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11 **Quantification of curium isotopes in environmental samples: drawbacks, speciation and**  
12 **specific tracer**

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18 **Keywords**

19 Curium, americium, environmental samples, speciation, <sup>248</sup>Cm

20 **Abstract**

21 In this study, drawbacks of the use of <sup>243</sup>Am as a tracer in order to quantify curium isotopes  
22 during a complex chemical procedure were highlighted. These drawbacks were investigated  
23 through a speciation computation simulation based on the compilation of over 50 stability  
24 constants. A new curium standard was then characterized and used to quantify a wide <sup>244</sup>Cm  
25 activities range in environmental samples. Obtained results were in excellent agreement with  
26 spiked activities and more consistent than those obtained when using <sup>243</sup>Am as tracer.

27 **Introduction**

28 Curium isotopes are mostly produced by irradiation of uranium and/or plutonium oxides with  
29 neutrons in nuclear power reactors [1]. In fact, during the nuclear fuel cycle, the production of  
30 transuranic elements with mass numbers exceeding 240 by multiple neutron capture of uranium  
31 and plutonium can be very substantial (e.g. ~ 20 g.tonne<sup>-1</sup> for curium isotopes) [2]. Over twenty  
32 isotopes of curium are known with mass numbers ranging from 232 to 252, all of these isotopes  
33 are radioactive and primarily  $\alpha$ -particle emitters, with <sup>242</sup>Cm and <sup>244</sup>Cm (respective half-lives  
34 of 163 days and 18.1 years) accounting for 90 % of those produced in the nuclear fuel cycle [2].

35 Indeed, in the fallout following the Chernobyl accident,  $^{242}\text{Cm}$  was the dominating alpha-  
36 particle emitter (14 times higher than  $^{239+240}\text{Pu}$ ) [2]. Furthermore, the high specific activity of  
37  $^{242}\text{Cm}$  and  $^{244}\text{Cm}$  ( $> 10^{12}$  Bq/g) has mainly been considered as an issue because it results in  
38 significant contribution to the radiotoxicity of nuclear waste. Regulatory and non-regulatory  
39 releases of curium in the environment, especially near reprocessing power plants such as La  
40 Hague (France), presents a considerable public health concern [1]. Curium isotopes  
41 quantification in environmental samples is then fundamental to monitor this releases.

42 Reliable detection and quantification of curium isotopes in complex environmental matrices  
43 require extensive removal of chemical and radiometric interferences. The procedure yield must  
44 be determined using an elemental or isotopic analog. The common yield monitor of curium  
45 separation is  $^{243}\text{Am}$  since considered as a chemical analog. The use of this isotope is therefore  
46 known for its drawbacks. A bias could indeed be observed between americium and curium  
47 behaviors [3–7]. This difference generates bias between chemical yields of americium and  
48 curium which leads to inexact results. To understand the observed bias and behaviors of  
49 americium and curium, their speciation during a complex purification procedure was  
50 investigated in this study by computer simulation. This simulation was executed using the  
51 MEDUSA software and the associated HYDRA equilibrium database, compiled with published  
52 data[8].

53 To avoid the risk of a bias between the chemical yields and therefore an incorrect curium  
54 isotopes activities determination in environmental samples, an alternative approach using  $^{248}\text{Cm}$   
55 as tracer to enable a determination based on the isotopic dilution technique was studied. The  
56 concentration and isotopic composition of a commercial curium solution with  $^{248}\text{Cm}$   
57 enrichment of 95.82 % (w/w) was standardized by alpha spectrometry. Various environmental  
58 samples, each spiked with known amounts of  $^{248}\text{Cm}$  and  $^{244}\text{Cm}$  were processed following our  
59 radiochemical procedure involving alpha spectrometry counting.

60 Experimental results and method performances observed when analyzing various types of  
61 environmental samples (water, vegetables and sediment) are presented. A detailed methodology  
62 including curium and americium speciation,  $^{248}\text{Cm}$  solution qualification, interferences  
63 corrections, results and uncertainties calculation are presented and discussed.

## 64 **Reagents and instrumentation**

### 65 **Reagents**

66 All used reagents were prepared from analytical-grade powders and analytical reagent-grade  
67 for acids. Extraction resins were from Triskem, Int. (FR) (TEVA resin and TRU resin). Anionic  
68 resin was purchased from BIO-RAD (AG<sup>®</sup> 1X4 50-100 mesh).

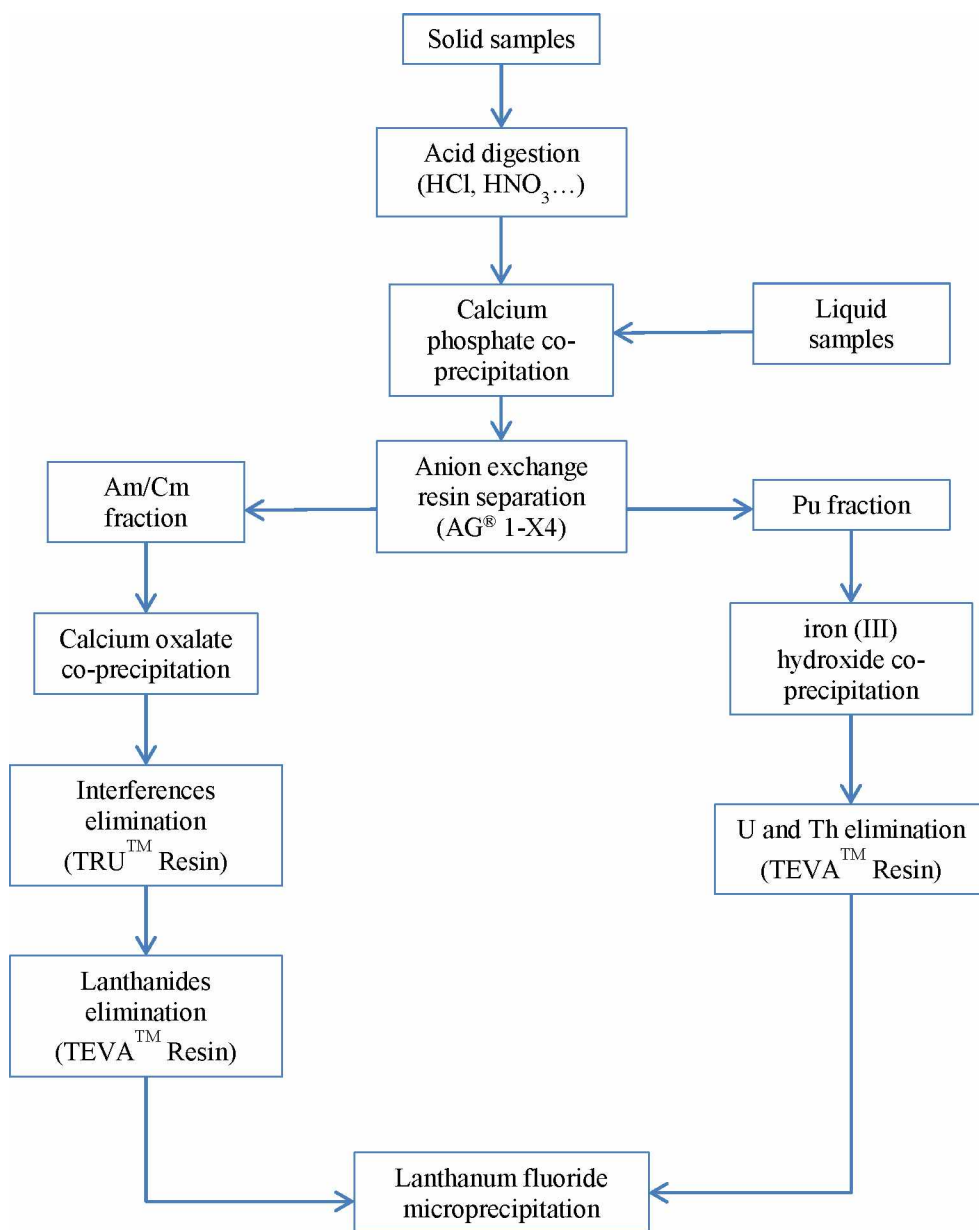
69 Tracer solutions were conserved in acidic media (1 – 4 M of  $\text{HNO}_3$ ) and purchased from the  
70 NIST, NPL, AEA Technology and ORNL for  $^{242}\text{Pu}$  (SRM 4334j),  $^{243}\text{Am}$  (A14063),  $^{244}\text{Cm}$   
71 (CLP 10010) and  $^{248}\text{Cm}$  (8R103CMPROD), respectively.

