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Determination of fission products in nuclear samples by capillary electrophoresis-inductively coupled plasma mass spectrometry (CE-ICP-MS)

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Abstract

Determination of fission products and of their isotopic composition is of high importance for the characterisation and complete inventory of nuclear fuels. Radiometric and mass spectrometric methods, which are currently used, enable only an incomplete determination of the fission products. Radiometric methods cannot be applied to all fission products and mass spectrometric methods are hindered by the existence of isobaric interferences, therefore a previous chemical separation is required before mass spectrometric analysis. Capillary electrophoresis (CE) has been coupled with inductively coupled plasma mass spectrometry (both ICP-QMS and ICP-SFMS). Typical detection limits of 6 ng/mL and 4 pg/mL for caesium as well as 8 ng/mL and 7 pg/mL for lanthanides have been obtained by CE-ICP-QMS and CE-ICP-SFMS, respectively. In addition to these very low detection limits, the procedures present the advantages to be fast (6 min for caesium and 13 min for lanthanides, respectively), to require a low microliter range sample volume and a nanoliter range injection volume. The radiation dose for the personnel as well as the volume of nuclear liquid wastes generated during the measurements are consequently reduced.

The procedures have been applied to nuclear samples from PUREX process and leachates from MOX fuels.

Keywords: Capillary electrophoresis; Inductively coupled plasma mass spectrometry; Fission products; Caesium; Lanthanide

1. Introduction

For a few years now inductively coupled plasma mass spectrometry has been increasingly used for precise and accurate determination of isotope ratios of long-lived radionuclides at the trace and ultratrace level due to its excellent sensitivity, good precision and accuracy. The application of ICP-MS for the determination of radionuclides in samples of different origin has been recently extensively reviewed by Becker [1] and applications have been exploited in her research group [2,3].

The determination of fission products is a major concern for the nuclear industry for the characterisation and complete inventory of nuclear fuels [4–12] and burn-up determination [13]. Elemental concentration and isotopic composition of fission products is not possible only using α, β or γ-spectrometry, in fact for long-lived radionuclides mass spectrometry is a choice. However, mass spectrometric methods are hindered by isobaric interferences as, for instance, radioactive caesium isotopes (masses 134, 135 and 137) are affected by isobaric interferences due to the natural barium isotopes (134, 135 and 137 with 2.4%, 6.6% and 11.2% natural abundance, respectively). When determining lanthanides their isobars can interfere each other as well as the formation of oxide can give place to overlapping at certain masses and it can be seen from the values reported in Table 1, even modern high resolution mass spectrometers cannot resolve these isobaric interferences [14,15]. To overcome them, a previous chemical separation of interfering elements is required before mass spectrometric analysis [16,17]. The hyphenation of a chromatographic separation technique such as ion chromatography (IC) with an ICP-MS has been already applied with success for the determination of fission products in nuclear spent fuels [9–12,18–20] and for the determination of radionuclides in an irradiated tantalum target of a spallation source [8]. Some authors have also hyphenated capillary electrophoresis

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Table 1
List of the most common isobaric interferences for lanthanides as radioactive or natural elements and resolution needed for the separation of the isotopes

Masses	Difference in mass	Isotopes	Resolution ($m/\Delta m$) needed for the separation of the elements
141.9092 – 141.9077	0.0015	^{142}Ce–^{142}Nd	93,238
143.9136 – 143.9101	0.0035	^{144}Ce–^{144}Nd	40,424
143.9101 – 143.9120	0.0019	^{144}Nd–^{144}Sm	75,149
147.9169 – 147.9148	0.0021	^{148}Nd–^{148}Sm	71,456
149.9209 – 149.9173	0.0036	^{150}Nd–^{150}Sm	41,483
150.9199 – 150.9197	0.0002	^{151}Sm–^{151}Eu	664,845
153.9222 – 153.9209	0.0013	^{154}Sm–^{154}Gd	114,524
154.9230 – 154.9226	0.0004	^{155}Eu–^{155}Gd	432,745
154.9226 – 154.9113	0.0113	^{155}Gd–^{139}La^{16}O	13,639
155.9221 – 155.9103	0.0118	^{156}Gd–^{140}Ce^{16}O	13,246
156.9240 – 156.9126	0.0014	^{157}Gd–^{151}Pr^{16}O	13,772
159.9270 – 159.9252	0.0018	^{160}Gd–^{160}Dy	86,167
163.92922 – 163.92920	0.00002	^{164}Dy–^{164}Er	6,071,451
169.9355 – 169.9348	0.0007	^{170}Er–^{170}Yb	242,072

Table 2
Experimental conditions for the capillary electrophoresis, the interface, the ICP-QMS and the ICP-SFMS

