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Alpha-spectrometry measurement of Am and Cm at trace levels in environmental samples using extraction chromatography

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Abstract

Various anthropogenic sources contribute to the presence of americium and curium isotopes in environmental samples. Incomplete radiochemical separations led to electrodeposited sources containing stable element impurities increasing auto-absorption effects. Other radioactive elements, such as ^{227}Ac and its daughters, interfered with ^{241}Am and ^{243,244}Cm emissions. These impurities are now completely eliminated using a Tru-Spec® column. Very low levels of ^{241}Am and ^{243,244}Cm in environmental samples (i.e. algae, mussels, sediment, etc.) from the Channel and the Rhône river, including its estuary, were investigated using a routine radiochemical process and measurement at levels as low as achievable with state of the art measuring technology. © 1998 Elsevier Science S.A.

Keywords: Alpha-spectrometry; Radiochemical separation; Americium; Curium; Environmental contamination

1. Introduction

Actinides are commonly present at trace levels in the environment due to global fallout of the atmospheric explosion of nuclear devices and satellite failures and reentry. On a regional scale, they can be found at slightly more significant levels, although still low, due to local discharges of effluents from nuclear reprocessing plants. These releases, both authorized and accidental, contribute to low levels of plutonium isotopes, ^{241}Am and ^{243,244}Cm in natural environments. The Institute for Protection and Nuclear Safety (IPSN) is studying the Am and Cm concentrations to constitute the baseline around nuclear sites. It is investigating the relevant transfer pathways and processes in components of natural and man-made ecosystems. The impact assessment of these radionuclides led the Laboratoire de Mesure de la Radioactivité de l'Environnement (LMRE) to focus on the measurement at levels in environmental matrices as low as achievable with state-of-the-art measuring technology.

Among nuclear techniques, α-spectrometry offers a high-energy resolution. The use of low-background semiconductor detectors makes this technique particularly sensitive for the measurement of very low activities of actinides. The simultaneous availability of new resins improves the element separation selectivity, particularly the development of sequential steps in a common scheme to extract and purify Pu isotopes, ^{241}Am and ^{243,244}Cm. Curium and Am have similar chemical properties but, in natural environments, ^{243,244}Cm is found at even lower levels than ^{241}Am. This requires the assay of samples of large size and the use of radiochemical procedures adapted to low-level activities. Environmental samples, such as soils and sediments, contain large amounts of natural α-emitters, mainly those of the Th and Ac series, that can interfere with Am and Cm when using α-counting methods. Artificial α-emitters, such as ^{238}Pu, must be eliminated since they interfere with the ^{241}Am lines. As for Pu measurement, biases may be introduced if those elements are not isolated in a pure form before measurement [1]. Trivalent metals and rare earth elements (R.E.E.) are, by virtue of their valence, III, far more stable, and have similar properties in respect of Am and Cm, and must therefore be specifically removed. A variety of procedures for Am and Cm separation were tested in order to optimize the radiochemical procedure to very low background equipment. Three different radiochemical procedures were chronologically implemented at LMRE and compared. The main constraint for the new protocol was to obtain a high recovery yield, a high-energy resolution and low interferences of other α-emitters. The work presented in this paper shows the effectiveness of improvements in terms of extraction chromatography to effect Am and Cm sepa-

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ration without any residual impurity from sediment samples. It likewise demonstrates the use of this method on biological samples.

2. Sample preparation

LMRE-Orsay is in charge of radionuclide measurements at trace levels in environmental matrices. The LMRE premises are thus provided with filtered air so as to limit the impact of a possible external source of contamination. The air is constantly renewed to reduce radon and radon daughters. Detectors are located in two rooms, two storeys below ground level, with a controlled atmosphere (filtration and temperature) under a 3-m thick borium concrete slab to reduce the highly unlikely impact of cosmic rays. In order to test different protocols on various matrices, samples of soil, sediment, milk, algae, molluscs and crustaceans were selected from a collection of samples gathered all over the French territory for different studies (see Fig. 1). Samples were dried, sifted to 0.2 mm, then ashed at 480°C during 10 h. The mass taken for analyses was within the range 100–200 g for soil and sediment, and 20–50 g for biological ashes. All samples were tested for Pu isotopes, ^{241}Am and ^{243,244}Cm. To determine the recovery yield of ^{241}Am and ^{243,244}Cm, all samples were spiked with ^{243}Am (Harwell Standard Reference Material 95/243/41) immediately after ashing.

