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

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Keywords

Curium, americium, environmental samples, speciation, ²⁴⁸Cm

Abstract

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

Introduction

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

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

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

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

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

Reagents and instrumentation

Reagents

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

Tracer solutions were conserved in acidic media (1 – 4 M of HNO_3) and purchased from the NIST, NPL, AEA Technology and ORNL for ^{242}Pu (SRM 4334j), ^{243}Am (A14063), ^{244}Cm (CLP 10010) and ^{248}Cm (8R103CMPROD), respectively.

Instrumentation

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

Experimental procedure

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

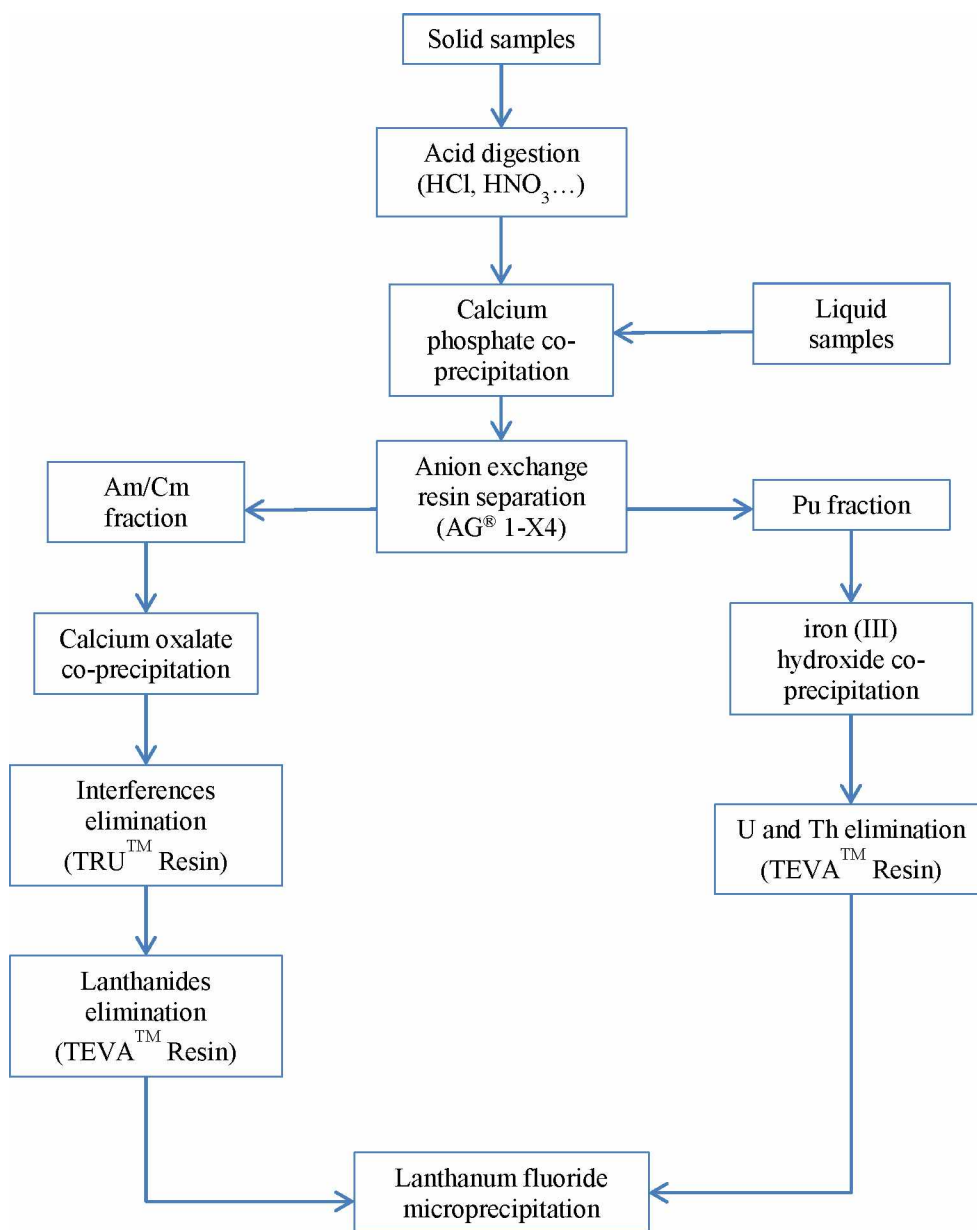


Figure 1: experimental procedure for americium and curium quantification in environmental samples

The first step of the experimental procedure consists on the addition of tracers (^{242}Pu and ^{243}Am) to 5 g of solid samples (e.g. soil, sediment, vegetables...) or 500 mL of liquid samples (e.g. drinking water, surface water...).