Capillary electrophoresis	Agilent 3D capillary electrophoresis
Capillary	Fused silica, 70 cm (CE-ICP-QMS), 90 cm (CE-ICP-SFMS) lengths, 75 μm i.d.
Buffer solution	Fifteen millimolar phosphate, pH 2.5 for the determination of caesium, 0.8 mM picolinic acid, 10 mM HIBA, 25 mM formic acid, pH 4.7 adjusted by TRIS for the determination of lanthanides. Marker: 1 μg/mL Rh (ICP-QMS); 10 ng/mL Rh (ICP-SFMS)
Temperature	20 °C
Voltage	30 kV
Injection	Hydrodynamic, 5 s, 50 mbar
CE-ICP-MS interface	CETAC CEI-100
Liquid flow rate	Self-aspiration, around 7 μL/min
Make-up liquid	One percent nitric acid. Marker: 100 ng/mL In (ICP-QMS); 1 ng/mL In (ICP-SFMS)
ICP-QMS	PerkinElmer ELAN 5000
RF power	1050 W
Cooling argon flow rate	15 L/min
Nebuliser argon flow rate	0.96 L/min
Auxiliary argon flow rate	0.85 L/min
Lens voltage	Optimised with Co, Rh, Tb and Th standard solutions
Scan mode	Peak hop
ICP-SFMS	Thermo Finnigan Element 2
Sampling cone	Nickel
Skimmer cone	Nickel
RF power	1250 W
Plasma argon flow rate	15.5 L/min
Nebuliser argon flow rate	0.92 L/min
Auxiliary argon flow rate	0.84 L/min
Resolution (10% valley definition)	Low, $m/\Delta m = 300$
Mass range of scan	Hundred percent peak width for each mass
Acquisition mode	E-Scan
Detection mode	Analogic and numeric

with ICP-MS for the determination of radionuclides in an irradiated tantalum target of a spallation source [21]. Respect to a chromatographic system, capillary electrophoresis reduces the sample volume to the low microliter range and the injection volume to the nanoliter range that is of high importance when high-radioactive samples such as nuclear spent fuel samples have to be characterised.

In this paper, the hyphenation of the capillary electrophoresis (CE) with ICP-MS instruments, both ICP-QMS and ICP-SFMS, is described as applied for the determination of fission products in different nuclear samples. The stability of the coupling CE-ICP-MS and the influence of different experimental parameters (interface argon flow rate, CE buffer molarity and CE buffer pH) have been studied. Two different analytical methods enabling the determination of both the concentration and the isotopic composition of the radioactive caesium as well as of the whole lanthanide series by CE-ICP-MS have been then developed. Applications of these analytical methods to nuclear samples such samples from PUREX process and leachates from MOX fuels are discussed.

2. Experimental

2.1. Instrumentation

2.1.1. CE-ICP-MS

The instrumental set-up consisted of an Agilent 3D capillary electrophoresis (Agilent Technologies, Waldbronn, Germany) coupled, respectively, with a PerkinElmer ELAN 5000 quadrupole ICP-MS (PerkinElmer Sciex, Thorhill, Ontario, Canada) or a Element 2 double focusing sector field ICP-MS (Thermo Finnigan MAT GmbH, Bremen, Germany) as element-specific detectors. Both instruments were coupled *via* an interface CETAC CEI-100 (CETAC Technologies, Omaha, Nebraska, USA), described elsewhere [22,23]. The ICP-QMS, respectively the ICP-SFMS, was linked to the spray chamber of the interface *via* a shielded teflon tube of a length of 70 cm, respectively 50 cm, and an inner diameter of 4 mm connected directly to the torch. The experimental conditions for the capillary electrophoresis, the interface, the ICP-QMS and the ICP-SFMS are summarised in Table 2.

2.2. Chemicals

Rubidium, indium, rhodium, caesium, barium and lanthanides standards (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were provided by SPEX CertiPrep (Metuchen, NJ, USA) as 1000 μg/mL stock standard solutions. Fifty millimolar phosphate buffer pH 2.5 for capillary electrophoresis was obtained from Agilent Technologies (Waldbronn, Germany). Picolinic acid (2-pyridinecarboxylic acid) and TRIS (Tris[hydroxymethyl]aminomethane) were provided by Sigma–Aldrich (Steinheim, Germany), HIBA (α-hydroxyisobutyric acid) by Fluka (Buchs, Switzerland) and formic acid by Merck (Darmstadt, Germany). Suprapure nitric acid was analytical-reagent grade from Merck (Darmstadt, Ger-