### 72 **Instrumentation**

73 Alpha source filters are counted by alpha spectrometry for approximately 69 h.

### 74 **Experimental procedure**

75 The major steps of the experimental procedure are summarized in figure 1.



76

77 *Figure 1: experimental procedure for americium and curium quantification in environmental*  
 78 *samples*

79 The first step of the experimental procedure consists on the addition of tracers (<sup>242</sup>Pu and <sup>243</sup>Am)  
 80 to 5 g of solid samples (e.g. soil, sediment, vegetables...) or 500 mL of liquid samples (e.g.  
 81 drinking water, surface water...).

82 When organic solid samples are analyzed (e.g. vegetables, fish, seaweed...), an acidic leaching  
 83 involving a mixture of concentrated nitric acid and hydrochloric acid is performed.

84 Furthermore, when soil or sediment samples are analyzed, the leaching is performed using 9 M  
85 hydrochloric acid.

86 After the elimination, by centrifugation, of the undissolved residue, plutonium and  
87 americium/curium phosphates are precipitated by adding 10 mL of calcium phosphates and  
88 ammonium hydroxide (20 %) to adjust the pH at 8-9. Once the precipitate is centrifuged, it's  
89 dissolved by adding 100 mL of 7 M HNO<sub>3</sub>. Valence adjustment is then performed with  
90 ~ 200 mg of NaNO<sub>2</sub>.

91 Plutonium is extracted from the sample using a column containing ~ 5 g of AG<sup>®</sup> 1-X4 50 – 100  
92 mesh (Anion Exchange Resin) previously washed with H<sub>2</sub>O and pre-conditioned with 30 mL  
93 of 7 M HNO<sub>3</sub>. The sample is loaded through the column. The resin is then rinsed with 2 x 30  
94 mL and 40 mL of 7 M HNO<sub>3</sub>. The loaded sample and the rinsing fractions are collected to be  
95 treated afterward since containing americium and curium (*fraction 2*). The column is then rinsed  
96 with 2 x 30 mL of 9 M HCl before plutonium elution with 2 x 30 mL of a solution of 0.2 M of  
97 hydroxylamine Hydrochloride. The elution fraction is evaporated to dryness and the residue is  
98 dissolved with 100 mL of 1 M HNO<sub>3</sub>. Plutonium is precipitated by adding 5 mL of iron (III)  
99 nitrate, previously prepared by dissolving 30 g of Fe(NO<sub>3</sub>)<sub>3</sub> in 1 L of 0.01 M of HNO<sub>3</sub>, and  
100 ammonium hydroxide (20 %) to adjust the pH at least at 9. The precipitate is centrifuged and  
101 dissolved with 30 mL of 7 M HNO<sub>3</sub>. 10 mL of 750 g/L of Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O and ~ 100 mg of  
102 NaNO<sub>2</sub> are then added to the previously dissolved precipitate. The sample is purified from the  
103 remaining uranium and thorium with a TEVA<sup>™</sup> resin. After the conditioning with 20 mL of 3  
104 M HNO<sub>3</sub> and the sample loading, the TEVA<sup>™</sup> resin is rinsed with 20 mL of 3 M HNO<sub>3</sub>, 20 mL  
105 of 0.5 M HNO<sub>3</sub> to eliminate uranium, 50 mL of 6 M HCl to eliminate thorium and again with  
106 20 mL of 3 M HNO<sub>3</sub>. Plutonium is finally eluted with 2 x 30 mL of a solution of 0.2 M of  
107 hydroxylamine Hydrochloride. The elution fraction is evaporated to dryness.

108 To the fraction containing americium and curium (*fraction 2*), ~ 100 mg of ascorbic acid, 3 mL  
109 of the previously used solution of iron (III) nitrate and 12 g of oxalic acid are added. The  
110 solution volume is then extended to 200 mL and the pH is adjusted to 1.48 - 1.5 with 20 %  
111 ammonium hydroxide. The precipitate is then collected by centrifugation, dissolved with 20  
112 mL of 7 M HNO<sub>3</sub> and heated to dryness in order to convert the oxalate complexes on carbonate  
113 complexes. Carbonate complexes are then dissolved with 20 mL of 1 M HNO<sub>3</sub>. Americium and  
114 curium are extracted using a TRU<sup>TM</sup> resin. The sample is loaded through a prepacked column  
115 purchased from Triskem international. The resin is rinsed with 2 x 10 mL of 1 M HNO<sub>3</sub> and 2  
116 mL of 9 M HCl. The loading and rinsing fractions are discarded. Americium and curium are  
117 eluted from the TRU resin with 10 mL of 4 M HCl. The elution fraction is heated to dryness  
118 and the residue is dissolved with 20 mL of a freshly prepared solution containing 0.1 M formic  
119 acid and 2 M ammonium thiocyanate. The sample is loaded and the TEVA<sup>TM</sup> resin is rinsed  
120 with 20 mL of 0.1 M formic acid and 2 M ammonium thiocyanate and 30 mL of 0.1 M formic  
121 acid and 1 M ammonium thiocyanate in order to remove the remaining lanthanides. Americium  
122 and curium are eluted from the TEVA<sup>TM</sup> resin with 30 mL of 0.25 M HCl. The elution fraction  
123 is evaporated to dryness.

124 Both residues containing plutonium and americium/curium are dissolved with 50 mL of 0.2 M  
125 HCl and lanthanum fluoride microprecipitation is performed by adding 1 mL of 0.29 g/L  
126 lanthanum oxide, prepared in 0.2 M HCl, and 1 mL of 40 % hydrofluoric acid. pH is then  
127 adjusted to 1.89 - 1.91.