3. Radiochemical procedure

3.1. Sample dissolution

Samples are leached (at 80–90°C during 24 h) with concentrated nitric acid and hydrogen peroxide, 200–400

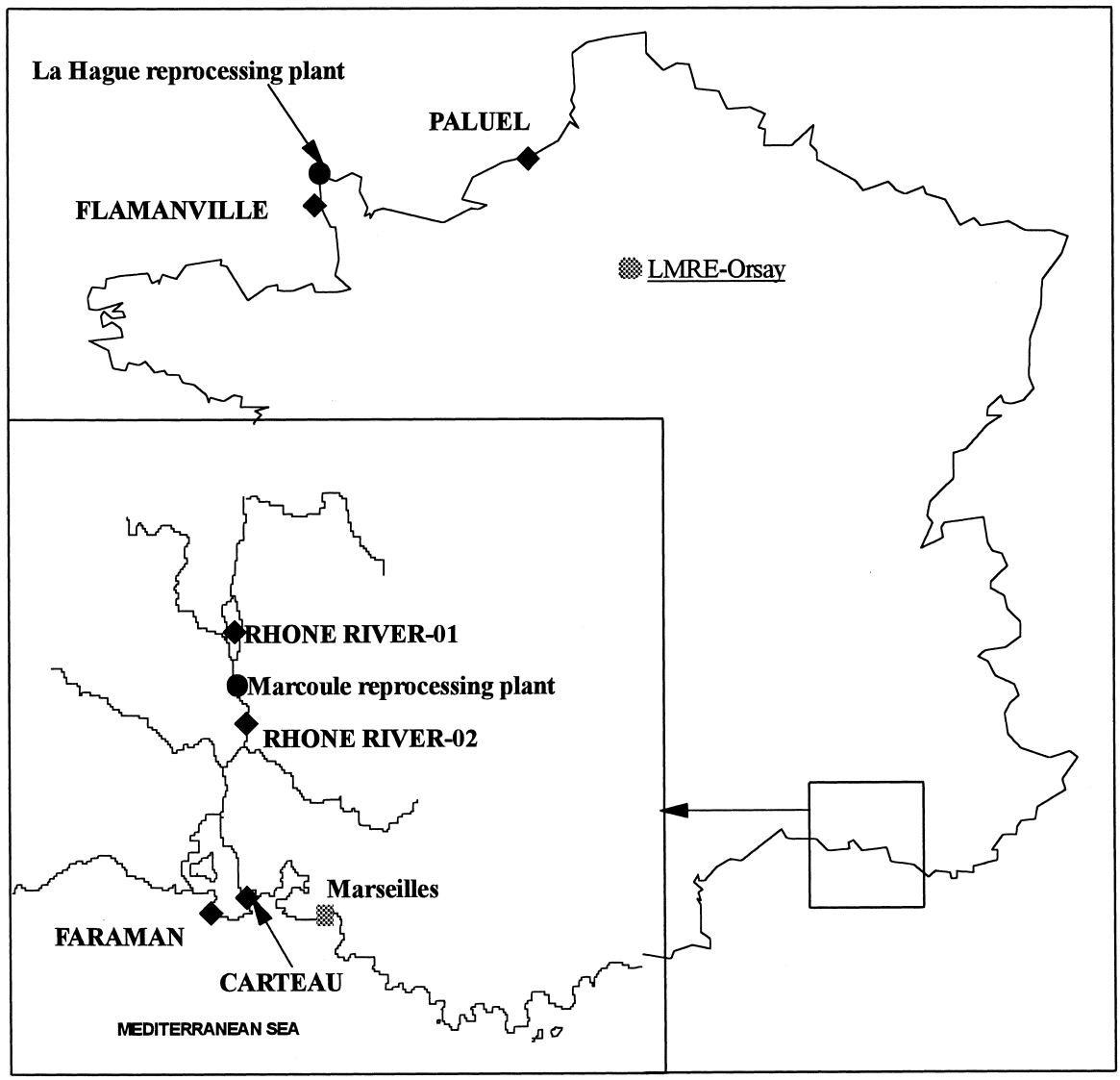

Fig. 1. Location of sampling sites (♦) and reprocessing plants (●).

and 50–100 ml for soil and sediment samples and for other matrices, respectively. After centrifugation, the residue is leached a second time with 8 M nitric acid. The acid solutions and the last deionized wash water of the insoluble fraction are combined and evaporated until colloidal silica appears. After centrifugation, silica is treated with hydrofluoric acid. Samples are then treated with two different protocols according to their stable element content: soils, sediments and vegetables with high iron content are distinct from meat, bones, fish and fruit with high calcium phosphate contents. Actinides in the leached samples with high iron contents are co-precipitated with three successive precipitation cycles. The first one yields calcium oxalate at pH 1.5. After drying, precipitates are decomposed into calcium carbonates at 550°C, which are dissolved in 9 M hydrochloric acid. Actinides are then co-precipitated with iron hydroxide at pH 8.5. The precipitate is dissolved in nitric acid, and a second calcium oxalate is formed at pH 1.5. The calcium oxalate is destroyed by heating with nitric acid and hydrogen peroxide. The solution is evaporated to dryness and the residue is dissolved in 8 M nitric acid.

