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Frédéric Chartier · Michel Aubert · Mireille Pilier

Determination of Am and Cm in spent nuclear fuels by isotope dilution inductively coupled plasma mass spectrometry and isotope dilution thermal ionization mass spectrometry after separation by high-performance liquid chromatography

Abstract Elemental and isotopic determination of americium and curium in spent nuclear fuels is necessary to validate neutronic calculation codes and for nuclear waste disposal purposes. Prior to mass spectrometric analysis, it is mandatory to perform separations in order to eliminate isobaric interferences between U, Pu, Am and Cm. In the spent fuels samples analyzed, a separation of U and Pu has been first realized with an anion-exchange resin. Then a rapid Am/Cm separation has been developed by high-performance liquid chromatography (HPLC) with an on-line detection using the Am and Cm α-emission. The influence of the different parameters on the chromatographic separation are described and discussed. Inductively coupled plasma mass spectrometry (ICP-MS) and thermal-ionization mass spectrometry (TIMS) have been used to measure the isotopic composition of U, Am and Cm and to determine the ^{241}Am/^{238}U and ^{244}Cm/^{238}U ratios with the double spike isotope dilution method. The measurement procedures and the accuracy and precision of the results obtained with a quadrupole ICP-MS on different spent fuels samples are discussed and compared with those obtained by TIMS, used as a reference technique.

Introduction

Americium and curium are strategic elements as part of the nuclear fuel cycle: they form a major source of radiation and a great part of long living radiotoxic wastes. The measurement of their abundances is of prime necessity for the management of nuclear wastes and for environmental monitoring. In other fields, such as transmutation studies or neutron calculation codes qualification, the isotopic composition and the amount of Am and Cm must also be known with high accuracy and precision.

Isotope dilution is a method that can provide the most accurate quantification coupled to mass spectrometric techniques (ID-MS). The principles of ID-MS have been reviewed in detail [1–4] and isotope dilution has been used in various domains, mainly with thermal ionization mass spectrometry (TIMS) [5–7] and inductively coupled plasma mass spectrometry (ICP-MS) [8–11].

TIMS has been utilized for the determination of actinides for a long time [12–15], but more often for U and Pu determination than for Am and Cm determination by isotope dilution [14, 15]. Although TIMS is one of the best techniques to perform isotope ratio measurements, it requires time consuming preparations as well as long analysis time.

ICP-MS has been increasingly applied to the analysis of nuclear samples [16–22] due to its high sensitivity, low matrix effects and its high throughput. For isotope ratio measurements these characteristics make up for its lesser precision and accuracy with respect to TIMS. Only little work has been performed on nuclear materials by ID-ICP-MS [19, 21] and on the determination of Am and Cm.

Measurements of actinides by ID-MS firstly require elemental separations between U, Pu, Am and Cm in order to eliminate isobaric interferences.

Actinides have been separated for many years by various methods such as solvent extraction or ion exchange resins. A literature review on Am recovery can be found in [23] and a review on the use of ion chromatography in nuclear applications in [24].

In this paper, the procedure used to separate U and Pu from spent fuels samples with an anion exchange resin and the development of a fast Am/Cm separation by HPLC with a complexing solution of 2-hydroxy-2-methylbutyric acid (HMB) are described. The Am and Cm detection was performed with an α-emitter detector. The influence of the main parameters on the Am/Cm separation are presented and discussed.

The isotopic measurements of U, Am and Cm and the determination of ^{241}Am/^{238}U and ^{244}Cm/^{238}U with the dou-

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F. Chartier (✉) · M. Aubert · M. Pilier
Commissariat à l'Energie Atomique, Saclay,
DCC/DPE/SPCP/LAIE, F-91191 Gif-sur-Yvette Cedex, France

ble spike isotope dilution method are presented for different irradiated nuclear samples. Two spike solutions containing, respectively, a mixture of ^{243}Am and ^{233}U and a mixture of ^{248}Cm and ^{233}U have been prepared and calibrated for this purpose.

Performances and results obtained with a nuclearized quadrupole ICP-MS are evaluated, discussed and compared to those obtained by TIMS which is used as a reference technique.

Experimental

Instrumentation

HPLC. The HPLC system consisted of a LC pump (Gilson Model 307), a six-way rotary valve (Rheodyne 7125) with a 50 µL sample loop and a 250 × 4 mm column filled with 5 µm diameter particles of Nucleosil SA 100 Å stationary phase (Touzart & Matignon). The column outlet was connected by a capillary tube (80 mm long, 0.25 mm i.d.) to a Si detector (Eurisys Mesures) to detect the α-emitters. The detector, protected by a mylar membrane, was connected to an electronic unit: preamplifier, amplifier, multichannel analyzer and ratemeter (Eurisys Mesures and Oxford) coupled with an integrator (Waters Model 471). This detection set-up was based on the work done by A. Billon [25]. In order to handle radioactive samples, the six-way rotary valve, the column and the detector were situated inside a glove-box. A schematic diagram of the HPLC system is shown in Fig. 1.