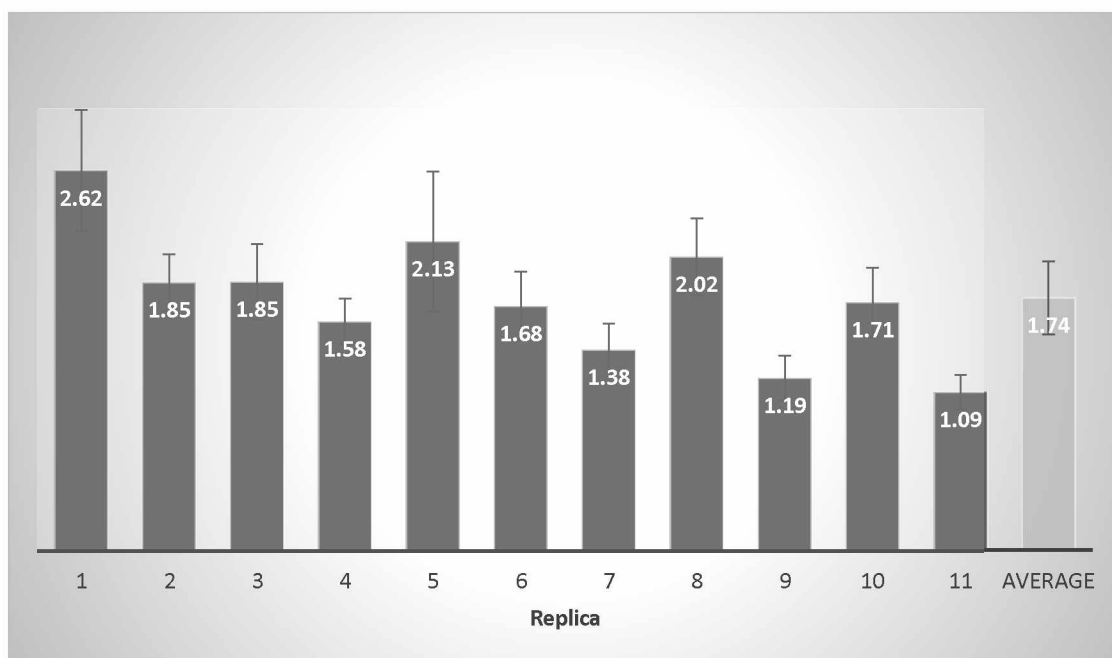
128 Quantification is based on isotopic dilution technique where <sup>242</sup>Pu tracer is used for <sup>238</sup>Pu and  
129 <sup>239+240</sup>Pu quantification and <sup>243</sup>Am tracer used for <sup>241</sup>Am, <sup>242</sup>Cm and <sup>243+244</sup>Cm quantification.  
130 Indeed, americium and curium have similar chemical properties in solution as a result of  
131 predominantly trivalent oxidation state with comparable ionic radii [9] and their extraction  
132 behavior is often perceived as indistinguishable [10]. Some differences were nonetheless

133 observed between americium and curium behaviors. These differences were then exploited in  
134 chromatographic systems to achieve separations of Cm from Am [3–7]. Due to these  
135 differences, the ISO 13167:2016 [11] recommended, if curium isotopes are needed in drinking  
136 water and  $^{243}\text{Am}$  is used as tracer, the determination of a correction factor (CF) using reference  
137 materials or spiked water samples.

138 
$$CF = \frac{\text{Cm isotope theoretical activity}}{\text{Cm isotope calculated activity with } ^{243}\text{Am tracer}} \quad \text{Eq. (1)}$$

139 The calculated correction factor (Eq. (1)) has then to be applied to curium isotopes measured  
140 activities.

141 An attempt to experimentally determine the correction factor was done by our team. This  
142 determination was done using 11 spiked water samples and samples from proficiency tests with  
143  $^{244}\text{Cm}$  activities ranging from 2 mBq.L<sup>-1</sup> to 10 Bq.mL<sup>-1</sup>. The calculated correction factors are  
144 presented in figure 2.



145

146

*Figure 2: experimentally determined correction factors*



147 The presented results were used to calculate the average correction factor which is  
148  $1.74 \pm 15 \%$ , the standard deviation is however relatively high ( $\sim 0.68$ ).

149 In order to determine the accuracy of the results when the determined correction factor (CF) is  
150 applied, 11 water samples, containing known activities of  $^{244}\text{Cm}$ , were analyzed using the  
151 procedure described in figure 1 and  $^{243}\text{Am}$  as a tracer. The standardized deviations (SD) (*Eq.*  
152 (2)) and relative deviations (RD) (*Eq.* (3)) between theoretical activities and experimentally  
153 determined ones when using the correction factor (e.g. 1.74) are then calculated. The SD and  
154 RD have to be, respectively, lower than 1 and 15 % in order to consider the experimental activity  
155 of  $^{244}\text{Cm}$  acceptable. The obtained calculated SD and RD [6], when the determined correction  
156 factor is applied, were compared to those obtained without the application of the correction  
157 factor (table 1).

$$158 \quad SD = \frac{|\text{calculated } ^{244}\text{Cm activity} - \text{theoretical } ^{244}\text{Cm activity}|}{\sqrt{(\text{uncertainty of the calculated activity})^2 + (\text{uncertainty of the theoretical activity})^2}} \quad \text{Eq. (2)}$$

$$159 \quad RD = \frac{|\text{calculated } ^{244}\text{Cm activity} - \text{theoretical } ^{244}\text{Cm activity}|}{\text{theoretical } ^{244}\text{Cm activity}} \times 100 \quad \text{Eq. (3)}$$

160 *Table 1: standardized and relative deviations obtained for <sup>244</sup>Cm activities with and without a*  
 161 *correction factor in water samples*

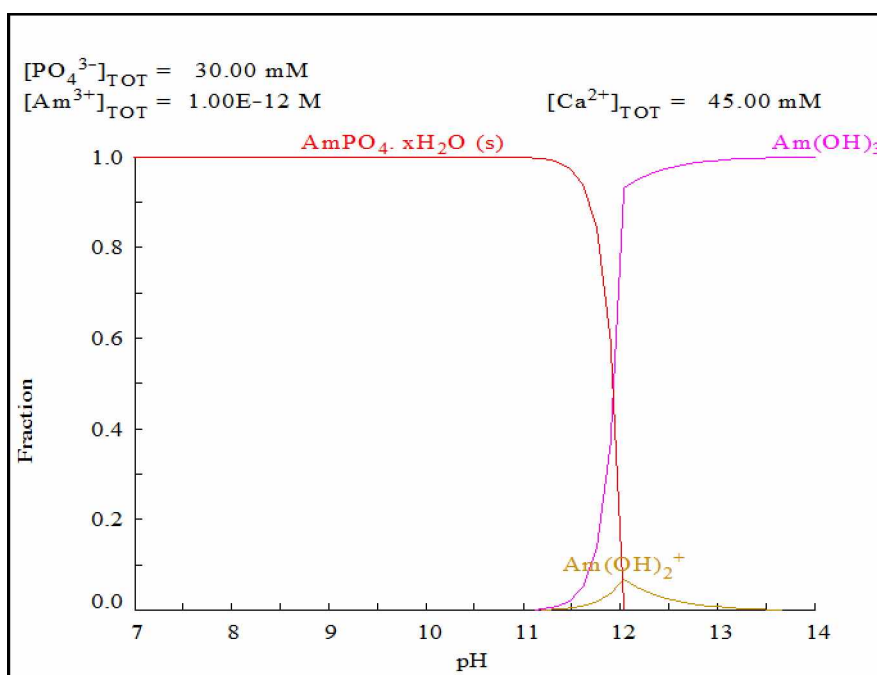
Sample	Theoretical <sup>244</sup> Cm activities, Bq/L (k=2)	Calculated <sup>244</sup> Cm activities, Bq/L (k=2)	SD of <sup>244</sup> Cm	SD of <sup>244</sup> Cm (With correction factor)	RD of <sup>244</sup> Cm	RD of <sup>244</sup> Cm (With correction factor)
<b>1</b>	14.6 ± 2.2	25.4 ± 5.4	7.96	2.22	62 %	34 %
<b>2</b>	213.0 ± 19.2	369.8 ± 65.8	6.33	0.34	46 %	6 %
<b>3</b>	2.2 ± 0.3	3.9 ± 0.8	5.30	0.32	46 %	6 %
<b>4</b>	6.8 ± 0.7	11.9 ± 2.2	5.75	0.50	37 %	10 %
<b>5</b>	20.2 ± 4.4	35.0 ± 9.4	4.55	0.82	53 %	18 %
<b>6</b>	106.7 ± 13.9	185.3 ± 37.3	4.39	0.14	41 %	3 %
<b>7</b>	2.4 ± 0.3	4.2 ± 0.9	2.93	1.02	28 %	26 %
<b>8</b>	7.8 ± 1.0	13.5 ± 2.7	6.38	0.81	51 %	14 %
<b>9</b>	197.1 ± 23.7	342.3 ± 66.7	1.46	1.57	16 %	46 %
<b>10</b>	9.1 ± 1.2	15.7 ± 3.2	4.53	0.07	42 %	2 %
<b>11</b>	2.4 ± 0.3	4.2 ± 0.8	0.84	1.97	8 %	59 %