For samples with high phosphate content, the first cycle of precipitation yields a manganese hydroxide at pH 8. The addition of $KMnO_4$ and then nitric acid, to reach pH 4.5, leads to the formation of manganese oxide. This stage is repeated after dissolution of the precipitate in nitric acid in order to eliminate as much as possible of the phosphate element. The second precipitate is dissolved in nitric acid. The solution is evaporated to 30–40 ml and titrated in order to adjust to a 60-ml solution of 8 M nitric acid. At this stage, the solution may contain the different actinides found in environmental samples, U, Th, Np, Pu, Am and Cm isotopes, that must now be separated.

3.2. Separation of Pu from the Am–Cm fraction

Pu(IV) is separated from Am and Cm using an 8 M nitric acid-conditioned anion exchange resin AG1X8 100–200 mesh. The eluate of the sample and 8 M HNO_3 wash may, under these circumstances, contain Am, Cm, U, iron, metals, calcium and R.E.E.

3.3. Purification of the Am–Cm fraction.

The Am–Cm fraction from the AG1X8 column is dissolved in 9 M HCl and loaded onto a double column of AG1X8 and AG50W [2]. Americium, Cm, calcium and R.E.E. are extracted with 9 M HCl, while Th, U, Po, Pu, Np, Fe and some metals are retained. Three different methods have been successively tested on the remaining fraction from the previous separation procedure in order to purify the Am–Cm fraction (see Fig. 2).

The eluate from the double column is evaporated to dryness and redissolved in 93% CH_3OH–1 M HNO_3 in order to separate Am–Cm from the R.E.E. using an