Table 3
Chemical composition of the simulated sample of nuclear spent fuel

Element	Concentration (μg/mL)
Rubidium	199 ± 12
Strontium	96 ± 5
Yttrium	217 ± 15
Zirconium	445 ± 18
Molybdenum	1460 ± 46
Ruthenium	1241 ± 55
Rhodium	235 ± 11
Palladium	268 ± 13
Silver	68 ± 4
Cadmium	109 ± 7
Tin	16 ± 1
Antimony	2.6 ± 0.3
Tellurium	642 ± 51
Caesium	4760 ± 181
Barium	1652 ± 88
Lanthanum	1171 ± 81
Cerium	2118 ± 114
Praseodymium	1030 ± 53
Neodymium	3964 ± 195
Samarium	916 ± 46
Europium	180 ± 10
Gadolinium	185 ± 11

many). All the other reagents were analytical-reagent grade. Water purified in a Milli-Q system (Millipore, Eschborn, Germany) was used throughout the procedure. All standard solutions and samples were prepared by dilution in mass in polyethylene bottles previously cleaned according to a procedure for trace element analysis. A CE buffer containing 15 mM phosphate at pH 2.5 was used for the determination of caesium. A CE buffer containing 0.8 mM picolinic acid, 10 mM HIBA and 25 mM formic acid at pH 4.7 adjusted by TRIS was employed for the determination of lanthanides. One microgram per milliliter and 10 ng/mL of rhodium were added as a marker to the CE buffer to monitor the electro-osmotic flow during the electrophoretic separation by CE-ICP-QMS and CE-ICP-SFMS, respectively. The fused silica capillaries were provided by Polymicro Technologies (Polymicro Technologies, Phoenix, AZ, USA). The capillary was flushed with running buffer for 15 min at the beginning of each day. A washing step of 5 min with running buffer was applied between each run. The capillary was also flushed with 1 M NaOH, Milli-Q water and air consecutively each for a 10-min duration at the end of each day. All system control, data acquisition and data evaluation were performed with G2201AA Agilent ChemStation software.

2.3. Sample preparation

The simulated sample of nuclear spent fuel corresponded to the chemical composition of a simulated high active concentrate (HAC). It contained, in addition to caesium, barium and lanthanides, a lot of other elements such as molybdenum, ruthenium, tellurium and zirconium as main elements. It was prepared by dissolving in mass standard powders of the different elements in 4 M nitric acid. The chemical composition of the simulated sample of nuclear spent fuel is given in Table 3.

PUREX (Plutonium Uranium Refining by EXtraction) is a hydrometallurgical process used in spent fuel reprocessing plants. It enables the separation of both uranium and plutonium from the other elements of the spent fuel [24]. This process operates in 4 M nitric acid. Fission products contribute mainly to the activity of the sample from PUREX process.

MOX (Mixed OXides) is used as a fuel in nuclear power plants. It is constituted of a mixture of uranium oxide and plutonium oxide. The simulation of the leaching of a MOX fuel by underground water is of high significance with respect to performance assessment, i.e., safety assessment modelling to evaluate the capacity of a possible underground storage site for nuclear wastes. The composition of the underground water has been simulated by a saline solution containing 12 mM Na^+, 10 mM Cl^- and 2 mM HCO_3^-.

All sample analyses have been obtained as the average of three replicate analyses.

3. Results and discussion

3.1. Determination of both concentration and isotopic composition of radioactive caesium by CE-ICP-MS

3.1.1. Stability of the coupling CE-ICP-MS

In order to check the stability of the coupling CE-ICP-MS, the electrical current, the electro-osmotic flow (EOF) and the nebulisation have been monitored during the electrophoretic separation of a test sample. A stable electrical current has been observed for a 30-kV voltage applied between the capillary electrophoresis and the interface: the electrical contact between the capillary electrophoresis and the interface is stable and continuous, and consequently the electrophoretic separations present a good repeatability. The electro-osmotic flow during the electrophoretic separation has been monitored through the signal of ^{103}Rh (1 μg/mL for CE-ICP-QMS, 10 ng/mL for CE-ICP-SFMS) added as a marker to the CE buffer. The nebulisation during the electrophoretic separation has been monitored observing the signal of ^{115}In (100 ng/mL for CE-ICP-QMS, 1 ng/mL for CE-ICP-SFMS) added as a marker to the interface make-up liquid (1% nitric acid). The electro-osmotic flow results stable during the electrophoretic separation. Consequently, the analyte transport from the CE capillary to the ICP-MS is stable as well as the nebulisation enabling a good accuracy for the signal obtained by ICP-MS.

3.1.2. Optimisation of CE-ICP-MS parameters

The influence of the argon flow rate necessary to the nebulisation at the interface as well as of the CE buffer molarity and CE buffer pH has been studied. Different interface argon flow rates from 0.7 L/min to 1.2 L/min as well as different CE buffer molarities (5 mM, 10 mM, 15 mM, 20 mM and 30 mM phosphate) and different CE buffer pH (pH 2.5, pH 5.1, pH 7.0 and pH 9.4) have been used to perform this study. The position of the capillary was first optimised to obtain the sharpest peak. It has been observed that the transport efficiency of the analyte between the spray chamber and the ICP-MS torch depends on the argon flow rate at the interface. Therefore, it was optimised

Table 4
Analytical figures of merit of the CE-ICP-MS methods for the caesium and barium determination