TIMS. The spectrometer used was a magnetic sector thermal ionization mass spectrometer Sector 54 (Micromass). The source was equipped with a twenty positions turret assembly. A glove-box was added around the source in order to handle radioactive samples.

Demountable triple filament arrangements were used for U, Am and Cm isotope ratio measurements in order to control independently the sample evaporation and ionization temperatures. The two evaporating filaments were made of tantalum and the ionizing filament was made of rhenium. Triple rhenium filaments were also used for Am and Cm determinations which were carried out by total evaporation. The detection system consisted of seven Faraday collectors and a Daly detector ion-counting system for the least abundant isotopes.

ICP-MS. The ICP-MS used for this study was a VG PlasmaQuad PQ2+ (Fisons Instruments) modified to handle radioactive samples. A two glove-box system was installed on the ICP-MS for this purpose. The sampling interface, the plasma torch, the torch box and the spray chamber with the nebulizer were located in the first glove-box. The second glove-box, coupled to the first, contained the peristaltic pump and was used for handling solutions.

High-efficiency filters were placed between the primary pump and the turbomolecular pumps and between the sampling interface and the second rotary pump. Due to this last filter, it was necessary to improve the expansion chamber pumping and the initial 25 m^3 h^{-1} mechanical rotary pump was replaced by a 65 m^3 h^{-1} pump. Two independent cooling systems were used, the first one for the spray chamber (maintained at 5 °C) and the second one for the interface, the RF coil and, with parallel connection, for the turbomolecular pumps.

Standard operating conditions and the data acquisition procedure used with the ICP-MS are summarized in Table 1.

Materials and reagents

Samples were supplied as diluted solutions of irradiated fuels with concentrations in the range of 4 mg mL^{-1} for U, 1 to 30 µg mL^{-1} for Am and 0.5 to 2 µg mL^{-1} for Cm.

For the preparation and calibration of the spike solutions, solutions of ^{243}Am, ^{248}Cm, ^{233}U and solutions of certified activity concentration of ^{241}Am and ^{244}Cm were supplied by the French Atomic Energy Commission. NIST SRM U930 uranium standard was used for the calibration of ^{233}U solution.

NIST SRM U005 and U500 uranium standards were used for bias factor determination in ICP-MS.

An anion-exchange Dowex AG1X4 (Bio-Rad Laboratories) resin, 100–200 mesh, was used for uranium and plutonium separation.

The americium/curium separation was performed with a Nucleosil SA column and 2-hydroxy-2-methylbutyric acid obtained from Sigma Aldrich as eluent. The pH of the mobile phase was adjusted with a 25% ammonia solution (Normatom, Prolabo).

Fig. 1 Schematic diagram of the HPLC system installed in the glove box for the Am/Cm separation
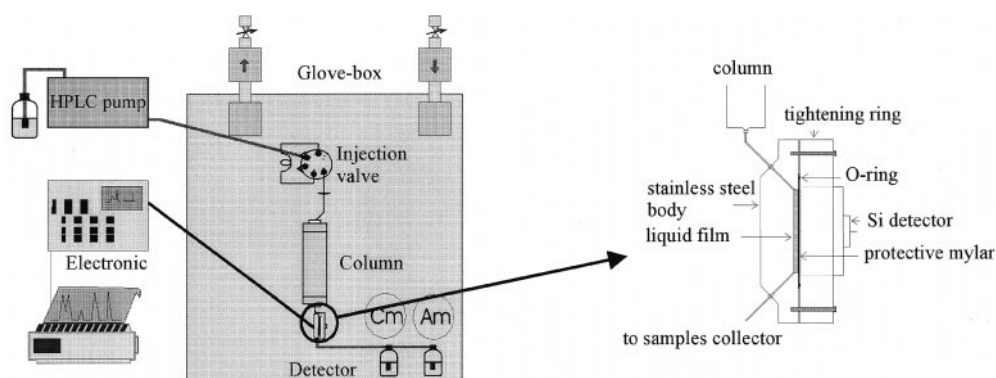
Table 1 Typical operating conditions and data acquisition procedure for ICP-MS measurements			
RF power	1350 W	detector type	Channeltron
Plasma gas flow rate	14 L min^{-1}	acquisition mode	peak jumping
Auxiliary gas flow rate	1 L min^{-1}	points/peak	5
Nebulizer gas flow rate	0.8 L min^{-1}	dwell time	10.24 ms
Sample uptake rate	1 mL min^{-1}	measurement time / replicate	30 s
Nebulizer type	Meinhard	number of replicates	6
Spray chamber type	Scott, double pass		

Nitric acid (Normatom Prolabo) and milli-Q water (Millipore) were used throughout for dilutions. All dilutions and spikings were performed by weight in a glove-box.

Preparation and calibration of spike solutions

The double spike isotope dilution technique allows to determine directly and in a very accurate way the concentration ratio of two elements present in a sample, with one of them used as a reference. Since this technique is only based on isotope ratio measurements, quantitative or constant elemental recovery is not required and accurate measurements of the amounts of sample and spike solutions are not necessary.