162 Although a downward trend of the standardized deviations and the relative deviations is  
 163 observed when the correction factor is applied, some calculated <sup>244</sup>Cm activities are not  
 164 acceptable since the associated SD is higher than 1 and/or the associated RD is higher than  
 165 15 %. For the sample n°11 the SD and the RD even increased after the correction. The use of  
 166 <sup>243</sup>Am when curium isotopes are analyzed could generate a bias even when a correction factor  
 167 is experimentally determined and applied.

168 In order to understand the physico-chemical causes of this bias during the analysis of spiked  
 169 aqueous solution, Cm and Am speciation, when using the previously described protocol, was  
 170 computed. This speciation was performed using the HYDRA database associated with the  
 171 MEDUSA software. Missing species and stability constants were added to complete the  
 172 database. Activity coefficients were calculated by using Davies equations [14]. This speciation  
 173 study was performed using a total of 50 stability constants.

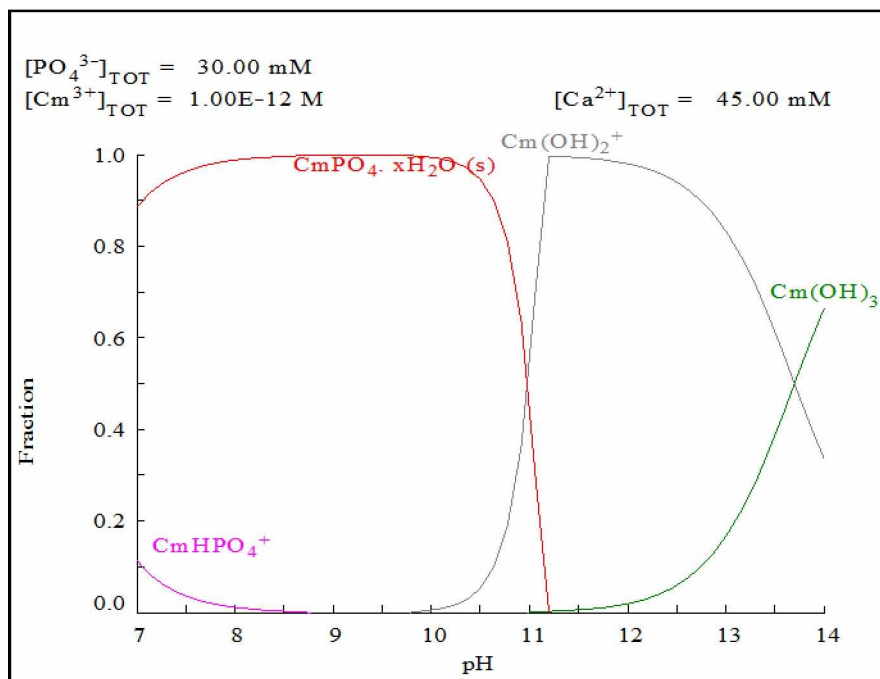
174 During the speciation computation, two hypotheses were made. The first hypothesis was that  
175 reactions between and with not studied ions were neglected. The second hypothesis was that  
176  $^{243}\text{Am}$  and  $^{244}\text{Cm}$  concentration is  $10^{-12}$  M (respectively,  $2.43 \times 10^{-10}$  g/L and  $2.47 \times 10^{-10}$  g/L)  
177 through the entire protocol.

178 The first studied step was the calcium phosphates co-precipitation (figures 3 and 4) [15–17].  
179 This co-precipitation is performed at  $\text{pH} \geq 8$ . According to the previously described procedure,  
180 during this step,  $\text{PO}_4^{3-}$  concentration is  $\sim 30$  mM and  $\text{Ca}^{2+}$  concentration is 45 mM. At pH higher  
181 than 8, the present calcium phosphate complex is  $\text{Ca}_5(\text{PO}_4)_3\text{OH}_{(s)}$ . Figures 3 and 4 show the  
182 fractions of Am and Cm complexes during the co-precipitation step.



183

184 *Figure 3: speciation of americium during the calcium phosphates co-precipitation step*

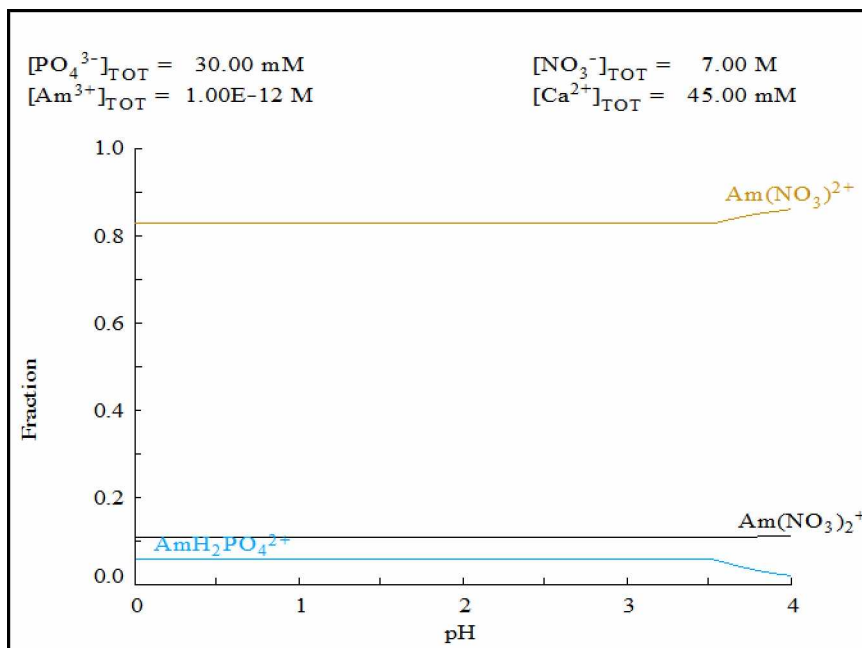


185

186 *Figure 4: speciation of curium during the calcium phosphates co-precipitation step*

187 Figures 3 and 4 show that at a pH between 8 and 10, Am and Cm phosphate complexes are  
 188  $\text{AmPO}_4 \cdot x \text{H}_2\text{O}(s)$  and  $\text{CmPO}_4 \cdot x \text{H}_2\text{O}(s)$ . At pH higher than 10,  $\text{Cm}(\text{OH})_2^+$  becomes a dominate  
 189 species and its fraction reach 100 % at pH 11.2. In this range of pH, almost all Am is precipitated  
 190 under the form of  $\text{Am}(\text{OH})_3$  while  $\text{Cm}(\text{OH})_3$  remains a minor species until pH 13.5. When a  
 191 calcium phosphates co-precipitation of Am and Cm is performed, the pH has a significant  
 192 influence on Am and Cm forms which are not necessarily the same and so can generate a bias.