Analytical figures of merit	CE-ICP-QMS method		CE-ICP-SFMS method	
	Caesium, Cs	Barium, Ba	Caesium, Cs	Barium, Ba
Analysis duration (min)	3.5	4.5	5	6
Detection limit (S/N = 3)	6 ng/mL	8 ng/mL	4 pg/mL	14 pg/mL
Quantification limit (S/N = 10)	19 ng/mL	26 ng/mL	13 pg/mL	44 pg/mL
Absolute quantity detectable	162 fg	216 fg	84 ag	273 ag

to obtain the best efficiency for the nebulisation process. On the other hand, the migration time does not depend on the argon flow rate, what means that there is no laminar suction effect within the CE capillary, but it depends on the CE buffer molarity and pH. The higher the CE buffer molarity is the longer the migration time is. In fact, when the CE buffer molarity is increased, the zeta potential is decreased and consequently the electro-osmotic flow is decreased. The higher the pH value is the shorter the migration time is. This because with increasing of pH, the ionisation of the silanol groups at the surface of the CE capillary and the potential zeta increase. Consequently the electro-osmotic flow is faster.

Optimised conditions correspond to a CE phosphate buffer of concentration 15 mM and of pH 2.5 and an argon flow rate of 0.96 L/min (CE-ICP-QMS).

3.1.3. Development of the method for caesium determination by CE-ICP-MS

The separation of natural caesium and barium by CE-ICP-MS has been performed in the experimental conditions previously optimised, i.e., a 15 mM phosphate CE buffer at pH 2.5 and a 1% nitric acid make-up liquid. Concentrations of caesium and barium of 1 μg/mL for CE-ICP-QMS and 10 ng/mL for CE-ICP-SFMS (referred to the isotope ^{133}Cs and ^{138}Ba) were used for the analysis. The two elements resulted to be very well separated. It could be remarked that the migration time for barium is longer than that for caesium. The barium ion is charged twice positively (Ba^{2+}) whereas the caesium ion is charged once positively (Cs^+). Consequently the migration time for barium should be shorter than the migration time for caesium, since the more charged the ion is, the faster it goes. This migration order can be explained by the fact that barium, contrary to caesium, can be complexed by the phosphate ion ($\log K(Ba(H_2PO_4)^+) = -7.40$). Caesium and barium may migrate in the CE capillary under the forms Cs^+ and $Ba(H_2PO_4)^+$. Analytical figures of merit (analysis duration, detection and quantification limits as well as absolute quantity detected) of the CE-ICP-MS methods for the determination of caesium and barium have been determined using natural caesium and barium standard solutions and are presented in Table 4. Intra-day and inter-day repeatabilities are 1% and 3%, respectively. The numbers of theoretical plates for caesium and barium are high (22,000 plates per meter and 26,000 plates per meter, respectively for CE-ICP-QMS, 56,000 plates per meter and 66,000 plates per meter, respectively for CE-ICP-SFMS) and the peaks are very thin ($\omega_{1/2} = 4$ s for CE-ICP-QMS, $\omega_{1/2} = 3$ s for CE-ICP-SFMS). This method enables the detection of caesium and barium absolute quantities corresponding to some hundreds of femtograms for CE-ICP-QMS and some hundreds of attograms for CE-ICP-SFMS, respectively. The detection and quantification limits obtained by CE-ICP-SFMS for the determination of caesium enable the high-radioactive nuclear spent fuel samples to be diluted to have a concentration of radioactive caesium corresponding to some decades of pg/mL before analysis. The activity of the sample is consequently limited. For example, the quantification limit for radiocaesium ^{137}Cs, 13 pg/mL, corresponds to an activity of about 39 Bq/mL. Moreover the small amount of sample (low microliter range) needed for the analysis reduces the radiation dose for the personnel. Another important issue to be considered is the reduced volume of nuclear liquid wastes generated during the measurements. As a result, this method can represent a valid alternative for the determination of radiocaesium in nuclear spent fuel samples. This CE-ICP-SFMS method can be compared to γ-spectrometry and to IC-ICP-MS, which are currently used for the determination of radioactive caesium in nuclear spent fuels. Only ^{134}Cs and ^{137}Cs, which are γ-emitters, can be measured by γ-spectrometry (^{135}Cs is difficult to measure due to its low β energy and its half-life of 2.3×10^6 years) and the determination of low activities requires long counting times. On the contrary, all the caesium isotopes can be rapidly determined by CE-ICP-SFMS. As for the IC-ICP-MS method [10], it needs a sample volume of 200 μL and it enables to quantify an absolute quantity of 3.2 pg for caesium, whereas the CE-ICP-SFMS method needs a sample volume of approximately 30 μL and enables to quantify an absolute quantity of 273 ag for caesium since the injection volume is only 21 nL.