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

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

After the elimination, by centrifugation, of the undissolved residue, plutonium and americium/curium phosphates are precipitated by adding 10 mL of calcium phosphates and ammonium hydroxide (20 %) to adjust the pH at 8-9. Once the precipitate is centrifuged, it's dissolved by adding 100 mL of 7 M HNO₃. Valence adjustment is then performed with ~ 200 mg of NaNO₂.

Plutonium is extracted from the sample using a column containing ~ 5 g of AG[®] 1-X4 50 – 100 mesh (Anion Exchange Resin) previously washed with H₂O and pre-conditioned with 30 mL of 7 M HNO₃. The sample is loaded through the column. The resin is then rinsed with 2 x 30 mL and 40 mL of 7 M HNO₃. The loaded sample and the rinsing fractions are collected to be treated afterward since containing americium and curium (*fraction 2*). The column is then rinsed 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 hydroxylamine Hydrochloride. The elution fraction is evaporated to dryness and the residue is dissolved with 100 mL of 1 M HNO₃. Plutonium is precipitated by adding 5 mL of iron (III) nitrate, previously prepared by dissolving 30 g of Fe(NO₃)₃ in 1 L of 0.01 M of HNO₃, and ammonium hydroxide (20 %) to adjust the pH at least at 9. The precipitate is centrifuged and dissolved with 30 mL of 7 M HNO₃. 10 mL of 750 g/L of Al(NO₃)₃ · 9H₂O and ~ 100 mg of NaNO₂ are then added to the previously dissolved precipitate. The sample is purified from the remaining uranium and thorium with a TEVA[™] resin. After the conditioning with 20 mL of 3 M HNO₃ and the sample loading, the TEVA[™] resin is rinsed with 20 mL of 3 M HNO₃, 20 mL of 0.5 M HNO₃ to eliminate uranium, 50 mL of 6 M HCl to eliminate thorium and again with 20 mL of 3 M HNO₃. Plutonium is finally eluted with 2 x 30 mL of a solution of 0.2 M of 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 HNO₃ 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 HNO₃. Americium and
114 curium are extracted using a TRUTM 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 HNO₃ 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 TEVATM 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 TEVATM 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 ²⁴²Pu tracer is used for ²³⁸Pu and
129 ²³⁹⁺²⁴⁰Pu quantification and ²⁴³Am tracer used for ²⁴¹Am, ²⁴²Cm and ²⁴³⁺²⁴⁴Cm 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

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

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

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

An attempt to experimentally determine the correction factor was done by our team. This determination was done using 11 spiked water samples and samples from proficiency tests with ^{244}Cm activities ranging from 2 mBq.L⁻¹ to 10 Bq.mL⁻¹. The calculated correction factors are presented in figure 2.

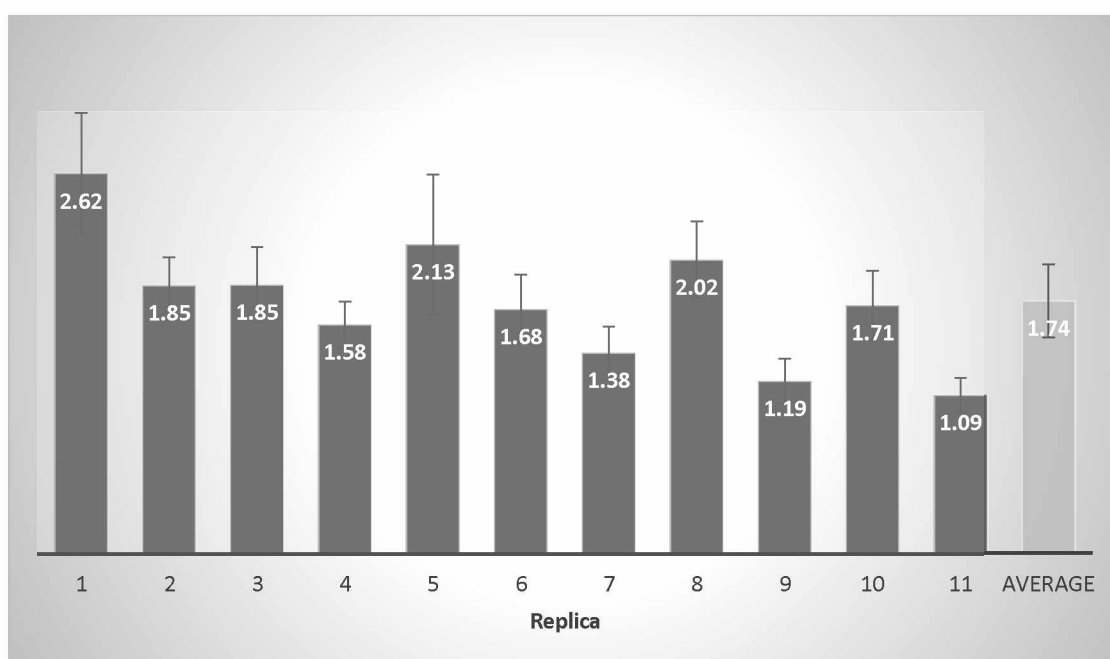


Figure 2: experimentally determined correction factors

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 (~ 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}Cm , were analyzed using the
 151 procedure described in figure 1 and ^{243}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}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 ^{244}Cm activities with and without a*
161 *correction factor in water samples*

