIE laboratory by thermal ionisation mass spectrometry using the  
282 procedures previously described [12,24]. It was enriched at around 93% in  $^{244}\text{Cm}$  with a  
283  $^{248}\text{Cm}/^{244}\text{Cm}$  isotope ratio around  $0.000127 \pm 3 \times 10^{-6}$  ( $k=2$ ) at the date of the measurement.  
284 The concentration of this spike was recalculated at the date of mixing between spike and  
285 sample by considering the half-life of Cm isotopes presented in Table 2.

286

## 287 4. Results and discussion

288

### 289 4.1. STEP 1: Cf, Bk, Cm chromatographic separation and Bk, Cf pure fractions recovery

290

291 All analytical developments and optimisations for rare earth elements separation were  
292 performed using a protocol previously available in the laboratory[12]. LUNA SCX column

293 which include benzene sulfonic acid group and 2-hydroxy-2-methylbutyric acid as a  
294 complexing agent in eluent solution were used for the separation of rare earth elements  
295 [11,25,26]. The analytical conditions were chosen to reach the best selectivity between Cf and  
296 Bk. These conditions were obtained by using HMB eluent at 0.085M with pH adjusted to 3.6.  
297 The monitoring of the element elution was performed by coupling the ionic chromatography  
298 with the ICP-QMS as previously described by Bourgeois et al.[14]. The yields of Cf and Bk  
299 were about 80% respectively. For the yield estimation, the injected concentrations of the two  
300 analytes of interest were calculated using the theoretical quantities predicted by the nuclear  
301 burn-up code CINDER'90 [4]. Several injections of irradiated  $^{248}\text{Cm}$  were performed and the  
302 retention times on the peaks apex for the Cf and the Bk were found to be reproducible and  
303 equal to ~11.5 min and ~17 min respectively (Figure 3). Sufficient time between the return to  
304 base line after Cf elution (at 14.5 min) and the beginning of the Bk elution (at 15.5 min)  
305 guaranties the high purity of the fractions. These well-defined retention times allowed the  
306 recovery of Cf and Bk pure fractions on two independent injections of around 5  $\mu\text{g}$  of  
307 irradiated  $^{248}\text{Cm}$ . During the first injection of  $^{248}\text{Cm}$ , the Cf was monitored by ICP-QMS.  
308 After the total Cf elution, the valve selector was turned towards a clean recipient for Bk  
309 recovery. For the second injection the valve selector was turned towards a second clean  
310 recipient for Cf recovery. Then, when full Cf recovery was achieved, the valve selector was  
311 turned towards the ICP-QMS in order to monitor the beginning of the Bk elution in order to  
312 prevent any Bk contamination of the Cf fraction. Pure Bk and Cf fractions were then dried  
313 before 0.5N  $\text{HNO}_3$  reconditioning.

314

315 4.2. STEP 2: Bk and Cf sensitivity control in the ICP-QMS

316

317 A total weight of 4.46 g of pure  $^{249}\text{Bk}$  solution was obtained. An aliquot of this solution  
318 ( $m_1=2.65$  g) was sent to the LNHB laboratory for the determination of the  $^{249}\text{Bk}$  activity by  
319 TDCR. The  $^{249}\text{Bk}$  concentration was then deduced using its half-life (Table 2). In the second  
320 aliquot ( $m_2=1.81$  g), the  $^{249}\text{Bk}$  concentration was measured using a  $^{249}\text{Cf}$  calibration curve.  
321  $^{238}\text{U}$  was used as an internal standard. The two independently measured  $^{249}\text{Bk}$  concentrations  
322 were found in good agreement ( $^{249}\text{Bk}_{\text{ICP-QMS}} = 0.0304 \pm 0.0012$  ng/g ;  $k=2$  and  $^{249}\text{Bk}_{\text{TDCR}} =$   
323  $0.0299 \pm 0.0011$  ng/g ;  $k=2$ ). This means that the measured  $^{249}\text{Bk}$  concentration using the  $^{249}\text{Cf}$   
324 calibration curve is correct and therefore we can consider that Bk and Cf have the same  
325 sensitivity in the ICP-QMS with an uncertainty of 4% ( $k=2$ ). This observation is also  
326 consistent with the very close first ionization potentials of Bk and Cf [27]. The validation of  
327 this step allowed the measurement of the  $^{249}(\text{Bk}+\text{Cf})$  concentration and of the  
328  $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$  atomic ratio in the third and fourth steps respectively.