3.1.4. Determination of caesium in nuclear samples by CE-ICP-MS

The CE-ICP-MS methods have been applied to different nuclear samples such as nuclear samples from PUREX process and leachates from MOX fuels. The CE-ICP-QMS method has been first applied to the determination of caesium in a simulated sample of nuclear spent fuel. Good agreement is obtained between the CE-ICP-QMS values (Cs: 4884 ± 249 μg/mL; Ba: 1703 ± 105 μg/mL) and the reference values (Cs: 4760 ± 181 μg/mL; Ba: 1652 ± 88 μg/mL). It demonstrates that the CE-ICP-MS method can be used to determine radioactive caesium in nuclear spent fuel samples. The CE-ICP-SFMS method has been then applied to the determination of caesium (natural caesium ^{133}Cs, radiocaesium ^{134}Cs, ^{135}Cs and ^{137}Cs) in a nuclear sample from PUREX process (Fig. 1). The nuclear sample from PUREX process has been diluted 70,000 times before CE-ICP-SFMS analysis

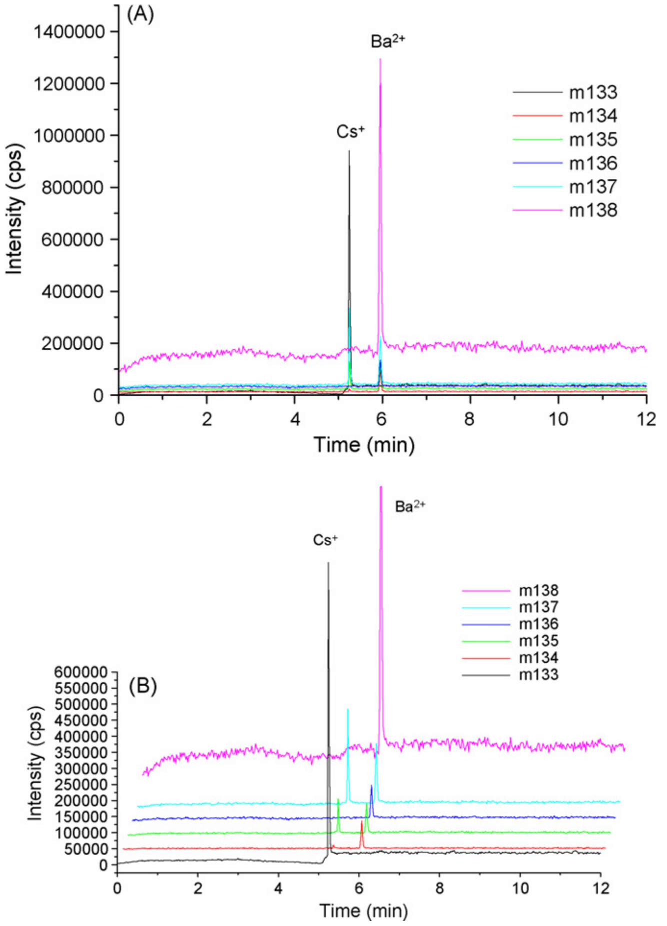

Fig. 1. Electropherograms obtained by CE-ICP-SFMS for the determination of caesium (natural caesium ^{133}Cs, radiocaesium ^{134}Cs, ^{135}Cs and ^{137}Cs) in a nuclear sample from PUREX process. Its separation from barium isotopes is also illustrated. The separation of the Cs and Ba as elements and isobars is shown. (A) 2D electropherogram and (B) 3D electropherogram. For Ba the charge +2 refers to the charge of the element in the species $Ba(H_2PO_4)^+$ as separated in the CE capillary. Experimental conditions—buffer: 15 mM phosphate pH 2.5; make-up liquid: HNO_3 1%.

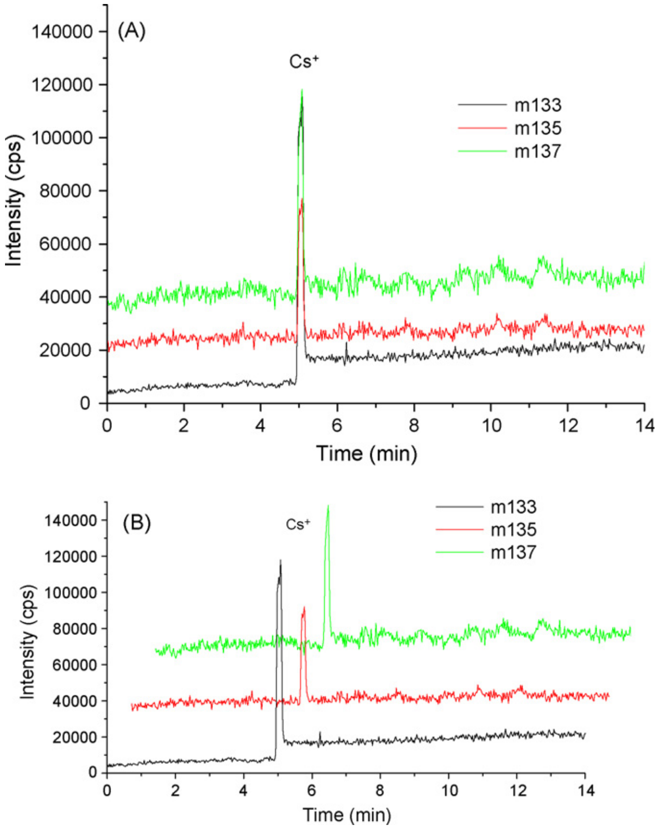

Fig. 2. Electropherograms obtained by CE-ICP-SFMS for the determination of caesium (natural caesium ^{133}Cs, radiocaesium ^{135}Cs and ^{137}Cs) in a leachate of MOX fuel. (A) 2D electropherogram and (B) 3D electropherogram. Experimental conditions—buffer: 15 mM phosphate pH 2.5; make-up liquid: HNO_3 1%.