Sample	Theoretical ^{244}Cm activities, Bq/L (k=2)	Calculated ^{244}Cm activities, Bq/L (k=2)	SD of ^{244}Cm	SD of ^{244}Cm (With correction factor)	RD of ^{244}Cm	RD of ^{244}Cm (With correction factor)
1	14.6 ± 2.2	25.4 ± 5.4	7.96	2.22	62 %	34 %
2	213.0 ± 19.2	369.8 ± 65.8	6.33	0.34	46 %	6 %
3	2.2 ± 0.3	3.9 ± 0.8	5.30	0.32	46 %	6 %
4	6.8 ± 0.7	11.9 ± 2.2	5.75	0.50	37 %	10 %
5	20.2 ± 4.4	35.0 ± 9.4	4.55	0.82	53 %	18 %
6	106.7 ± 13.9	185.3 ± 37.3	4.39	0.14	41 %	3 %
7	2.4 ± 0.3	4.2 ± 0.9	2.93	1.02	28 %	26 %
8	7.8 ± 1.0	13.5 ± 2.7	6.38	0.81	51 %	14 %
9	197.1 ± 23.7	342.3 ± 66.7	1.46	1.57	16 %	46 %
10	9.1 ± 1.2	15.7 ± 3.2	4.53	0.07	42 %	2 %
11	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 ^{244}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 ^{243}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.

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

The first studied step was the calcium phosphates co-precipitation (figures 3 and 4) [15–17]. This co-precipitation is performed at $\text{pH} \geq 8$. According to the previously described procedure, during this step, PO_4^{3-} concentration is ~ 30 mM and Ca^{2+} concentration is 45 mM. At pH higher than 8, the present calcium phosphate complex is $\text{Ca}_5(\text{PO}_4)_3\text{OH}_{(\text{s})}$. Figures 3 and 4 show the fractions of Am and Cm complexes during the co-precipitation step.

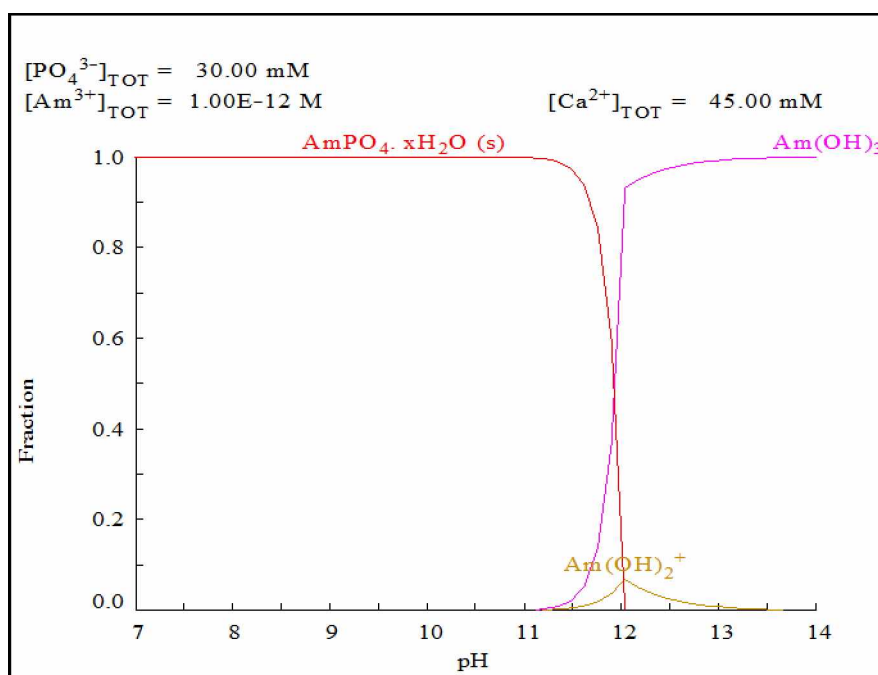


Figure 3: speciation of americium during the calcium phosphates co-precipitation step