329

### 330 4.3. STEP 3: $^{249}(\text{Bk}+\text{Cf})$ concentration measurement

331

332 The  $^{249}(\text{Bk}+\text{Cf})$  concentration was measured by using the same  $^{249}\text{Cf}$  calibration curve based  
333 on the similar sensitivities observed between the two elements (within analytical  
334 uncertainties) as demonstrated in the previous step. This measurement allowed the  
335 determination of the “a” parameter (Figure 2).

336

### 337 4.2. STEP 4: $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$ atomic ratio (initial $^{248}\text{Cm}$ sample) and Cf isotope ratios 338 measurement (purified fraction)

339

340 In this step the measurements of  $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$  and of  $^{249, 251, 252}\text{Cf}/^{250}\text{Cf}$  were performed by  
341 ICP-QMS based on previously developed methodologies for isotope ratio measurements by

342 ICP-QMS[5,17-19]. According to these methods, all ratios were corrected for memory blank,  
 343 peak centre, hydride level, instrumental mass bias and detector dead time. The results are  
 344 presented in Table 3. These measurements lead to the determination of the “b” and “c”  
 345 parameters (Figure 2). The good consistency of the analytical procedure for isotope ratio  
 346 measurements by ICP-QMS was confirmed by comparing the  $^{251}\text{Cf}/^{250}\text{Cf}$ ,  $^{252}\text{Cf}/^{250}\text{Cf}$ ,  
 347  $^{249}(\text{Bk+Cf})/^{250}\text{Cf}$  ratios obtained in this work with previously obtained results[5] for the same  
 348 sample of irradiated  $^{248}\text{Cm}$ . As can be seen in Figure 4, a good agreement within analytical  
 349 uncertainties was observed.

350

#### 351 4.4. STEP 5: Determination of $^{248}\text{Cm}$ concentration using ID technique

352

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

$$355 \quad [Cm]_S = [Cm]_{Sp} \times \frac{m_{Sp}}{m_S} \times \frac{M_S}{M_{Sp}} \times \frac{(244)_{Sp}}{(248)_S} \times \left[ \left( \frac{^{248}\text{Cm}}{^{244}\text{Cm}} \right)_{Mix} - \left( \frac{^{248}\text{Cm}}{^{244}\text{Cm}} \right)_{Sp} \right] \quad 3$$

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

359 Two mixtures of the spike and sample solutions were prepared by weight to determine the  
 360  $(^{248}\text{Cm}/^{244}\text{Cm})_{Mix}$  ratio in the sample by TIMS. Each solution was evaporated after mixing,  
 361 and then redissolved in  $\text{HNO}_3$  2 % media. The relative difference obtained between the two  
 362 mixtures is 0.13 %. The uncertainty on the  $^{248}\text{Cm}$  sample concentration was evaluated by  
 363 calculating the combined uncertainties of each contributing term [28]. The value found for the  
 364 Cm concentration in the sample was  $1.729 \pm 0.008 \mu\text{g}\cdot\text{g}^{-1}$  ( $k=2$ ) corresponding to a  $^{248}\text{Cm}$

365 concentration of  $1.685 \pm 0.008 \mu\text{g.g}^{-1}$  ( $k=2$ ). This measurement leads to the determination of  
366 the “d” parameter (Figure 2).