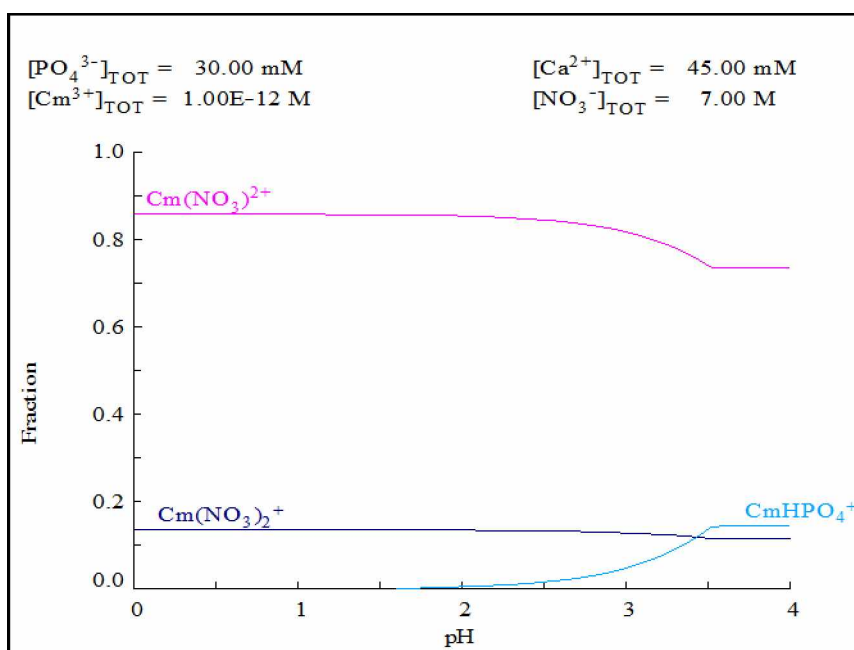
193 The second studied step is the precipitated complexes dissolution using 7 M  $\text{HNO}_3$  [18–20].  
 194 During this step we suppose that all the present  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  are under the forms  $\text{AmPO}_4 \cdot x$   
 195  $\text{H}_2\text{O}(s)$  and  $\text{CmPO}_4 \cdot x \text{H}_2\text{O}(s)$ . However, since during the previous step, 100 % of Ca is  
 196 precipitated under the form  $\text{Ca}_5(\text{PO}_4)_3\text{OH}(s)$ ,  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  concentrations are respectively at  
 197 45 mM and 30 mM during this step.  $\text{NO}_3^-$  concentration is 7 M during this step. The aim of  
 198 this step is to convert the solid  $\text{AmPO}_4 \cdot x \text{H}_2\text{O}(s)$  and  $\text{CmPO}_4 \cdot x \text{H}_2\text{O}(s)$  to aqueous complexes.  
 199 Figures 5 and 6 present the speciation of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  during this step as a function of the  
 200 pH.



201

202

Figure 5: speciation of americium during the phosphates dissolution step



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204

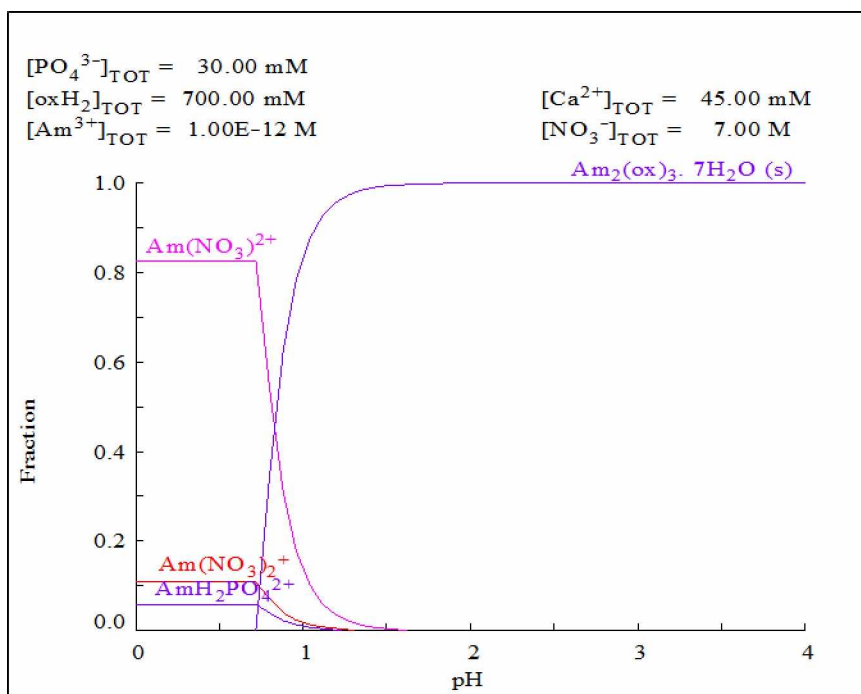
Figure 6: speciation of curium during the phosphates dissolution step

205 Figures 5 and 6 shows that during the phosphate complexes dissolution with 100 mL 7 M HNO<sub>3</sub>  
 206 (pH < 1), 100 % of curium is under the form of aqueous nitrate complexes. On the other hand,  
 207 ~ 6 % of Am is not under the form of aqueous nitrate complexes but remains under the form

208  $\text{AmH}_2\text{PO}_4^{2+}$ . This aqueous americium complex fraction will not have the same behavior during  
209 the separation step on the AG<sup>®</sup> 1-X4 resin.

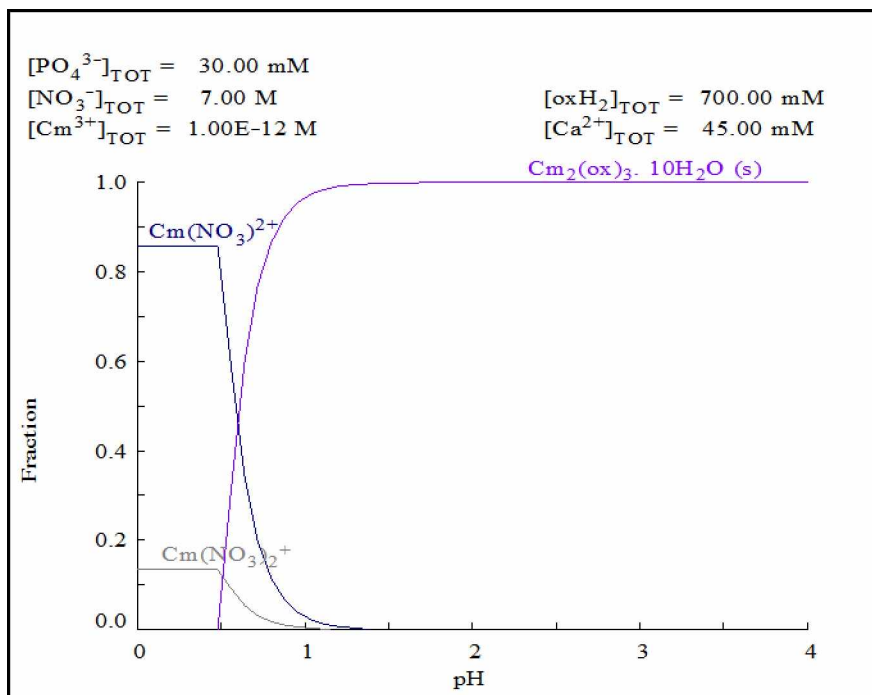
210 The third studied step was the calcium oxalates co-precipitation [20, 21]. Figures 7 and 8 show  
211 the speciation of americium and curium in function of the pH.