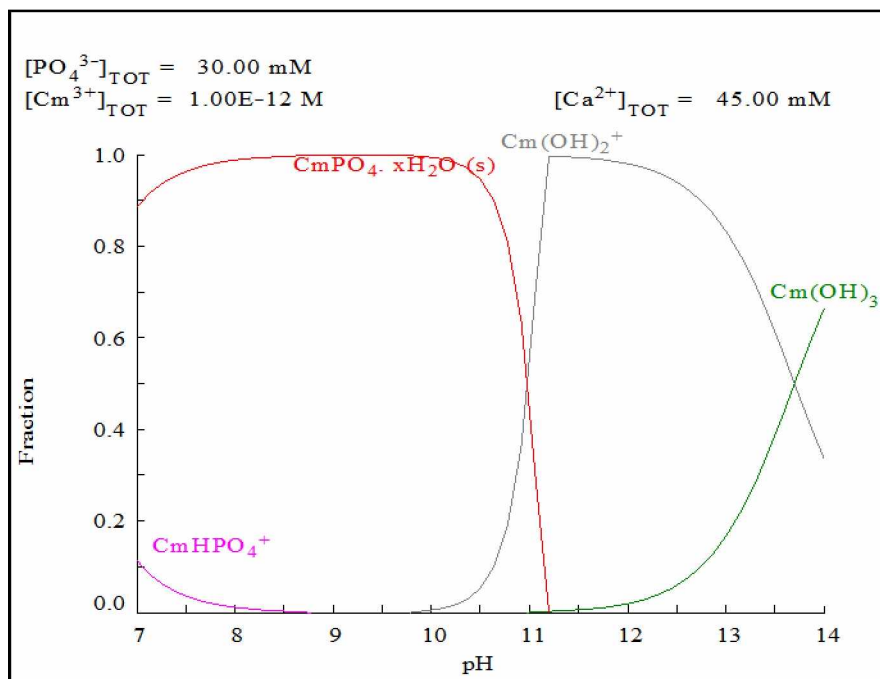


Figure 4: speciation of curium during the calcium phosphates co-precipitation step

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

The second studied step is the precipitated complexes dissolution using 7 M HNO_3 [18–20]. During this step we suppose that all the present Am^{3+} and Cm^{3+} are under the forms $\text{AmPO}_4 \cdot x \text{H}_2\text{O(s)}$ and $\text{CmPO}_4 \cdot x \text{H}_2\text{O(s)}$. However, since during the previous step, 100 % of Ca is precipitated under the form $\text{Ca}_5(\text{PO}_4)_3\text{OH(s)}$, Ca^{2+} and PO_4^{3-} concentrations are respectively at 45 mM and 30 mM during this step. NO_3^- concentration is 7 M during this step. The aim of 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. Figures 5 and 6 present the speciation of Am^{3+} and Cm^{3+} during this step as a function of the pH.