For neutronic studies requiring the knowledge of the ^{241}Am/^{238}U and ^{244}Cm/^{238}U ratios in irradiated fuels samples, two double spike solutions were prepared. The first one contained a mixture of ^{243}Am and ^{233}U and the second one a mixture of ^{248}Cm and ^{233}U. To characterize these solutions, it was necessary to determine the different isotopic compositions and concentrations of the enriched spikes or of the ^{243}Am/^{233}U and ^{248}Cm/^{233}U ratios.

The isotopic distributions of individual solutions of enriched ^{244}Cm, ^{248}Cm and ^{243}Am were determined with at least eight independent measurements by TIMS, after two independent chromatographic isolations of each element. Eight isotopic determinations of a solution of enriched ^{233}U were also performed by TIMS.

In the first double spike solution, the ^{243}Am and ^{233}U concentrations were measured by TIMS by simple reverse isotope dilution analysis with respectively a pure ^{241}Am reference solution of certified activity concentration and a ^{235}U isotopic reference solution (U930) prepared by weight. Eight mixtures of ^{243}Am–^{241}Am and ^{233}U–^{235}U were analyzed after a chromatographic isolation of Am and U.

In the second double spike solution, the ^{248}Cm and ^{233}U concentrations were measured in the same way with a ^{244}Cm reference solution of certified activity concentration and a ^{235}U reference solution (U930) prepared by weight. Eight mixtures of ^{248}Cm–^{244}Cm and ^{233}U–^{235}U were analyzed after a chromatographic isolation of Cm and U.

With these two spike solutions, characterized in Table 2, the ^{241}Am/^{238}U and ^{244}Cm/^{238}U ratios can be measured in nuclear fuel samples with the double spike isotope dilution technique using the isotopic balance equations:

$$\left(\frac{^{241}Am}{^{238}U}\right)_S = \left(\frac{^{243}Am}{^{233}U}\right)_{Sp} \times \frac{\left[\left(\frac{^{241}Am}{^{243}Am}\right)_M - \left(\frac{^{241}Am}{^{243}Am}\right)_{Sp}\right] \times \left[1 - \left(\frac{^{238}U}{^{233}U}\right)_M \times \left(\frac{^{233}U}{^{238}U}\right)_S\right]}{\left[\left(\frac{^{238}U}{^{233}U}\right)_M - \left(\frac{^{238}U}{^{233}U}\right)_{Sp}\right] \times \left[1 - \left(\frac{^{241}Am}{^{243}Am}\right)_M \times \left(\frac{^{243}Am}{^{241}Am}\right)_S\right]}$$

$$\left(\frac{^{244}Cm}{^{238}U}\right)_S = \left(\frac{^{248}Cm}{^{233}U}\right)_{Sp} \times \frac{\left[\left(\frac{^{244}Cm}{^{248}Cm}\right)_M - \left(\frac{^{244}Cm}{^{248}Cm}\right)_{Sp}\right] \times \left[1 - \left(\frac{^{238}U}{^{233}U}\right)_M \times \left(\frac{^{233}U}{^{238}U}\right)_S\right]}{\left[\left(\frac{^{238}U}{^{233}U}\right)_M - \left(\frac{^{238}U}{^{233}U}\right)_{Sp}\right] \times \left[1 - \left(\frac{^{244}Cm}{^{248}Cm}\right)_M \times \left(\frac{^{248}Cm}{^{244}Cm}\right)_S\right]}$$

S: sample, M: mixture, Sp: spike; all the ratios are expressed in atoms.

As there is no ^{233}U and very little ^{248}Cm in the samples (the correction factor due to the presence of ^{248}Cm in the sample is less than 1.0003 on the ^{244}Cm/^{238}U determination), these equations are simplified to:

$$\left(\frac{^{241}Am}{^{238}U}\right)_S = \left(\frac{^{243}Am}{^{233}U}\right)_{Sp} \times \frac{\left[\left(\frac{^{241}Am}{^{243}Am}\right)_M - \left(\frac{^{241}Am}{^{243}Am}\right)_{Sp}\right]}{\left[\left(\frac{^{238}U}{^{233}U}\right)_M - \left(\frac{^{238}U}{^{233}U}\right)_{Sp}\right] \times \left[1 - \left(\frac{^{241}Am}{^{243}Am}\right)_M \times \left(\frac{^{243}Am}{^{241}Am}\right)_S\right]}$$

$$\left(\frac{^{244}Cm}{^{238}U}\right)_S = \left(\frac{^{248}Cm}{^{233}U}\right)_{Sp} \times \frac{\left[\left(\frac{^{244}Cm}{^{248}Cm}\right)_M - \left(\frac{^{244}Cm}{^{248}Cm}\right)_{Sp}\right]}{\left[\left(\frac{^{238}U}{^{233}U}\right)_M - \left(\frac{^{238}U}{^{233}U}\right)_{Sp}\right]}$$

Results and discussion

Chromatographic separations

To perform isotopic determinations of U, Am and Cm from a spent fuel sample, it is mandatory to eliminate first the isobaric interferences at masses 238 (U, Pu), 241 (Pu, Am), 242 (Pu, Am) and 243 (Am, Cm).