367

#### 368 4.5. Evaluation of uncertainties

369

370 All the results obtained in this work are presented in Table 3. Uncertainties of “a”, “b”, “c”  
371 and “d” parameters have been taken into account for the calculation of  $^{249}\text{Bk}/^{248}\text{Cm}$  and  
372  $^{249}\text{Cf}/^{248}\text{Cm}$  ratio uncertainties and were found to be 6.1% and 3.2% ( $k=2$ ), respectively. Due  
373 to the low Bk amount compared to that of Cf in our sample ( $\text{Bk}/\text{Cf} \sim 1/6.6$ ), the uncertainty  
374 on the Bk sensitivity (4%;  $k=2$ ) in the ICP-QMS has not an important contribution on the  
375 uncertainties of “a” and “b” parameters and for this reason has not been taken into account.  
376 This calculation was based on the spreadsheet method for uncertainties propagation [29,30].  
377 As can be seen in the Figure 5, the major uncertainty contribution regarding to the  
378  $^{249}\text{Bk}/^{248}\text{Cm}$  ratio uncertainty comes from the “b” parameter ( $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$ ) whereas the  
379 “a” parameter ( $^{249}(\text{Bk}+\text{Cf})$  concentration) is dominant on the uncertainty budget of the  
380  $^{249}\text{Cf}/^{248}\text{Cm}$  elemental ratio. These results are of major importance for future experimental  
381 procedures design as the “key” parameters governing the uncertainties budget are highlighted.  
382 The isotope and elemental ratio uncertainties reached in this work are perfectly adapted for  
383 actinide neutron capture cross-section calculation since they are significantly below other  
384 sources of uncertainty (e.g., neutron fluence during irradiation). These results will allow  
385 reducing significantly the  $^{248}\text{Cm}$  and  $^{249}\text{Bk}$  capture cross-section uncertainties, which are  
386 larger than 10% ( $k=1$ ) with significant discrepancies between the available data. The  
387 comparison between theoretical and experimental data will be given in a further work.  
388 However, if lower uncertainties are required in the future on  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$   
389 elemental ratios for nuclear applications, both high transmission MC-ICP-MS and isotope

390 dilution approaches can be envisioned, together with a better definition of  $^{249}\text{Bk}$  and  $^{249}\text{Cf}$   
391 respective sensitivities.

392

### 393 **5. Conclusion**

394

395 This work is the second part of the analytical development that was performed for the  
396 measurement of the elemental and isotope ratio composition of an irradiated  $^{248}\text{Cm}$  sample.

397 The major drawback for the determination of  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$  elemental ratios  
398 was the isobaric interference of  $^{249}\text{Bk}$  and  $^{249}\text{Cf}$  in the irradiated sample. For this reason, the

399 previously developed protocol in the laboratory for lanthanides separation by ion  
400 chromatography was adapted for Cf, Bk and Cm separation. The element elution was

401 monitored by coupling the ionic chromatography with the ICP-QMS. After several number of  
402 irradiated sample injections, well-defined retention times for Cf, Bk and Cm were obtained. A

403 second critical point in this work was the measurement of  $^{249}(\text{Bk}+\text{Cf})$  concentration and of  
404  $^{249}(\text{Bk}+\text{Cf})/^{250}\text{Cf}$  atomic ratio. In order to proceed in this measurement, Cf and Bk sensitivities

405 were tested in the ICP-QMS and found to be similar with an uncertainty of 4%. All parameter  
406 uncertainties were propagated for the uncertainty calculation of  $^{249}\text{Bk}/^{248}\text{Cm}$  and  $^{249}\text{Cf}/^{248}\text{Cm}$

407 elemental ratios. Furthermore, the “key” parameters governing the uncertainties budget were  
408 identified for future experimental procedures improvement.

409

410

411

412

413

414

415  
416  
417  
418  
419  
420  
421  
422  
423  
424  
425  
426  
427  
428  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443  
444  
445  
446  
447  
448  
449  
450  
451  
452  
453  
454  
455  
456  
457  
458  
459