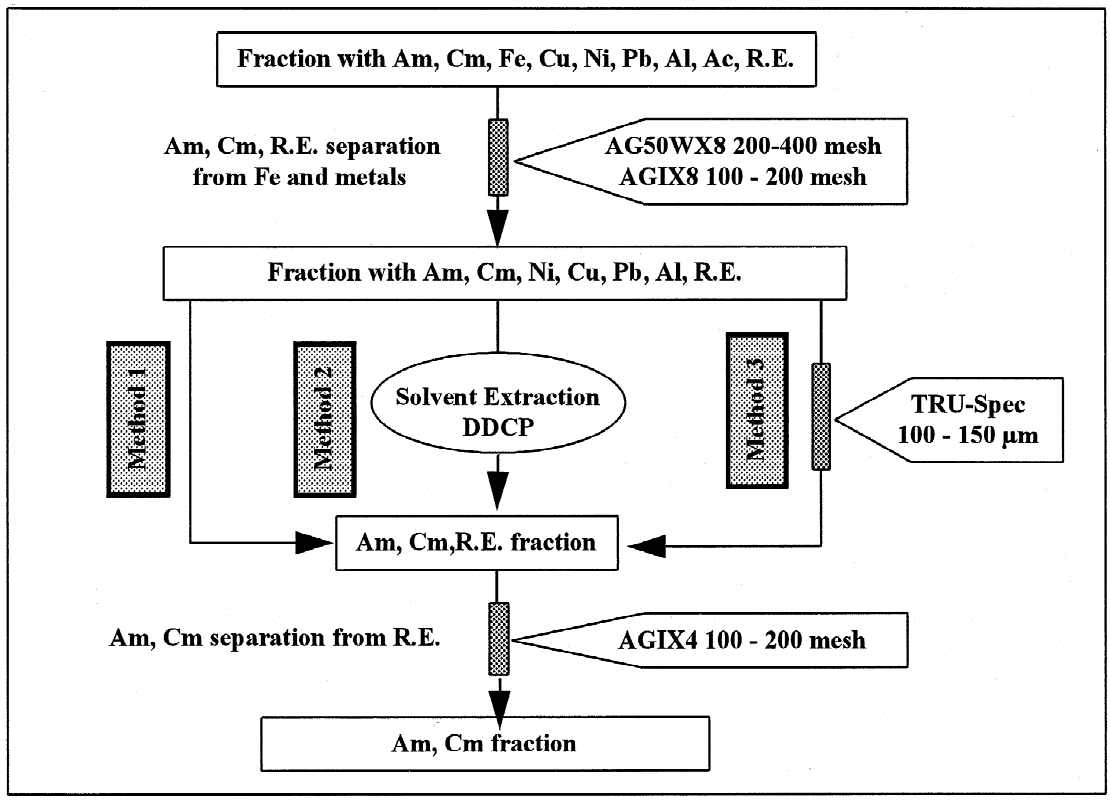

Fig. 2. Schematics of the three methods tested to impove the simultaneous Am and Cm purification.

AG1X4 anion exchange column. The R.E.E. are removed by washing the column with a 0.5 N NH_4SCN–0.1 N HCl–80% CH_3OH system. Thiocyanate ions are removed by washing the column with 93% CH_3OH–1 M HNO_3 before extracting the Am–Cm fraction with 1.5 N HCl–93% CH_3OH. $NaHSO_4$ (5%) solution is added as a carrier before evaporation to dryness [3].

The second method consists of adding a solvent extraction step with DDCP [3]. The sample is dissolved in 12 M nitric acid, and the Am–Cm fraction is extracted in the DDCP organic phase, which is then diluted with toluene. Americium, Cm and R.E.E. are back-extracted with 2 M nitric acid.

The third method consists of replacing the solvent extraction step with an extraction chromatography column, using the commercially available Eichrom material: Truspec® prepacked column. The sample is dissolved in 2 M HNO_3–0.5 M $Al(NO_3)_3$ solution. This column is used to separate the Am, Cm and R.E.E. from the cations (Ca, Cu, Ni, Pb, Zr) remaining at this stage of the protocol. After washing the column with 2 M HNO_3, the Am fraction is extracted with 0.03 M HNO_3.

4. Measurements

The Am–Cm fraction is dissolved with concentrated HNO_3, in deionized water, with 15% Na_2SO_4 and DTPA with pH adjusted to 1.8. The Am and Cm sources are prepared by electrolytic plating onto stainless steel discs: 1 A current during 7200 s with a 5-mm distance between the electrodes. Sources are counted for a minimum of 5×10^5 s for soils and sediments and 10^6 s for biological samples using a low-level background α-spectrometer Oasis® (Eurysis) and Alpha-Analyst® (Canberra). Detectors are 300- and 450-mm^2 passivated implanted planar silicon.