The following procedure was defined and used. First a Dowex AG1X4 resin was pretreated by washing with 8 M HNO$_3$ and water and then dried at about 60 °C. Then, in a glove-box, a fuel solution aliquot was passed through the resin in 8 M HNO$_3$ medium. Anionic complexes of uranium and plutonium were fixed on this quaternary ammonium type resin. The bulk sample, containing Am and Cm, was not retained with 8 M HNO$_3$ and uranium was then eluted with 3 M HNO$_3$. The column temperature was maintained at 60 °C during the separation.

The uranium fraction was evaporated to dryness and the residue was then redissolved in 0.2 M HNO$_3$. The uranium was then ready for subsequent loading on a filament for TIMS measurements or dilution in ICP-MS measurements.

The fraction not retained by the resin and containing Am and Cm, but also the fission products and the Zr cladding, was collected, evaporated to dryness and redissolved with 0.2 M HNO$_3$. This fraction was then ready to be used for separation and collection of Am and Cm.

The separation of Am and Cm was performed with a strong cation-exchange silica based stationary phase (Nucleosil SA) and a test solution containing 90 µg mL^{-1} of ^{241}Am and 25 µg mL^{-1} of ^{244}Cm. A solution of HMB was

Table 2 Concentrations and isotope abundances of spike isotopes in the two spike solutions (n = 8; 95% confidence limits, TIMS measurements)

Isotope enriched	Am – U spike solution		Cm – U spike solution	
	^{243}Am	^{233}U	^{248}Cm	^{233}U
Abundance of spike isotopes (at. %)	98.648 ± 0.005	99.537 ± 0.005	89.511 ± 0.010	99.537 ± 0.005
Concentration of spike isotopes (µg/g)	0.8541 ± 0.0025	1065.1 ± 1.1	0.7347 ± 0.0012	1034.8 ± 1.5
Isotope ratios (at.)	^{241}Am/^{243}Am 0.013628 ± 0.000014	^{238}U/^{233}U 0.000208 ± 0.000002	^{244}Cm/^{248}Cm 0.001353 ± 0.000007	^{238}U/^{233}U 0.000208 ± 0.000002

used as eluting solution. All the separations were performed at room temperature and under isocratic conditions.

The influence of operating conditions such as the HMB concentration and the pH of the mobile phase were tested in order to optimize the separation between Am and Cm.

The mobile phase flow rate was fixed to 1.5 mL min^{-1} for this study.

First, the effect of the HMB concentration on the chromatographic separation of Am and Cm has been evaluated at a constant pH value of 4.1. The pH was adjusted by an ammonia solution.

The increase of the HMB concentration between 0.14 and 0.26 M results in a decrease of the capacity factors k′ from 2.5 to 0.4 for Am and from 1.6 to 0.3 for Cm. The capacity factor k′ is defined as $\dfrac{t_R - t_0}{t_0}$ with t_R: retention time and t_0: dead time. The dead time was determined with H_2O and a conductivity detector (Waters Model 432).
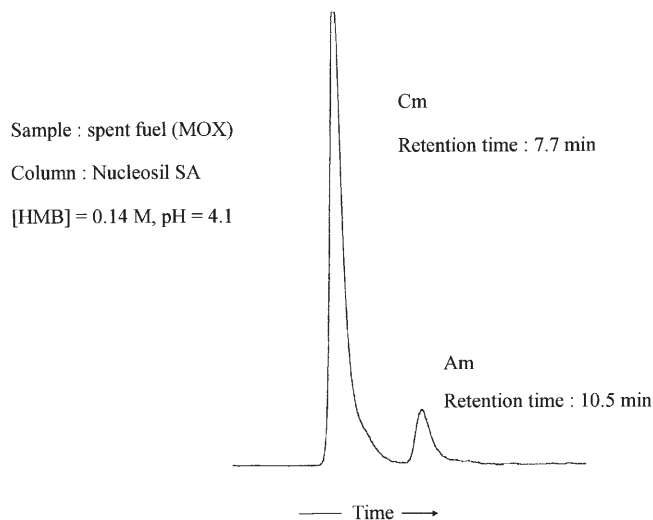
Then, the effect of the pH of the mobile phase on the Am/Cm separation was evaluated with a concentration of HMB set to 0.14 M. When the pH is increased from 3.5 to 4.5, the capacity factors decrease from 60 to 1.1 for Am and from 36 to 0.7 for Cm.

Therefore, as expected, the retention times greatly depend on the HMB concentration and on the pH of the mobile phase, i.e. on the concentration of the complex-forming anion (the 2-hydroxy-2-methyl butyrate anion). In the column, there is a competition of the Am and Cm ions between the ligand and the ion exchange sites. When concentration of HMB or the pH are increased, there is a higher rate of complex formation during the passage through the column, the effective charge of the analyte ions is decreased and the retention times on the stationary phase decrease.

The conditions yielding the necessary and sufficient separation (HMB concentration = 0.14 M, pH = 4.1 and mobile phase flow rate = 0.8 mL min^{-1}) have been used for the subsequent separations of Am and Cm. The chromatographic behavior of Am and Cm was identical in the spent fuels samples and in the synthetic Am/Cm mixture used for the development of the separation.