and as a consequence, the activity of the nuclear sample has been highly decreased: the radiation dose for the personnel is inferior to 20 μSv per hour after the dilution. The CE-ICP-SFMS results are presented in Table 5. The CE-ICP-SFMS method overcomes the isobaric interferences for radiocaesium with natural barium at masses 134, 135 and 137. The isotopic ratios of 0.041 ± 0.009 and of 0.385 ± 0.057 were obtained for ^{134}Cs/^{137}Cs and ^{135}Cs/^{137}Cs, respectively. These values are characteristic of the nuclear fuel from which the sample originates. The values of the isotopic ratios ^{134}Cs/^{137}Cs and ^{135}Cs/^{137}Cs obtained experimentally can be compared with those given by the calculation codes. Barrero Moreno et al. [10] have measured by IC-ICP-MS the isotopic ratio ^{134}Cs/^{137}Cs in a nuclear spent fuel with different burn-ups. They have compared their results to the values given by the calculation code KORIGEN [25]. Their values are between 0.013 for a burn-up of 45 GWd/t and 0.053 for a burn-up of 67 GWd/t. The value obtained by CE-ICP-SFMS for the nuclear sample from PUREX process belongs to this range.

Table 5
Results obtained by CE-ICP-SFMS for the determination of caesium (natural caesium ^{133}Cs, radiocaesium ^{134}Cs, ^{135}Cs and ^{137}Cs) and barium in a nuclear sample from PUREX process

Mass	Element	CE-ICP-SFMS results (μg/mL)
133	Cs	87.5 ± 2.7
134	Cs	1.2 ± 0.2
134	Ba	12.7 ± 1.1
135	Cs	11.2 ± 1.0
135	Ba	6.0 ± 0.4
136	Ba	8.8 ± 0.6
137	Cs	29.1 ± 1.5
137	Ba	18.6 ± 1.2
138	Ba	124.9 ± 3.6

The CE-ICP-SFMS method has been also applied to a leachate of MOX fuel (Fig. 2). It has been observed experimentally that ^{134}Cs is not present in this leachate of MOX fuel. The results obtained by CE-ICP-SFMS for the determination of the radiocaesium ^{137}Cs have been compared with the results obtained by γ-spectrometry and ICP-SFMS (fission products ^{137}Cs and ^{137}Ba). The results obtained by CE-ICP-SFMS and by γ-spectrometry for the determination of radiocaesium ^{137}Cs are in excellent agreement: 3.56 ± 0.19 and 3.56 ± 0.07, respectively. The value obtained by ICP-SFMS for the determination of total fission products at mass 137 is slightly superior to the values obtained by CE-ICP-SFMS and by γ-spectrometry for the determination of ^{137}Cs since clearly is relevant to the sum of Cs and Ba at mass 137. The result obtained for the isotopic ratio ^{135}Cs/^{137}Cs by CE-ICP-SFMS has been also compared with those obtained by ICP-SFMS as well as by the calculation code ORIGEN [26]. The value obtained by CE-ICP-SFMS of 0.77 ± 0.06 resulted in a good agreement with that of 0.72 calculated by the code. By ICP-SFMS without CE separation, a value of 0.86 ± 0.05 was obtained.

3.2. Determination of both concentration and isotopic composition of lanthanides by CE-ICP-MS

3.2.1. Development of the method for lanthanide determination by CE-ICP-MS

The technique of partial complexation is often used for the separation of metal ions by capillary electrophoresis. The competition between two different ligands enables to attain differences in the degree of complexation and consequently different electrophoretic mobilities. Öztekin and Erim [27] performed partial complexation of lanthanides with picolinic acid and HIBA employing a CE buffer composed of 0.8 mM picolinic acid, 10 mM HIBA and 25 mM formic acid at pH 4.7 adjusted by TRIS [27]. Lanthanides were detected by direct UV–vis absorption spectrophotometry. However, a detection limit of some μg/mL could be obtained. The detection by ICP-MS presents the advantage to have lower detection limits (from the ng/mL to the pg/mL) and the isotopic composition is obtained.