The detection limit is calculated as follows: $K^2+4.5\times K\sqrt{B}$, where K is equal to 1.645 for a 95% confidence value, and B is the background (counts) in the channels of the region of interest [4].

5. Result and discussion

Most soils and sediments contain high Th contents relative to Am and Cm found at ultra-trace levels. When method 1 was used, Th isotopes were not completely removed (see Fig. 3a). The ^{230}Th and the ^{232}Th were identified with the 4010- and 4687-keV lines, respectively. On the other hand, ^{228}Th (α-energy, 5424 keV) could not be directly separated from ^{241}Am (α-energy, 5443 and 5486 keV). Its presence could be suspected from the detection of its daughters: ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Bi and, above all, ^{212}Po, but its contribution to the ^{241}Am region of interest could not be inferred because this isotope is not in radioactive equilibrium with its daughters. The ^{241}Am

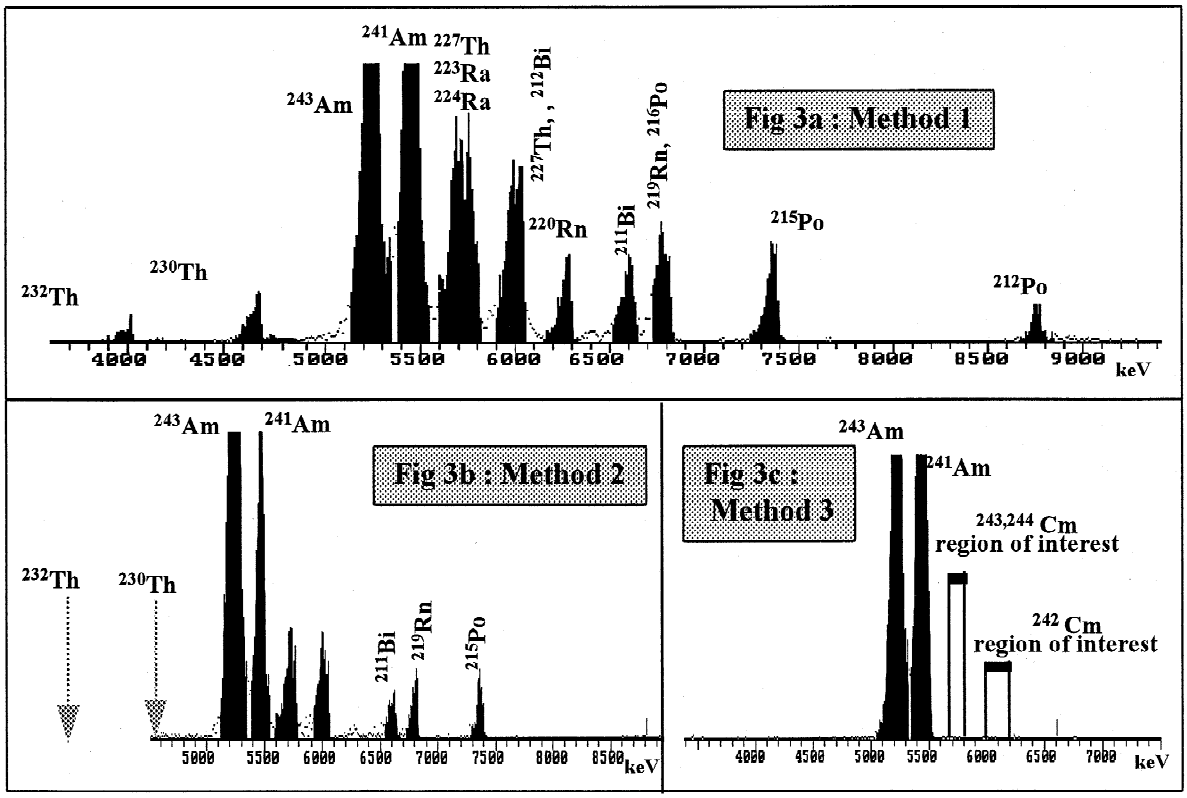

Fig. 3. Spectra obtained with the three radiochemical methods used to eliminate the impurities.