The chromatogram obtained under these optimized conditions for a diluted solution of an irradiated mixed uranium – plutonium oxide (MOX) sample is shown in Fig. 2. Retention times are 7.7 min for Cm and 10.5 min for Am.

Reproducibility of the Am/Cm separation was determined by measuring the net retention times on ten injections of Am and Cm on different days, under the same conditions. This reproducibility, expressed as the relative standard deviation (RSD in %), was 1.2% for both Am and Cm. The purity of the Am and Cm fractions obtained was verified by ICP-MS qualitative measurements. The mass spectra of the collected fractions are reported in Fig. 3 and the whole separation procedure is schematized in Fig. 4.

Sample : spent fuel (MOX)

Column : Nucleosil SA

[HMB] = 0.14 M, pH = 4.1

Cm
Retention time : 7.7 min

Am
Retention time : 10.5 min

Time ⟶

Fig. 2 Chromatographic separation of an Am/Cm mixture with α-emitter detection

Determination of U, Am and Cm in spent fuels by TIMS and ICP-MS

The purified fractions of U, Am and Cm were analyzed by TIMS with deposits of 2 μg, 500 ng and 40 ng, respectively, on the side filament of the previously outgassed triple filament arrangement.

Sample aliquot size, filament loading and drying procedures were strictly controlled to minimize analytical biases.

All measurements were based on the completion of 30 cycles of 5 s integration time.

Due to the very different ion beam sizes to measure, peak-jumping or static multi-collection modes, with the Faraday buckets or the Faraday buckets and the Daly electrode, were used. When both Faraday and Daly detectors were used simultaneously, the relative gain between these detectors was monitored and calibrated.

One of the main bias factors impairing accuracy in TIMS is isotope fractionation [26]. Even if this phenomenon is weaker for heavy elements (such as the actinides) than for light elements, it must be taken into account. For U and Pu, the availability of isotope standards permits the adaptation of the analytical procedures to obtain highly precise and accurate isotope ratios. For Am and Cm, due to the non-availability of isotopic standards, it was assumed that the isotope fractionation was the same as for Pu.

To verify this assumption, Am and Cm isotopic measurements were also performed with the flash evaporation method. With this method, the sample is entirely volatilized while the signal from each isotope is integrated. Thus, the effects of isotope fractionation are eliminated.

Deposits of 40 ng of Am or Cm on triple Re filaments were performed from the ^{243}Am and ^{248}Cm spike solutions. The bias obtained on the ^{241}Am/^{243}Am and ^{244}Cm/^{248}Cm ratios with respect to the conventional procedures