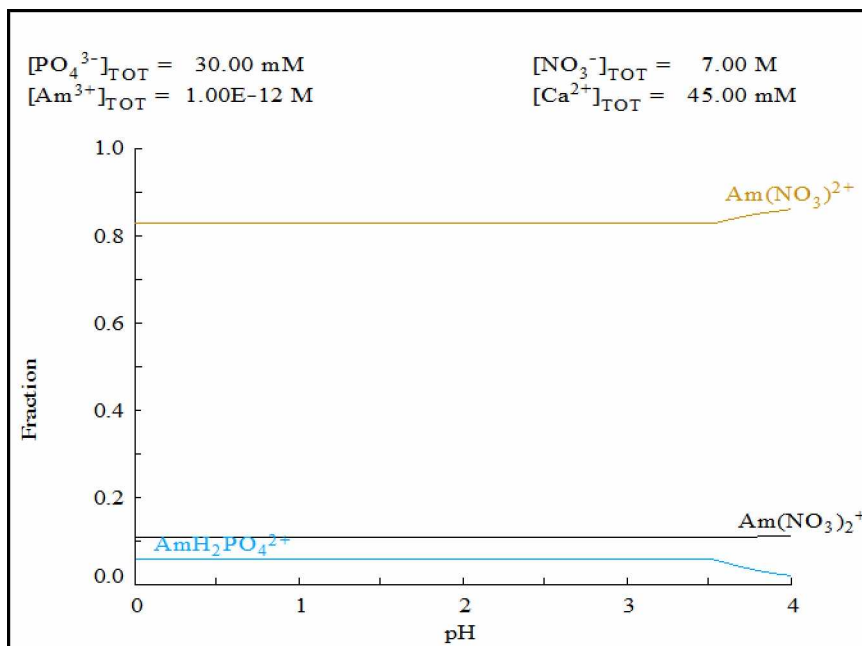


Figure 5: speciation of americium during the phosphates dissolution step

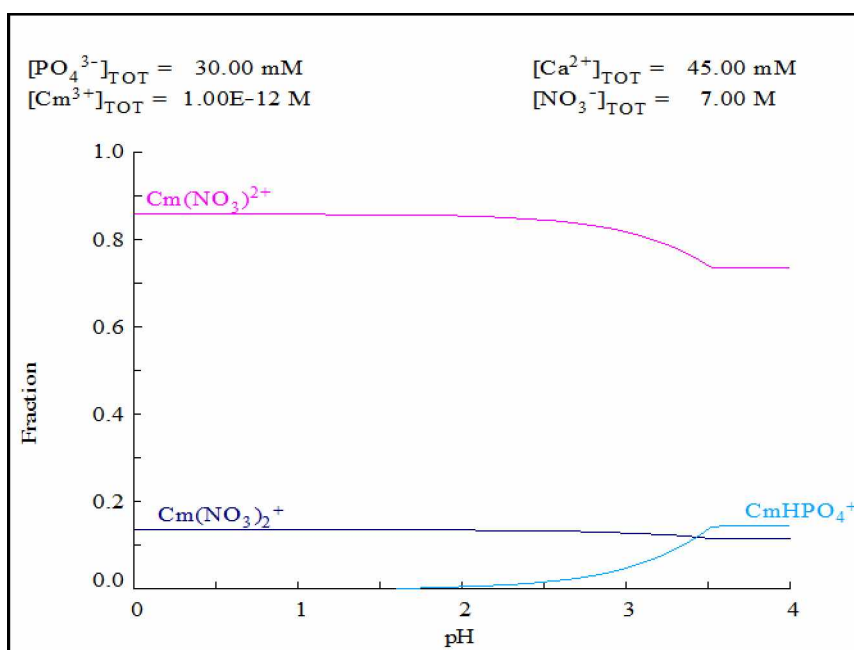


Figure 6: speciation of curium during the phosphates dissolution step

Figures 5 and 6 shows that during the phosphate complexes dissolution with 100 mL 7 M HNO₃ (pH < 1), 100 % of curium is under the form of aqueous nitrate complexes. On the other hand, ~ 6 % of Am is not under the form of aqueous nitrate complexes but remains under the form

AmH₂PO₄²⁺. This aqueous americium complex fraction will not have the same behavior during the separation step on the AG[®] 1-X4 resin.

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

During this step, NO₃⁻, Ca²⁺ and PO₄³⁻ concentrations are still at respectively 7 M, 45 mM and 30 mM. Moreover, according to the previously described procedure, oxalic acid (OxH₂) concentration is at 0.7 M.

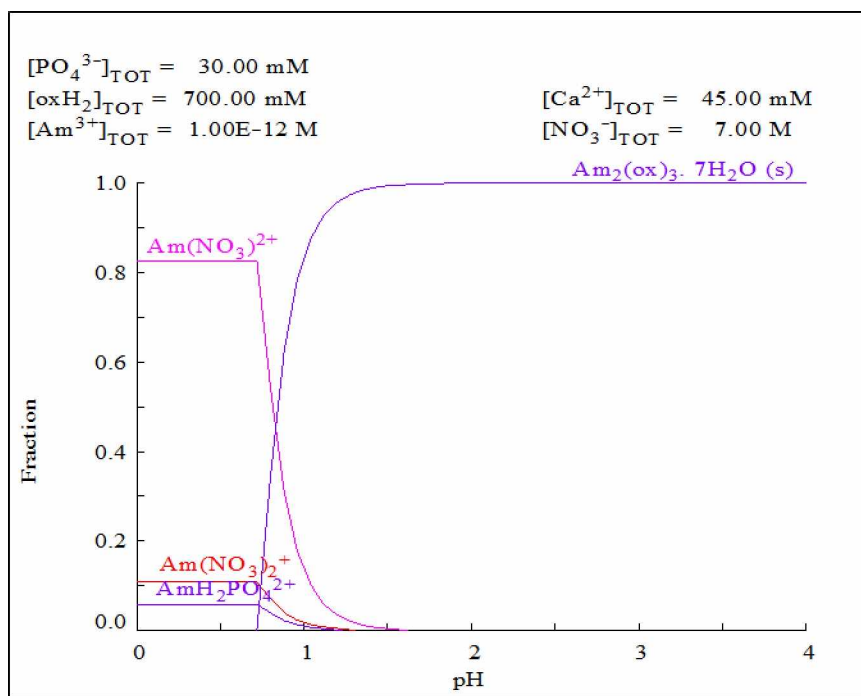


Figure 7: speciation of americium during the calcium oxalates co-precipitation step