## References

- [1] 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) 468-486.
- [2] M. Salvatores, A. Zaetta, C. Girard, M. Delpech, I. Slessarev, J. Tommasi, Appl. Radiat. Isot. 46 (1995) 681-687.
- [3] A. Takibayev, M. Saito, V. Artisyuk, H. Sagara, Prog. Nucl. Energy 47 (2005) 354-360.
- [4] W.B. Wilson, S.T. Cowelle, T.R. England, A.C. Hayes, P. Moller, LA-UR-07-8412 (2007).
- [5] A. Gourgiotis, H. Isnard, M. Aubert, E. Dupont, I. AlMahamid, G. Tiang, L. Rao, W. Lukens, P. Cassette, S. Panebianco, A. Letourneau, F. Chartier, Int. J. Mass Spectrom. 291 (2010) 101-107.
- [6] E.P. Horwitz, C.A.A. Bloomquist, D.J. Henderson, D.E. Nelson, J. Inorg. Nucl. Chem. 31 (1969) 3255.
- [7] J. Kooi, R. Boden, H. Wijkstra, J. Inorg. Nucl. Chem. 26 (1964) 2300.
- [8] F.L. Moore, A. Jurriaanse, Anal. Chem. 39 (1967) 733.
- [9] A. Ikeda, T. Suzuki, M. Aida, K. Otake, Y. Fujii, K. Itoh, T. Mitsugashira, M. Hara, M. Ozawa, J. Nucl. Sci. Technol. 41 (2004) 915-918.
- [10] L.A. Firsova, E.A. Chuveleva, O.V. Kharitonov, Radiochem. 38 (1996) 407-409.
- [11] M. Vobecky, J. Chromatogr. 478 (1989) 446-448.
- [12] F. Chartier, M. Aubert, M. Pilier, Fresenius J. Anal. Chem. 364 (1999) 320-327.
- [13] F. Goutelard, C. Caussignac, R. Brennetot, G. Stadelmann, C. Gautier, J. Radioanal. Nucl. Chem. 282 (2009) 669-675.
- [14] M. Bourgeois, H. Isnard, A. Gourgiotis, G. Stadelmann, C. Gautier, S. Mialle, A. Nonell, F. Chartier, J. Anal. At. Spectrom. 26 (2011) 1549-1688.
- [15] C. Gautier, M. Bourgeois, H. Isnard, A. Nonell, G. Stadelmann, F. Goutelard, J. Chromatogr. A 1218 (2011) 5241-5247.
- [16] G. Favre, R. Brennetot, F. Chartier, P. Vitorge, Int. J. Mass Spectrom. 265 (2007) 15-22.
- [17] E. Margui, M. Iglesias, I. Queralt, M. Hidalgo, Talanta 73 (2007) 700-709.
- [18] C.C. Shen, H.T. Lin, M.F. Chu, E.F. Yu, X.F. Wang, J.A. Dorale, Geochem. Geophys. Geosyst. 7 (2006) -.
- [19] J. Zheng, M. Yamada, Talanta 68 (2006) 932-939.
- [20] E.L. Callis, R. Abernathy, Int. J. Mass Spectrom. Ion Process. 103 (1991) 93-105.
- [21] J.C. Dubois, G. Retali, J. Cesario, Int. J. Mass Spectrom. Ion Process. 120 (1992) 163-177.
- [22] R. Fiedler, Int. J. Mass Spectrom. Ion Process. 146-147 (1995) 91-97.
- [23] R. Broda, P. Cassette, K. Kossert, Metrologia 44 (2007) S36-S52.
- [24] F. Chartier, M. Aubert, J.P. Degros, J.M. Duda, Radioprotection 39 (2004) 1-11.
- [25] T. Nishi, I. Fujiwara, J. Atom. Energy Soc. Jpn. 6 (1964) 15.

- 460 [26] N.M. Raut, P.G. Jaison, S.K. Aggarwal, *J. Chromatogr. A* 959 (2002) 163-172.  
461 [27] N. Erdmann, M. Nunnemann, K. Eberhardt, G. Herrmann, G. Huber, S. Kohler, J.V.  
462 Kratz, G. Passler, J.R. Peterson, N. Trautmann, A. Waldek, *J. Alloys Compd.* 271  
463 (1998) 837-840.  
464 [28] ISO, 1995 Guide of the Expression of Uncertainty in Measurements, ISBN 92-67-  
465 10188-9, CP 56, CH 1211 Geneve 20, Switzerland.  
466 [29] J. Kragten, *Analyst* 119 (1994) 2161-2165.  
467 [30] J. Kragten, *Chemometr. Intelligent Laborat. Systems* 28 (1995) 89-97.  
468  
469