Fig. 3 ICP-MS spectra of a
spent nuclear fuel sample be-
fore and after actinide separa-
tion
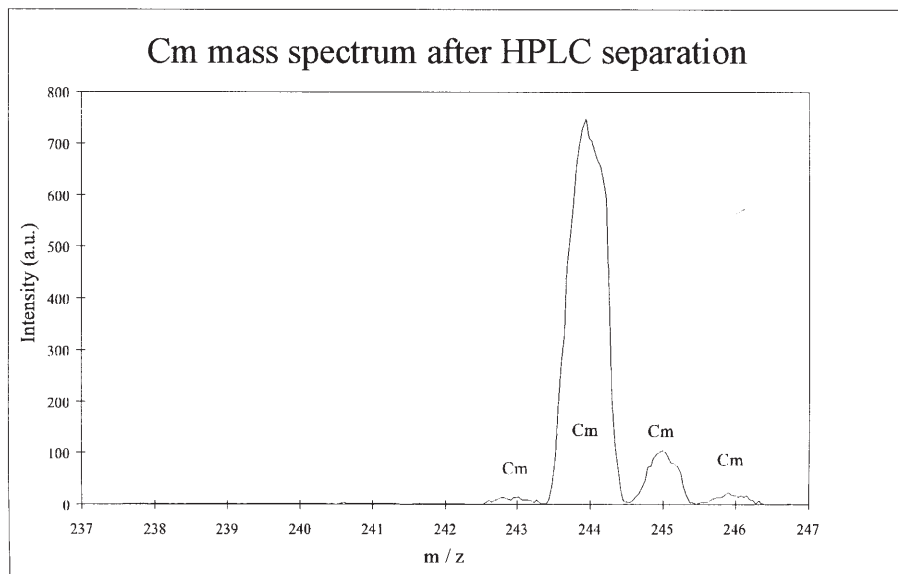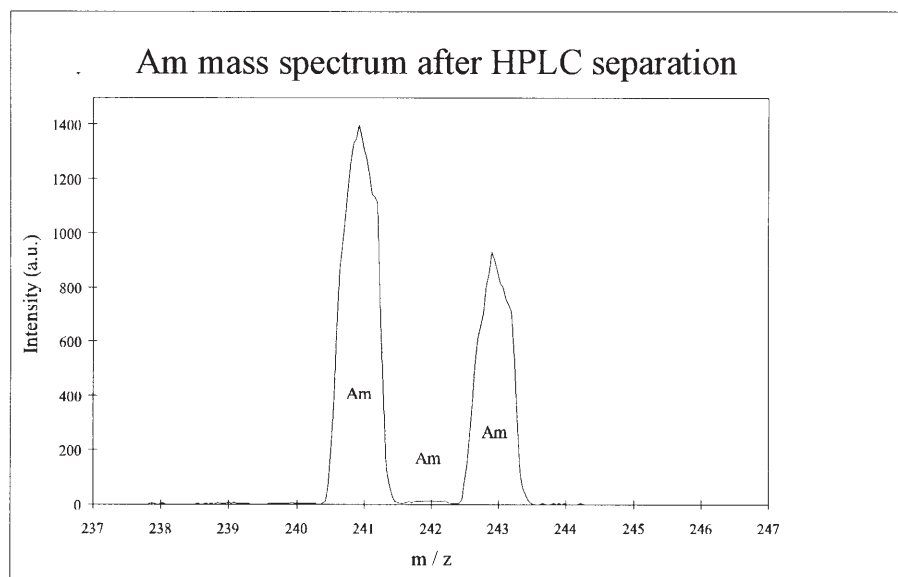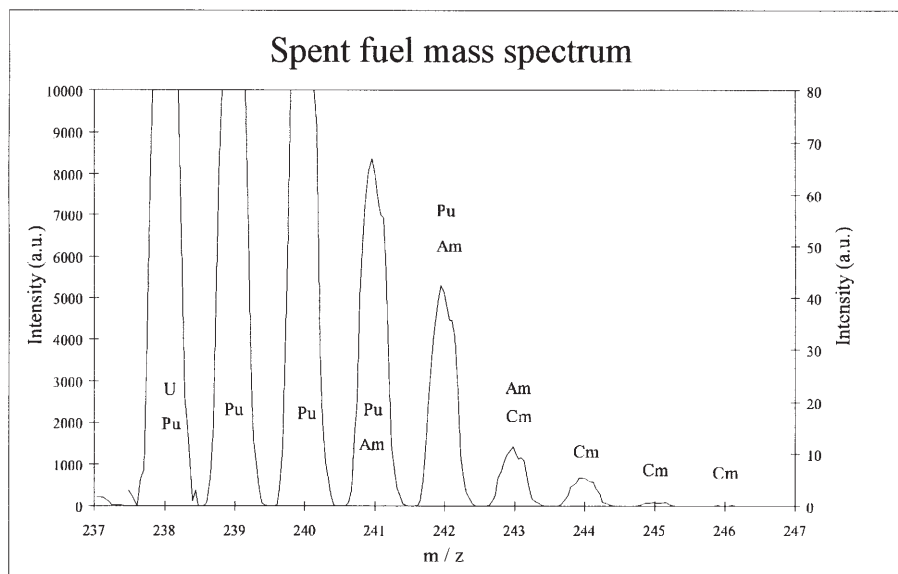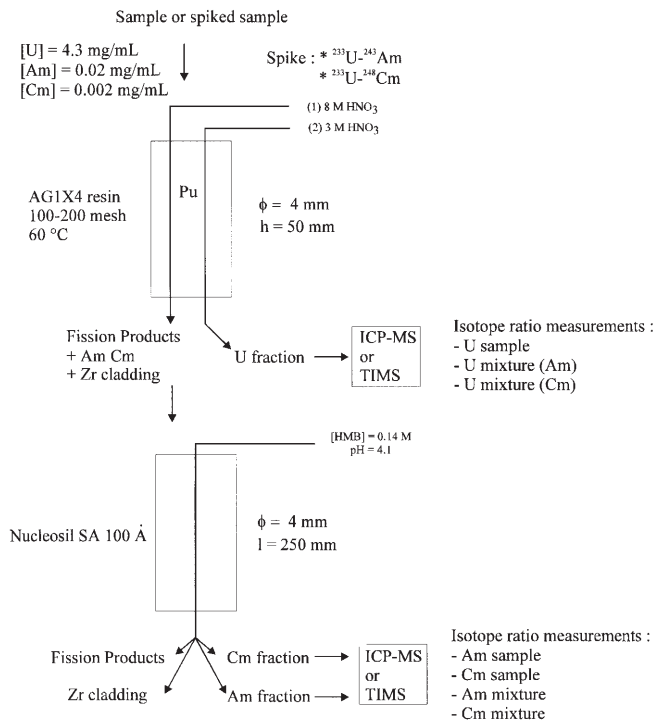
Fig. 4 Analytical procedure used for U, Am and Cm determination in spent fuel samples

was 0.1% and 0.3%, respectively. These discrepancies were within the uncertainty limits of the measured ratios and showed that the adjustment of the different parameters (filament heating, time of analysis etc.) in the conventional procedures was satisfactory.

Due to the relatively short half-life of some isotopes, the same U, Am and Cm fractions were analyzed simultaneously by ICP-MS.

Optimization of operating conditions was performed every day by nebulizing a 100 µg/L solution of uranium and adjusting the torch position, the ion lens setting and the nebulization gas flow rate in order to maximize the ^{238}U signal. Blanks were negligible for actinide measurements and carefully rinsing was performed between sample analyses to avoid memory effects.