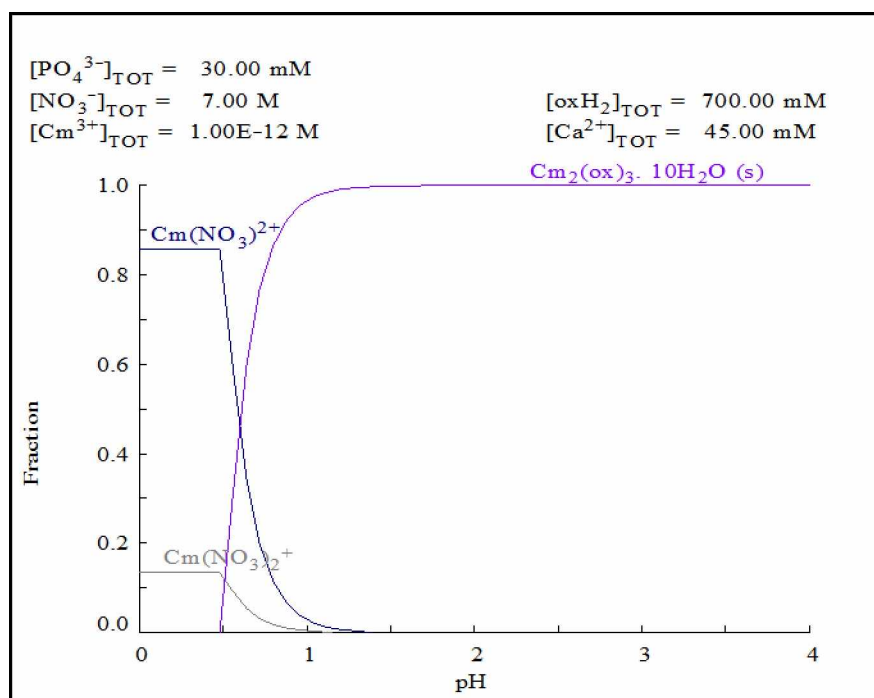


Figure 8: speciation of americium during the calcium oxalates co-precipitation step

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 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 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 difference. Cm and Am remaining in solution are under the form of aqueous nitrate complexes. Furthermore at pH 1.5, 99.9 % of both Cm and Am precipitate as oxalate complexes. The pH adjustment step is then very important and a slight variation could influence Am and Cm forms.

After the recovery of the carrier, oxalate complexes were converted to carbonate complexes with 7 M HNO_3 under heating [20, 22, 23]. Speciation of americium and curium during this step are presented in figures 9 and 10. Since during the previous step, 100 % of Ca^{2+} is precipitated under the form of $\text{CaC}_2\text{O}_4(\text{s})$, Ca^{2+} concentration is still at 45 mM during this step. At $[\text{NO}_3^-] = 7 \text{ M}$, ~ 99 % of curium and americium are present as aqueous nitrate complexes. In contrary to the previously steps, the dissolution of the carbonate complexes carrier does not imply any differences between americium and curium behaviors.