212 During this step,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  concentrations are still at respectively 7 M, 45 mM and  
213 30 mM. Moreover, according to the previously described procedure, oxalic acid ( $\text{OxH}_2$ )  
214 concentration is at 0.7 M.



215

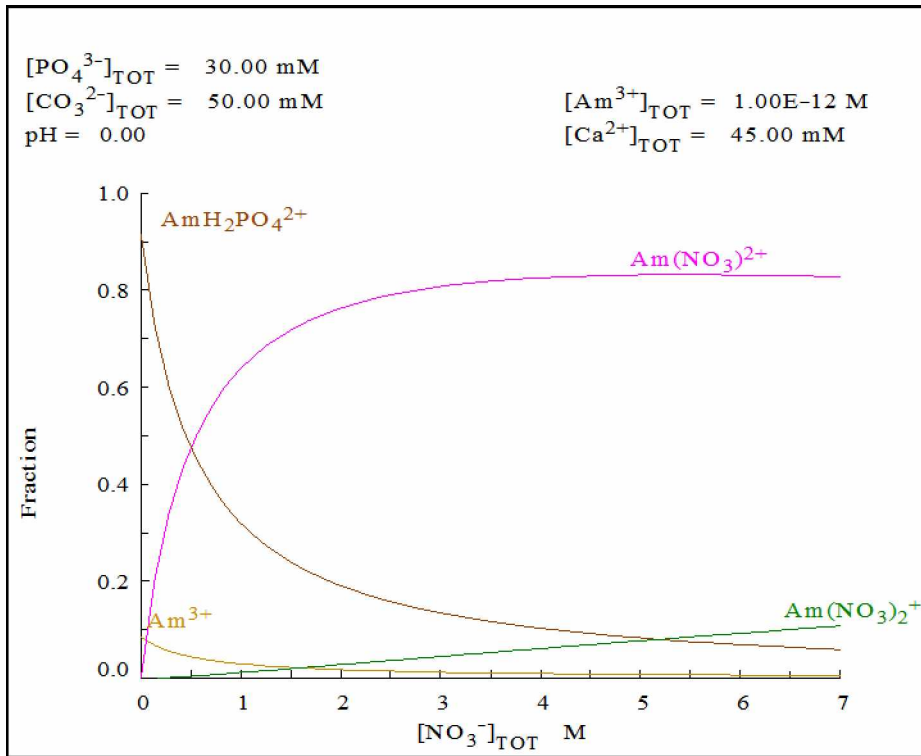
216 *Figure 7: speciation of americium during the calcium oxalates co-precipitation step*



217

218 *Figure 8: speciation of americium during the calcium oxalates co-precipitation step*

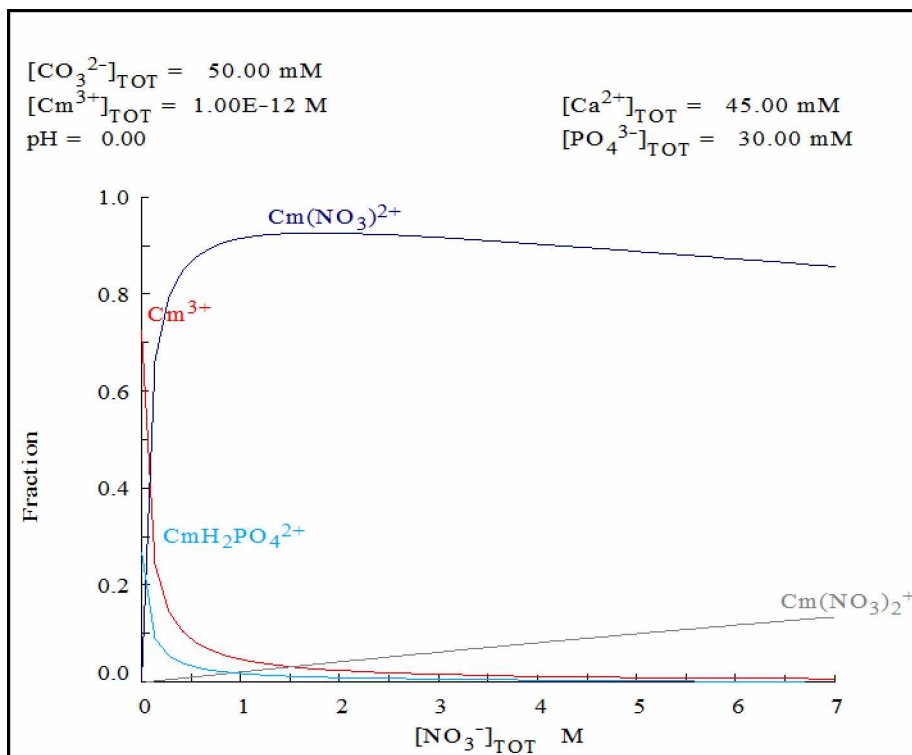
219 For  $\text{pH} \geq 1$ , 100 % of the present calcium is precipitated as  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}(\text{s})$ . According to figures  
 220 7 and 8, at pH 1, 97 % of Cm is precipitated as  $\text{Cm}_2(\text{ox})_3 \cdot 10\text{H}_2\text{O}(\text{s})$  while only 83.2 % of Am is  
 221 precipitated as  $\text{Am}_2(\text{ox})_3 \cdot 7\text{H}_2\text{O}(\text{s})$ . Once again, Am and Cm behaviors present a slight  
 222 difference. Cm and Am remaining in solution are under the form of aqueous nitrate complexes.  
 223 Furthermore at pH 1.5, 99.9 % of both Cm and Am precipitate as oxalate complexes. The pH  
 224 adjustment step is then very important and a slight variation could influence Am and Cm forms.  
 225 After the recovery of the carrier, oxalate complexes were converted to carbonate complexes  
 226 with 7 M  $\text{HNO}_3$  under heating [20, 22, 23]. Speciation of americium and curium during this  
 227 step are presented in figures 9 and 10. Since during the previous step, 100 % of  $\text{Ca}^{2+}$  is  
 228 precipitated under the form of  $\text{CaC}_2\text{O}_4(\text{s})$ ,  $\text{Ca}^{2+}$  concentration is still at 45 mM during this step.  
 229 At  $[\text{NO}_3^-] = 7 \text{ M}$ , ~ 99 % of curium and americium are present as aqueous nitrate complexes.  
 230 In contrary to the previously steps, the dissolution of the carbonate complexes carrier does not  
 231 imply any differences between americium and curium behaviors.