ICP-MS is subject to mass discrimination and the magnitude of this bias depends on operating conditions. In practice, it is difficult to minimize this mass discrimination and as stability of the bias over time is more important than the magnitude, the mass bias was regularly measured and corrected with the use of external standards of known isotopic composition.

The correction factor was calculated with the following equation [27]:

$$R_m = R_t(1+am)$$

where R_t: true value, R_m: measured value, a: bias factor per mass unit and m: mass difference between the measured isotopes.

The correction factor was then applied to sample results to correct them for instrumental mass discrimination.

Due to the very different ranges of the U isotope ratios to measure, the $^{235}U/^{238}U$ ratio was measured on U reference NIST U005 standard in order to determine a bias factor which was then applied to correct the U isotope ratios in the samples. In the same way, the $^{235}U/^{238}U$ ratio in a U500 standard was used for the correction of the $^{238}U/^{233}U$ ratios in the spiked samples.

For the measurement of Am and Cm isotope ratios in samples, and due to the lack of available standards, the Am isotope ratios were measured on a sample by TIMS and the result was considered as a reference value for ICP-MS determination. This sample was then analyzed by ICP-MS and the bias factors obtained were then applied to all further samples. The same procedure was used for Cm isotope ratios.

For the Am and Cm spiked samples, the $^{235}U/^{238}U$ ratio measured in the U500 standard was used for the determination of the correction factor.

Results obtained by TIMS and ICP-MS for two different samples in the determination of the isotopic composition of U, Am and Cm are shown in Table 3.

As mentioned before, in these samples only the measurement of the $^{243}Am/^{241}Am$ ratio is directly involved in the $^{241}Am/^{238}U$ and $^{244}Cm/^{238}U$ determination.

Table 3 Uranium, americium and curium isotopic ratios determined by TIMS and ICP-MS from spent nuclear fuel samples

Isotopic ratios	Sample 1				Sample 2			
	TIMS	ICP-MS	RSD_{ICPMS}(%)	Δ (%)	TIMS	ICP-MS	RSD_{ICPMS} (%)	Δ (%)
$^{234}U/^{238}U$	0.000029	0.000040	8.0	+ 38	0.000043	0.000055	3.7	+ 28
$^{235}U/^{238}U$	0.000619	0.000635	1.5	+ 2.6	0.000893	0.000925	1.2	+ 3.6
$^{236}U/^{238}U$	0.000319	0.000303	2.1	− 5.0	0.000314	0.000327	1.5	+ 4.1
$^{242}Am/^{241}Am$	0.003137	0.00315	1.3	+ 0.4	0.004378	0.00434	1.2	− 0.9
$^{243}Am/^{241}Am$	0.6735	0.6772	0.5	+ 0.5	0.4699	0.4672	0.5	− 0.6
$^{243}Cm/^{244}Cm$	0.01151	0.01130	1.1	− 1.8	0.01692	0.01655	1.4	− 2.2
$^{245}Cm/^{244}Cm$	0.1081	0.1087	0.6	+ 0.6	0.1208	0.1190	0.6	− 1.5
$^{246}Cm/^{244}Cm$	0.01817	0.01773	0.7	− 2.4	0.01484	0.01479	2.4	− 0.3
$^{247}Cm/^{244}Cm$	0.000326	0.000344	4.5	+ 5.5	0.000255	0.000266	13.7	+ 4.3

RSD_{ICPMS} (%) represents the internal precision obtained with ICP-MS from 6 repetitive measurements on the sample. Δ (%) is the relative deviation: the deviation between the mean obtained by ICP-MS and the TIMS value relative to the TIMS value. A minus sign indicates a value inferior to TIMS value and a plus sign a value superior to TIMS value

Table 4 Uranium, americium and curium isotopic ratios determined by TIMS and ICP-MS in the spiked samples

Isotopic ratios	Sample 1				Sample 2			
	TIMS	ICP-MS	RSD$_{ICPMS}$ (%)	Δ (%)	TIMS	ICP-MS	RSD$_{ICPMS}$ (%)	Δ (%)
^{238}U/^{233}U mixture (Am)	1.790	1.793	0.4	+ 0.2	0.3949	0.3961	0.6	+ 0.3
^{238}U/^{233}U mixture (Cm)	1.973	1.980	0.2	+ 0.4	1.820	1.798	0.2	− 1.2
^{241}Am/^{243}Am mixture	0.9791	0.9823	0.6	+ 0.3	0.6755	0.6891	0.4	+ 2.0
^{244}Cm/^{248}Cm mixture	1.338	1.324	0.5	− 1.0	1.258	1.257	0.6	− 0.1

RSD$_{ICPMS}$ and Δ (%) as in Table 3

Table 5 Calculation of the ^{241}Am and ^{244}Cm atom numbers formed with respect to the ^{238}U atom number in the two samples

Ratios	Sample 1			Sample 2		
	TIMS	ICP-MS	Δ (%)	TIMS	ICP-MS	Δ (%)
^{241}Am/^{238}U (ppm)	1207	1230	+ 1.9	1872	1917	+ 2.4
^{244}Cm/^{238}U (ppm)	406.8	401.2	− 1.4	414.5	419.3	+ 1.2

Δ (%) as in Table 3

Results for the different spiked sample solutions are presented in Table 4 for the ^{238}U/^{233}U ratios measurements in mixtures with the two spike solutions and for the ^{241}Am/^{243}Am and ^{244}Cm/^{248}Cm ratio measurements in the two spiked samples.