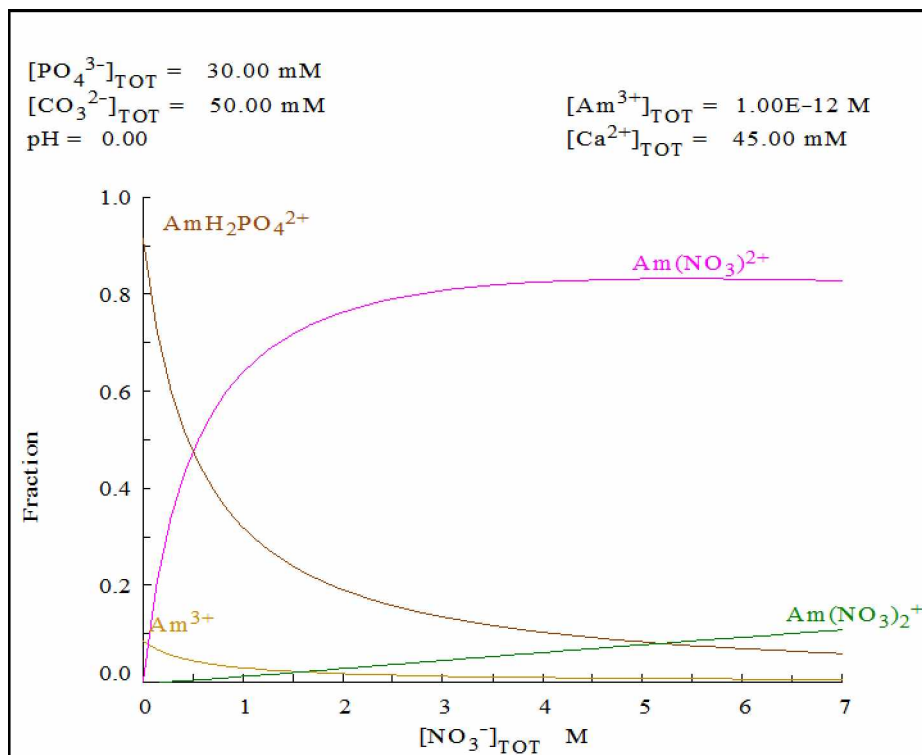


Figure 9: speciation of americium during the carbonates dissolution step

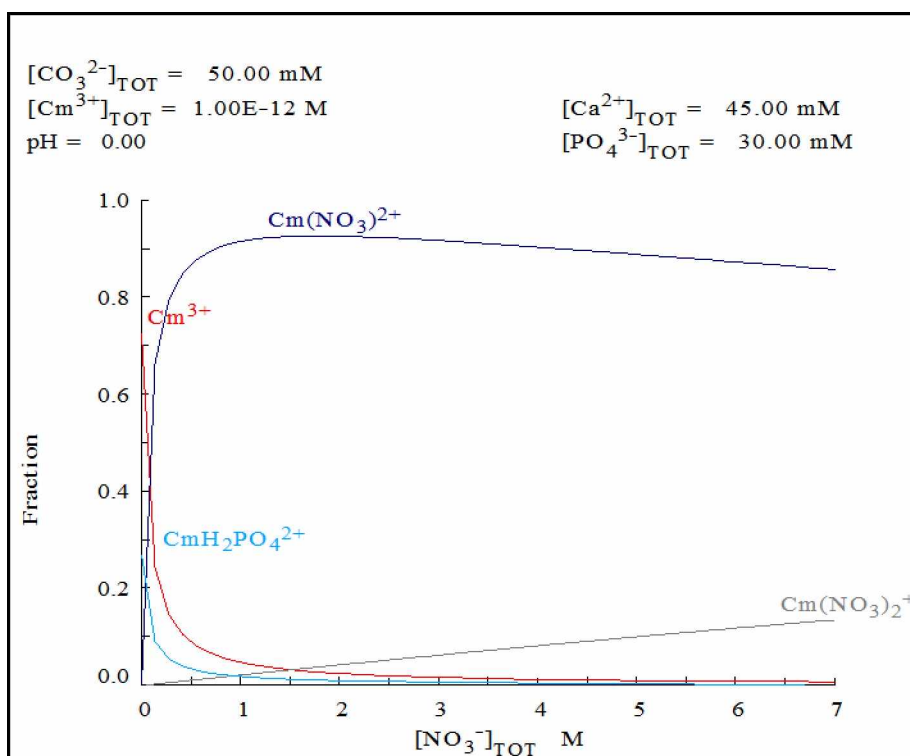


Figure 10: speciation of curium during the carbonates dissolution step

236 Speciation of americium and curium during the separation using the TRUTM 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 TRUTM resin were studied
239 by Gharibyan et al.[10]. In this study, minor variations between Cm and Am behaviors at 1 M
240 HNO₃ 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 TRUTM 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 HNO₃.

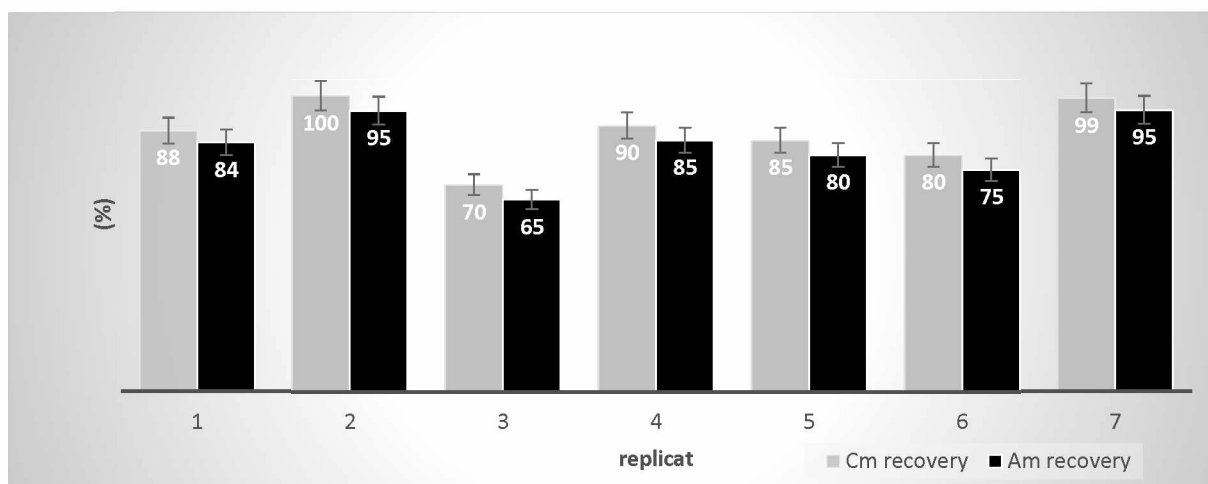


Figure 11: Am and Cm extracted fraction with the TRU™ resin

This speciation computation study points up a noticeable difference in the hydrolysis constants 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 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 observed. The literature described a higher affinity of americium to the TRU™ resin [10]. Cm and Am behaviors are indistinguishable during all the other steps of our protocol. In fact, in spite of a slight difference between extractions of Am and Cm by ammonium dinonylnaphthalene sulphonate in moderate thiocyanate concentration solutions [26], behaviors of Am and Cm during the separation using TEVA™ resin were similar. Finally, since americium and curium complexes are not retained on the AG® 1-X4 resin over the entire HNO_3 concentration range, any difference between their behaviors during this step can be dismissed [27].