232

233

Figure 9: speciation of americium during the carbonates dissolution step



234

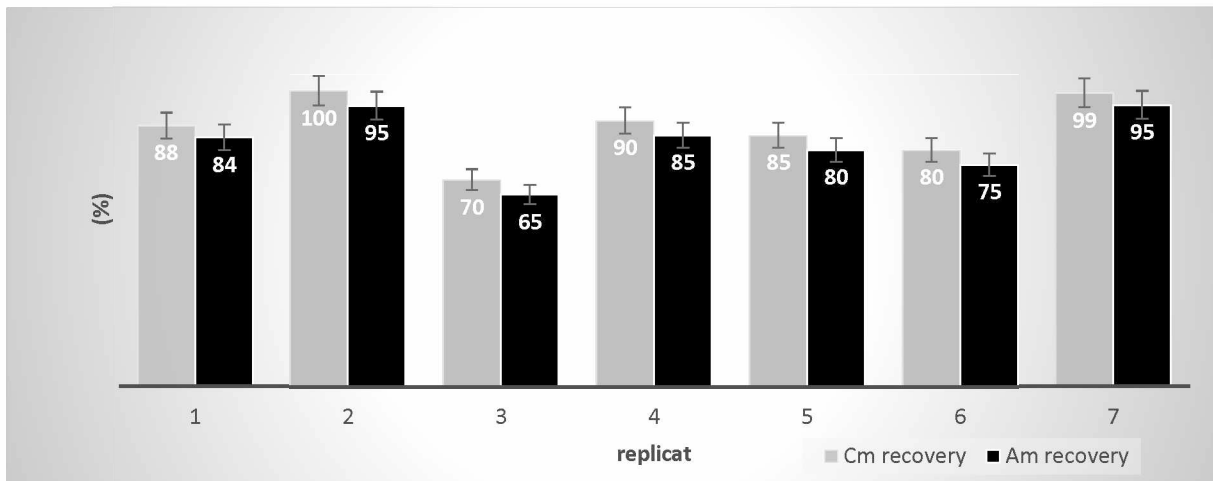
235

Figure 10: speciation of curium during the carbonates dissolution step



236 Speciation of americium and curium during the separation using the TRU<sup>TM</sup> resin is not possible  
237 without a perfect knowledge of the resin properties (e.g. quantity of coated CMPO, packing  
238 procedure...). However, behaviors of americium and curium on the TRU<sup>TM</sup> resin were studied  
239 by Gharibyan et al.[10]. In this study, minor variations between Cm and Am behaviors at 1 M  
240 HNO<sub>3</sub> were described. This medium is the most common one used for the sample loading when  
241 analyzing Am and Cm. The authors described batch studies and deduced a separation factor of  
242 Am from Cm of 1.45. This type of behavior, where a heavier neighboring element has a lower  
243 retention factor than its lighter neighbor, is also observed in the lanthanide series between Eu  
244 (III) and Gd (III) which are isoelectronic to Am (III) and Cm (III), respectively. This separation  
245 factor was then confirmed by column studies and other publications [24].

246 In order to verify if this behavior difference is impacting in our case, several water samples  
247 spiked with Am and Cm were analyzed using TRU<sup>TM</sup> resin. Conditions of the separation were  
248 the same as our routine protocol (e.g. 2 mL pre-packed columns, a flow of 1.5 mL/min  
249 controlled by a peristaltic pump). Elution fractions (4 M HCl) were analyzed by ICP-MS in  
250 order to prevent any behavior difference due to the lanthanum fluoride co-precipitation step.  
251 Figure 11 presents the obtained results. These results highlight that, within the uncertainties,  
252 extraction results obtained for Am and Cm are similar. A slight trend of higher Am recoveries  
253 is nonetheless observed. Since both actinides are not retained over the entire HCl concentration  
254 range [24, 25], this difference is obviously due to a difference between retention factors during  
255 the sample loading in 1 M HNO<sub>3</sub>.



256

257

*Figure 11: Am and Cm extracted fraction with the TRU<sup>TM</sup> resin*

258 This speciation computation study points up a noticeable difference in the hydrolysis constants  
 259 of Am and Cm. Moreover,  $\text{AmH}_2\text{PO}_4^{2+}$  seems to be more stable than  $\text{CmH}_2\text{PO}_4^{2+}$  and a small  
 260 difference between formation's constants of  $\text{Cm}_2(\text{Ox})_3 \cdot 10 \text{ H}_2\text{O}$  and  $\text{Am}_2(\text{Ox})_3 \cdot 7 \text{ H}_2\text{O}$  was  
 261 observed. The literature described a higher affinity of americium to the TRU<sup>TM</sup> resin [10]. Cm  
 262 and Am behaviors are indistinguishable during all the other steps of our protocol. In fact, in  
 263 spite of a slight difference between extractions of Am and Cm by ammonium  
 264 dinonylnaphthalene sulphonate in moderate thiocyanate concentration solutions [26], behaviors  
 265 of Am and Cm during the separation using TEVA<sup>TM</sup> resin were similar. Finally, since  
 266 americium and curium complexes are not retained on the AG<sup>®</sup> 1-X4 resin over the entire  $\text{HNO}_3$   
 267 concentration range, any difference between their behaviors during this step can be dismissed  
 268 [27].

269 When analyzing environmental samples, difference between Am and Cm behaviors could be  
 270 more noticeable and not predictable. Due to the importance of curium analysis in some of the  
 271 environmental samples (e.g. samples from the surrounding of reprocessing plants), the  
 272 quantification has to be reliable. The only known standard containing  $^{248}\text{Cm}$  was then bought  
 273 from the Oak Ridge National Laboratory. Activity concentrations of this standard are not

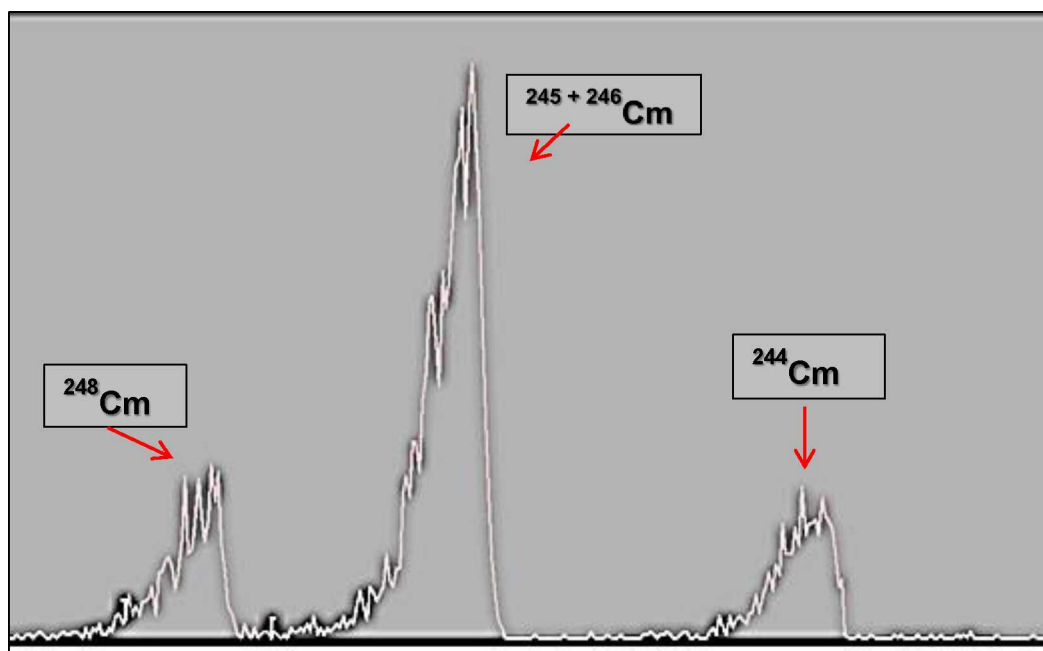
274 certified and associated uncertainties are not communicated. The total  $^{248}\text{Cm}$  content was  
275 however measured to be  $6.6\ \mu\text{g}$  ( $\sim 1012\ \text{Bq}$ ) and the total volume of the solution was  $5\ \text{mL}$  at  
276  $2.0\ \text{M HCl}$ . Table 2 presents the announced isotopic composition of the material.