As already said in the introduction, the determination of a specific lanthanide is also very often hindered by the presence of isobaric interferences from other lanthanides as well as from the formation of the lanthanide oxides (Table 1). Therefore, they have to be chemically separated before mass spectrometric analysis. Fourteen lanthanides (La–Lu) are separated by CE-ICP-MS with a resolution of 100% except europium and gadolinium, which are overlapping on 20% of their heights (Fig. 3A and B for CE-ICP-QMS and CE-ICP-SFMS, respectively). The concentration of each lanthanide used for the analysis is 1 μg/mL for CE-ICP-QMS, respectively 10 ng/mL for CE-ICP-SFMS, as referred to the major isotope (^{139}La, ^{140}Ce, ^{141}Pr, ^{142}Nd, ^{152}Sm, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb and ^{175}Lu). The presence of the different isobaric interferences is highlighted in Fig. 4. As it can be seen on the electropherogram, all the lanthanide isobaric interferences ^{142}Ce–^{142}Nd, ^{144}Nd–^{144}Sm, ^{148}Nd–^{148}Sm, ^{150}Nd–^{150}Sm, ^{154}Sm–^{154}Gd, ^{160}Gd–^{160}Dy, ^{164}Dy–^{164}Er, ^{170}Er–^{170}Yb and ^{176}Yb–^{176}Lu are resolved. The presence of oxide molecular ions for lanthanum (m/z 155), cerium (m/z 156 and m/z 158) and praseodymium (m/z 157) is observed. These oxide molecular ions could interfere with the determination of other heavier lanthanides such as gadolinium without previous chemical separation. Analytical figures of merit of the CE-ICP-MS methods have been determined using lanthanide standard solutions and are presented in Tables 6 and 7 for CE-ICP-QMS and CE-ICP-SFMS, respectively. Intra-day and inter-day repeatabilities are 1% and 3%, respectively. The separation efficiency is high (between 72,000 plates per meter for lanthanum and 109,000 plates per meter for ytterbium for CE-ICP-QMS, respectively, between 93,000 plates per meter for lutetium and 165,000 plates per meter for ytterbium for CE-ICP-SFMS), and the peaks are very thin ($\omega_{1/2} = 5$ s for CE-ICP-QMS, $\omega_{1/2} = 4$ s for CE-ICP-SFMS).

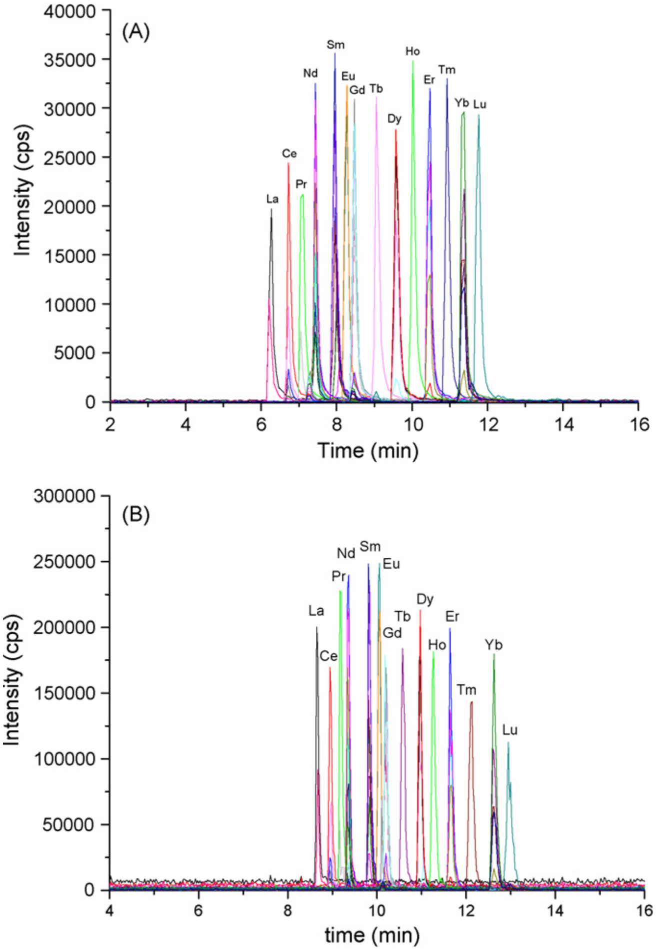

Fig. 3. Electropherogram obtained for the separation of the 14 lanthanides. Ions detected by ICP-MS: ^{139}La^{+}, ^{140,142}Ce^{+}, ^{141}Pr^{+}, ^{142,143,144,145,146,148,150}Nd^{+}, ^{144,147,148,149,150,152,154}Sm^{+}, ^{151,153}Eu^{+}, ^{154,155,156,157,158,160}Gd^{+}, ^{159}Tb^{+}, ^{160,161,162,163,164}Dy^{+}, ^{165}Ho^{+}, ^{164,166,167,168,170}Er^{+}, ^{169}Tm^{+}, ^{170,171,172,173,174,176}Yb^{+}, ^{175,176}Lu^{+}. (A) CE-ICP-QMS and (B) CE-ICP-SFMS. Experimental conditions—Ln: 1 μg/mL (CE-ICP-QMS), 10 ng/mL (CE-ICP-SFMS); buffer: 0.8 mM picolinic acid, 10 mM HIBA, 25 mM formic acid, pH 4.7 adjusted by TRIS; make-up liquid: HNO_3 1%.