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

certified and associated uncertainties are not communicated. The total ^{248}Cm content was 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 $2.0\ \text{M HCl}$. Table 2 presents the announced isotopic composition of the material.

Table 2: certified isotopic composition of the material

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

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

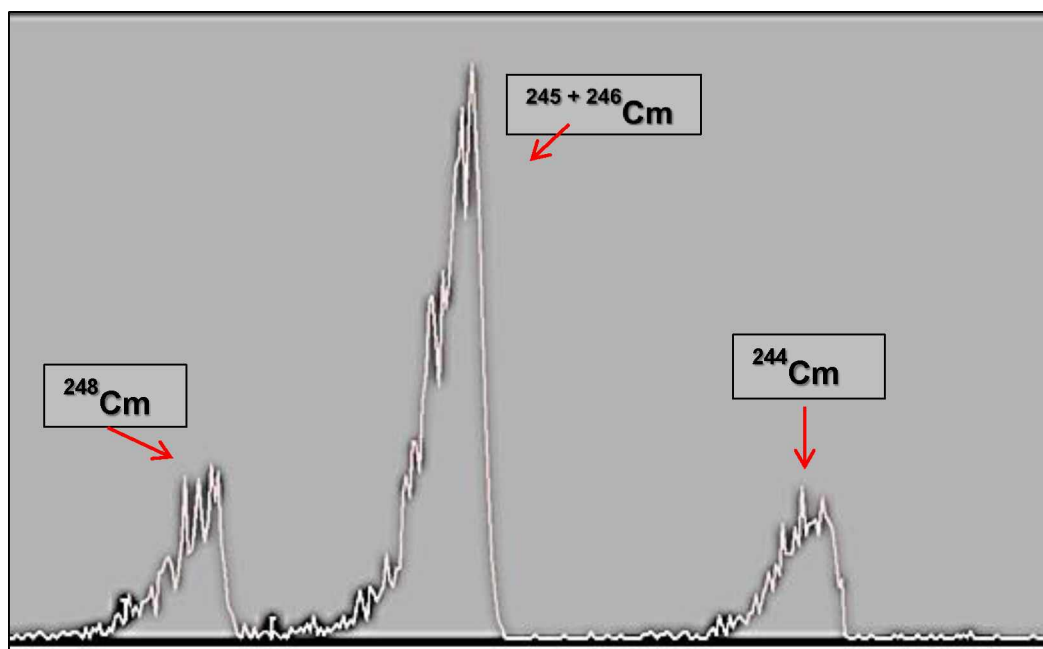


Figure 12: alpha spectra of the used standard

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

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

Table 3: expected and measured activity concentrations

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

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

In order to validate the use of the newly purchased ^{248}Cm tracer solution for curium isotopes 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}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
$$A = \frac{A_T \times N_{net} \times E_T}{N_{netT} \times m \times E} \quad \text{Eq. (4)}$$

309 Where A_T is the added activity of the tracer (^{248}Cm), N_{net} are counts of the studied isotope
310 (^{244}Cm) corrected from the background and from the impurity in the tracer solution, N_{netT} are
311 the counts of the tracer (^{248}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}Cm in tea, soil and water samples.

314 *Table 4: spiked and measured activity concentrations of ^{244}Cm in tea, soil and water samples*

Spiked activity, ²⁴⁴ Cm (k=2)			Experimental activity, ²⁴⁴ Cm (k=2)			Standard deviation	Relative deviation
Tea samples (Bq/kg, ashes)							
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 %
Soil samples (Bq/kg, ashes)							
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 %
Water samples (Bq/L)							
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 ^{248}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.

Conclusion

Curium origins in environmental samples are mostly due to regulatory releases from fuel reprocessing plants (e.g. La Hague, Sellafield...) and fallout following major nuclear accidents. Quantification of curium isotopes in environmental samples is frequently based on isotopic dilution using ^{243}Am as a tracer. This procedure shows a few drawbacks since it generates a bias between americium and curium behaviors. The speciation computation studied in this work permitted to conclude that this bias is mostly due to differences in the hydrolysis constants of americium and curium, in the formation constants of $\text{Cm}_2(\text{Ox})_3 \cdot 10 \text{ H}_2\text{O}$ and $\text{Am}_2(\text{Ox})_3 \cdot 7 \text{ H}_2\text{O}$, 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 curium for the TRUTM resin in 1 M HNO_3 solution. In order to prevent the observed bias in quantified curium activities, a new standard was reliably characterized and used to quantify curium isotopes in spiked environmental samples (e.g. water, tea and soil samples). The new procedure is based on isotopic dilution using ^{248}Cm as tracer. Excellent results were obtained for the analyzed samples. The characterization and the use of a specific curium tracer, even when it's not reliably certified, to quantify curium isotopes is then recommended since it allows having more consistent results.

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