activity or its detection limit could ultimately be corrected considering that the ^{228}Th contribution is equal to the ^{232}Th activity. The presence of ^{223}Ra, ^{219}Rn, ^{215}Po and ^{211}Bi generated by ^{227}Th, and the absence of ^{231}Pa, coming from ^{235}U chain, could also indicate that the ^{227}Th or/and ^{227}Ac are not completely eliminated.

Furthermore, metals such as Cu, Ni, Pb and Zr, present in concentrations of about 10–100 ppm in soils and sediments, are not completely removed after the double-column anionic–cationic step and compromise the Am/R.E.E. separation. The recovery yields are weak, between 15 and 25%, and there is spectrum distortion due to the auto-absorption effect.

For the same type of samples, soils and sediments, method 2 led to the elimination of ^{230}Th and ^{232}Th (see Fig. 3b). The ^{227}Th and its short-lived decay products remained, coming from ^{227}Ac which was not completely eliminated. The detection limit for ^{241}Am was about 1 mBq kg^{-1} ashes. However, the presence of ^{227}Ac daughters in the ^{243,244}Cm region of interest made its quantitative determination impossible. In fact, the ^{243,244}Cm line (5763 keV, 23%; −5805 keV, 77%) was between the ^{227}Th ones (5757 keV, 20%; −5976 keV, 23%; −6037 keV, 24%).

By using the Tru-Spec® column, instead of DDCP solvent extraction, method 3 produces an Am, Cm and R.E.E. fraction apparently free from all residual mineral salts thus far responsible for the auto-absorption effect (see Fig. 3c). In that case, yield recoveries range from 80 to 90% for biological matrices and 60 to 75% for soils and sediments. The total removal of Th and Ac isotopes enables the quantification of ^{243,244}Cm and a detection limit of 1 mBq.kg^{-1} ashes, similar to those of ^{241}Am.

6. Conclusion

Over the past 2 years, the method using the Tru-Spec® column step has routinely been implemented at LMRE on various environmental matrices and blanks (reagents) (see Table 1). This separation process scheme appears well adapted to avoid interference induced by the presence of all natural α-emitters found in large amounts in environmental samples. It gives thin α-sources with no traces of the Th series elements and produces high-quality spectra, in terms of good energy resolution and without interference lines. These improvements are particularly important for sediments where contamination of the sources with ^{228}Th and ^{227}Ac was a major problem when measuring ^{241}Am and ^{243,244}Cm, respectively. This scheme, including the Pu isotope separation step, ensures a good reliability in the reproducibility of the measurement, even at very low levels. The recovery yield is usually higher than 60% for sediment and up to 90% for biological samples. The combination of radiochemical improvements and spectrometer performance allows a detection limit of 0.2 mBq in the electrodeposited source. These levels are adapted to those currently measured in environments contaminated by global fallout for ^{241}Am and under the industrial influence for ^{243,244}Cm.

Samples collected over French territory and analysed for Pu isotopes, ^{241}Am and ^{243,244}Cm may be categorized into two groups using the well-known ^{238}Pu/$^{239+240}$Pu ratio: samples contaminated at global fallout level and samples predominantly contaminated by industrial discharges.