277 *Table 2: certified isotopic composition of the material*

Isotope	Atom (%)	Weight (%)
$^{244}\text{Cm}$	< 0.02	< 0.02
$^{245}\text{Cm}$	0.06	0.06
$^{246}\text{Cm}$	4.12	4.09
$^{247}\text{Cm}$	0.02	0.02
$^{248}\text{Cm}$	95.78	95.82

278

279 Figure 12 presents the alpha spectra of the material. This spectra was obtained by counting a  
280 lanthanum fluoride precipitate of  $\sim 0.02\ \text{Bq}$  of the material during 69h.



281

282 *Figure 12: alpha spectra of the used standard*

283 Alpha spectrometry highlighted that despite the fact  $^{244}\text{Cm}$  presence is low, it represents 5.4 %  
 284 of  $^{248}\text{Cm}$  net count.  $^{244}\text{Cm}$  presence in the radioactive material has then to be taken into account.  
 285 However,  $^{243}\text{Am}$  emits at 5275.3 keV with an intensity of 93.2 % while  $^{245}\text{Cm}$  and  $^{246}\text{Cm}$  emit  
 286 at respectively 5361.8 keV (93.2 %) and 5387.5 keV (86.74 %). The addition of both tracers  
 287 ( $^{243}\text{Am}$  and  $^{248}\text{Cm}$ ) is then not possible and two replicates of the sample are needed in order to  
 288 analyze americium and curium.

289 In order to verify activity concentrations of curium isotopes and determine uncertainties  
 290 associated to each concentration, a diluted fraction of the purchased radioactive material was  
 291 doped with a known amount of a certified  $^{244}\text{Cm}$  tracer solution and analyzed. This  $^{244}\text{Cm}$  tracer  
 292 solution was previously analyzed and no significant  $^{248}\text{Cm}$  activity concentration was detected  
 293 above our detection limit. Table 3 shows expected and measured activities concentrations of  
 294  $^{248}\text{Cm}$  and  $^{245+246}\text{Cm}$ .

295 *Table 3: expected and measured activity concentrations*

	expected activity concentrations		Measured activity concentrations	
	Activity ( $\text{Bq.g}^{-1}$ )	Uncertainty (%)	Activity ( $\text{Bq.g}^{-1}$ )	Uncertainty (%)
$^{248}\text{Cm}$	$6.29 \times 10^{-2}$	-	$6.26 \times 10^{-2}$	7.52
$^{245+246}\text{Cm}$	$2.29 \times 10^{-1}$	-	$2.27 \times 10^{-1}$	6.81

296  
 297 Results presented in table 3 show that the measured activity concentrations are consistent with  
 298 the calculated ones. Furthermore, this characterization step allowed the determinations of  
 299 associated uncertainties.

300 In order to validate the use of the newly purchased  $^{248}\text{Cm}$  tracer solution for curium isotopes  
 301 quantification, water, soil and tea samples were spiked to be analyzed. In fact, although a few

302 environmental reference materials are containing curium, none has been reliably certified. Tea  
303 and soil samples were from previous proficiency tests intended to americium isotopes analysis.  
304 Water, soil and tea samples were analyzed before the spike and no significant  $^{244}\text{Cm}$  activity  
305 concentration was detected above our detection limit.

306 The quantification was based on the isotopic dilution technique, where the activity of each  
307 isotope is calculated using equation 4 [11].

$$308 \quad A = \frac{A_T \times N_{net} \times E_T}{N_{netT} \times m \times E} \quad \text{Eq. (4)}$$

309 Where  $A_T$  is the added activity of the tracer ( $^{248}\text{Cm}$ ),  $N_{net}$  are counts of the studied isotope  
310 ( $^{244}\text{Cm}$ ) corrected from the background and from the impurity in the tracer solution,  $N_{netT}$  are  
311 the counts of the tracer ( $^{248}\text{Cm}$ ),  $m$  is the sample quantity,  $E$  and  $E_T$  are respectively emitting  
312 rates of the studied isotope and the tracer.

313 Table 4 presents spiked and measured activities of  $^{244}\text{Cm}$  in tea, soil and water samples.

314 *Table 4: spiked and measured activity concentrations of <sup>244</sup>Cm in tea, soil and water samples*

Spiked activity, <sup>244</sup> Cm (k=2)			Experimental activity, <sup>244</sup> Cm (k=2)			Standard deviation	Relative deviation
<b>Tea samples (Bq/kg, ashes)</b>							
0,29	±	0,01	0,32	±	0,09	0,34	11 %
0,28	±	0,01	0,28	±	0,08	0,05	1 %
0,91	±	0,05	0,90	±	0,18	0,04	1 %
0,91	±	0,05	0,92	±	0,17	0,06	1 %
4,28	±	0,21	4,32	±	0,78	0,05	1 %
4,11	±	0,21	4,07	±	0,81	0,05	1 %
<b>Soil samples (Bq/kg, ashes)</b>							
0,29	±	0,01	0,31	±	0,09	0,31	10 %
0,91	±	0,05	0,82	±	0,17	0,47	9 %
4,18	±	0,21	3,68	±	0,74	0,66	12 %
<b>Water samples (Bq/L)</b>							
5,00	±	0,25	4,88	±	0,49	0,23	2 %
1,20	±	0,06	1,15	±	0,10	0,42	4 %
1,20	±	0,06	1,09	±	0,10	0,96	9 %
1,20	±	0,06	1,12	±	0,10	0,68	7 %
0,50	±	0,03	0,48	±	0,05	0,34	4 %
0,50	±	0,03	0,45	±	0,05	0,90	10 %
0,50	±	0,03	0,52	±	0,05	0,35	4 %
0,20	±	0,01	0,18	±	0,03	0,69	10 %
0,20	±	0,01	0,23	±	0,03	0,89	14 %

315

316 According to results obtained when analyzing tea, soil and water samples, the use of <sup>248</sup>Cm as  
317 a tracer allows having excellent compatibility between spiked and measured activities even  
318 when analyzing complex matrices such as soil samples. These performances are characterized  
319 by standard deviations lower than 1 and relative deviations lower than 15 %. Results presented  
320 in table 4 are more reliable and accurate since activity concentrations determination is based on  
321 an isotopic tracer.

## 322 **Conclusion**

323 Curium origins in environmental samples are mostly due to regulatory releases from fuel  
324 reprocessing plants (e.g. La Hague, Sellafield...) and fallout following major nuclear accidents.  
325 Quantification of curium isotopes in environmental samples is frequently based on isotopic  
326 dilution using  $^{243}\text{Am}$  as a tracer. This procedure shows a few drawbacks since it generates a  
327 bias between americium and curium behaviors. The speciation computation studied in this work  
328 permitted to conclude that this bias is mostly due to differences in the hydrolysis constants of  
329 americium and curium, in the formation constants of  $\text{Cm}_2(\text{Ox})_3 \cdot 10 \text{H}_2\text{O}$  and  $\text{Am}_2(\text{Ox})_3 \cdot 7 \text{H}_2\text{O}$ ,  
330 in the stability constants of  $\text{AmH}_2\text{PO}_4^{2+}$  and  $\text{CmH}_2\text{PO}_4^{2+}$  and in affinities of americium and  
331 curium for the TRU<sup>TM</sup> resin in 1 M  $\text{HNO}_3$  solution. In order to prevent the observed bias in  
332 quantified curium activities, a new standard was reliably characterized and used to quantify  
333 curium isotopes in spiked environmental samples (e.g. water, tea and soil samples). The new  
334 procedure is based on isotopic dilution using  $^{248}\text{Cm}$  as tracer. Excellent results were obtained  
335 for the analyzed samples. The characterization and the use of a specific curium tracer, even  
336 when it's not reliably certified, to quantify curium isotopes is then recommended since it allows  
337 having more consistent results.

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