Final calculations of ^{241}Am/^{238}U and ^{244}Cm/^{238}U atomic ratios for the two samples are compiled in Table 5.

As can be observed in Table 3, the range of the U isotope ratios measured is very large. One advantage of TIMS is that high-precise and accurate isotope ratios can be determined even within these very large ratios. ICP-MS results show that if the internal precision, expressed as the relative standard deviation (RSD) from six repetitive measurements, remains acceptable for the ^{235}U/^{238}U and ^{236}U/^{238}U ratios (around 2%), for the least abundant ratio, the number of counts on the 234 isotope (less than 1000) gives a RSD between 4 and 8%. The value obtained for this ratio in ICP-MS is only indicative and for the two other ratios the bias between TIMS and ICP-MS results reaches up to 5%. The range of these ratios was too large for a more precise determination with the quadrupole ICP-MS.

Comparison between Am isotope ratios determined by TIMS and ICP-MS (Table 3) shows an excellent agreement. The accuracy of ICP-MS results with respect to TIMS is better than 1% in all cases due to the relatively weak range of the ratios to measure. The repeatability obtained for the different isotope ratios and for the two samples varied from 0.5 to 1.3%. For the ^{241}Am/^{243}Am ratio, which is used for the final calculation of ^{241}Am/^{238}U, the RSDs and the accuracy were less than 0.6%.

For the Cm isotopic composition in the two samples (Table 3), except for the weakest ratio where the number of counts in ICP-MS was not high enough, the RSDs were between 0.6 and 2.4% and bias with respect to the TIMS results was between 0.3 and 2.4%.

For the determination of the ^{241}Am/^{238}U and ^{244}Cm/^{238}U ratios, it is also necessary to measure the ^{238}U/^{233}U and the ^{241}Am/^{243}Am ratios in the mixtures of each sample with the first spike solution and the ^{238}U/^{233}U and the ^{244}Cm/^{248}Cm ratios in the mixture of each sample with the second spike solution. The results (Table 4) show that for all the isotope ratios the precision obtained by ICP-MS was excellent; the RSDs were always equal or inferior to 0.6%. The isotope ratios measured with the two techniques compared well with each other. For the two spiked samples analyzed, the accuracy reached in ICP-MS was better than 1.2% except for one ^{241}Am/^{243}Am measurement which presented a higher bias of 2%.

Final calculations of ^{241}Am/^{238}U and ^{244}Cm/^{238}U with these results are reported in Table 5, where the very good agreement between results obtained by TIMS and ICP-MS can be seen. The discrepancies between these techniques were around 2% for the ^{241}Am/^{238}U ratio and 1% for the ^{244}Cm/^{238}U ratio for the two samples analyzed.

These good results are due to the higher precision achievable in ICP-MS when the atom ratios are close to unity, which is the case for the U, Am and Cm sample-spike mixtures. The determination of the U, Am and Cm isotopic composition in the samples shows that for ratios ranging from unity to 0.001, agreement between ICP-MS and TIMS measurements, after bias correction, is better than 2.5%. For isotope ratios between 0.001 and 0.0003 agreement was within 5%.

Conclusions

A rapid and efficient Am/Cm separation has been achieved by ion-exchange chromatography with the aid of HMB as complexing agent and an on-line α-emitter detector. The procedure described allows the recovery of pure Am and Cm fractions from spent nuclear fuels.

Comparison of the results obtained with nuclearized ICP-MS and TIMS has been possible by U, Am and Cm isotope abundance measurements and for the determination of ^{241}Am/^{238}U and ^{244}Cm/^{238}U by double spike isotope dilution. Two spike solutions of ^{243}Am–^{233}U and

^{248}Cm–^{233}U have been realized and calibrated. Concentrations can also be measured, if necessary, with the same spike solutions by using single isotope dilution.

Although the accuracy of isotope ratio measurements by ICP-MS is not as good as that obtained by TIMS, it is still adequate for isotope dilution analysis.

Results obtained for U, Am and Cm isotopic compositions showed that ICP-MS measurements agree with respect to TIMS within 2.5% for isotope ratios ranging from 1 to 0.001 and within 5% for ratios ranging from 0.001 and 0.0003.

Comparison of the results obtained with the double spike isotope dilution method demonstrates that ID ICP-MS is accurate and reliable for the determination of ^{241}Am/^{238}U and ^{244}Cm/^{238}U in spent reactor fuels. The final accuracy obtained is better than 2.5% as determined by TIMS.

Isotope dilution quadrupole ICP-MS is consequently an attractive alternative to techniques such as TIMS for the Am and Cm determination in spent fuels, due to its higher throughput and shorter analysis time. Its use is still more interesting when precision requirements are less stringent as for waste management or environmental monitoring.

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