Samples contaminated at global fallout levels show a ^{238}Pu/$^{239+240}$Pu ratio close to 0.05 with the ^{241}Am/

Table 1
Am and Cm results for environmental samples collected in 1995 at various sites in France

Location	Nature	Quality	Recovery yield (%)	mBq kg^{-1} ashes or dry (see Quality) (confidence level=95%)				
				^{238}Pu/$^{239+240}$Pu	^{241}Am	^{241}Am/$^{239+240}$Pu	^{243,244}Cm	^{243,244}Cm/$^{239+240}$Pu
Flamanville	Soil	Dry	50	0.039±0.001	65±4	0.52±0.04	<1	<0.008
	Milk	Ash	58	0.21±0.21	5.7±2.8	0.98±0.65	1.8±1.6	0.31±0.3
	Moss terr.	Ash	85	0.042±0.007	365±20	0.39±0.03	21±4	0.023±0.004
	Sediment	Dry	50	0.67±0.03	1251±52	1.83±0.1	225±11	0.33±0.11
	Algae	Ash	48	0.68±0.05	383±22	0.53±0.04	110±9	0.15±0.01
	Limpet	Ash	59	0.58±0.05	524±31	2.3±0.2	102±9	0.43±0.04
	Lobster	Ash	61	0.69±0.11	298±18	11.5±0.19	85±7	3.26±0.46
	Crab	Ash	72	0.60±0.11	60±5	2.4±0.3	19±3	0.76±0.15
	Fish	Ash	64	0.25±0.14	10±2	0.83±0.21	3.2±2.1	0.27±0.18
Paluel	Soil	Dry	64	0.03±0.01	57.2±8	0.42±0.07	<1	<0.007
	Sediment	Dry	43	0.45±0.07	1298±185	1.29±0.24	113±12	0.11±0.02
	Mussel	Ash	90	0.49±0.07	247±35	1.03±0.17	43±5	0.18±0.03
	Lobster	Ash	43	0.67±0.37	67.4±13	5.3±1.9	10.5±2	0.82±0.3
Rhône, river, 1	Sediment	Dry	64	0.06±0.01	42±6	0.34±0.06	<1	<0.008
Rhône, river, 2	Sediment	Dry	63	0.24±0.03	777±100	1.21±0.21	10±3	0.016±0.005
Rhône, estuary, 10–20 cm	Sediment	Dry	72	0.30±0.04	2064±142	0.97±0.11	22.2±6.3	0.010±0.003
Rhône, estuary, 90–100 cm	Sediment	Dry	68	0.24±0.02	2662±289	0.86±0.11	14.8±3.5	0.005±0.001
Rhône, estuary, 390–400 cm	Sediment	Dry	61	0.10±0.01	1728±184	1.16±0.14	5.6±1.6	0.004±0.001
Faraman	Mussel	Ash	79	0.12±0.04	118±18	0.93±0.18	<1	<0.007
Carteau	Mussel	Ash	93	0.07±0.01	60±10	0.33±0.06	<1	<0.005

$^{239+240}$Pu ratio one order of magnitude higher and ^{243,244}Cm lower than 1 mBq kg^{-1}. This is observed on a majority of samples collected in the terrestrial environments, even those close to nuclear plants. Samples from the Rhône River and the Channel under the influence of low-level radioactive liquid effluents released by the nuclear reprocessing plants of Marcoule and La Hague, respectively, show different ratios. The ^{238}Pu/$^{239+240}$Pu ratio ranges from 0.1 to 0.7 and the ^{241}Am/$^{239+240}$Pu ratio is close or higher than 1. ^{243,244}Cm fluctuates from 5 to 25 mBq kg^{-1} in the lower part of the Rhône river to 250 mBq kg^{-1} in the Channel, with the higher value applying to sediment samples, and the ^{243,244}Cm/$^{239+240}$Pu ratio is one order of magnitude lower than samples from the Rhône River and its estuary. In the same area, fluctuation of the ^{243,244}Cm, $^{239+240}$Pu, as well as their ratio in different layers of the vertical profile obtained from a sediment core indicate modification with time of the Marcoule radioactive liquid effluent composition.

The reliability of the process, irrespective of the type of environmental matrix analysed, encouraged us to develop an automated system at present being tested. The purpose is to run all the ionic chromatographic steps, in line, up to the Pu and Am–Cm fractions to be electrodeposited.

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