This method can detect absolute quantities of lanthanides in the range of some hundreds of femtograms for CE-ICP-QMS and some hundreds of attograms for CE-ICP-SFMS, respectively. Both concentration and isotopic composition are obtained. ^{148}Nd can be easily determined to evaluate the burn-up of the nuclear spent fuel, since its isobaric interference with ^{148}Sm is resolved. The detection and quantification limits obtained by CE-ICP-SFMS for the determination of lanthanides enable the high-radioactive nuclear spent fuel samples to be diluted to have a concentration of each lanthanide corresponding to some decades of pg/mL before analysis and as a consequence the activity of the sample is limited.

This CE-ICP-SFMS method can be compared to γ-spectrometry and to IC-ICP-MS, which are currently used for

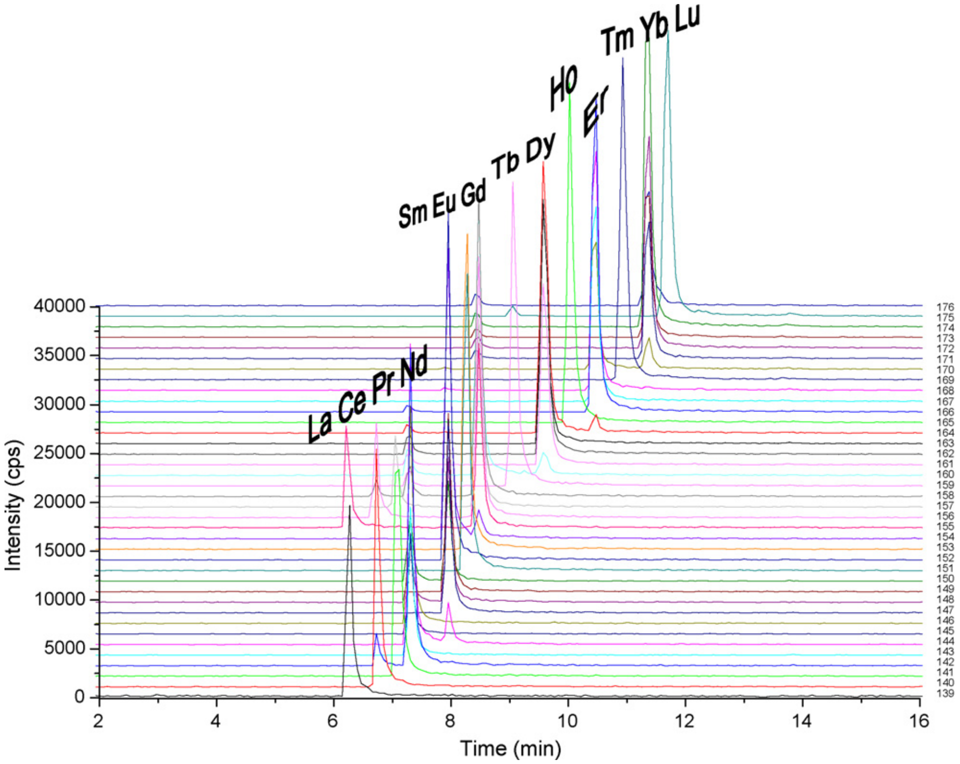

Fig. 4. Resolution of the isobaric interferences for lanthanides by CE-ICP-QMS in the sequence from left to right: $^{139}La^{+}$, $^{140,142}Ce^{+}$, $^{141}Pr^{+}$, $^{142,143,144,145,146,148,150}Nd^{+}$, $^{144,147,148,149,150,152,154}Sm^{+}$, $^{151,153}Eu^{+}$, $^{154,155,156,157,158,160}Gd^{+}$, $^{159}Tb^{+}$, $^{160,161,162,163,164}Dy^{+}$, $^{165}Ho^{+}$, $^{164,166,167,168,170}Er^{+}$, $^{169}Tm^{+}$, $^{170,171,172,173,174,176}Yb^{+}$, $^{175,176}Lu^{+}$.

Table 6
Analytical figures of merit of the CE-ICP-QMS method for the determination of lanthanides

Analytical figures of merit	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Analysis duration (min)	Thirteen minutes for the determination of all lanthanides													
Detection limit (S/N = 3) (ng/mL)	5	4	3	14	15	5	12	3	8	3	8	4	6	3
Quantification limit (S/N = 10) (ng/mL)	16	13	9	47	50	16	38	10	26	10	27	12	18	8
Absolute quantity detected (fg)	135	108	81	378	405	135	324	81	216	81	216	108	162	81

the determination of lanthanides in nuclear spent fuels. Only γ-emitters, such as ^{155}Eu, can be measured by γ-spectrometry. On the contrary, all the lanthanide isotopes can be determined by CE-ICP-SFMS.

As for the IC-ICP-MS method [9], it needs a sample volume of 250 μL and it enables to quantify a typical absolute quantity of 208 pg for the lanthanides, whereas the CE-ICP-SFMS method needs a sample volume of approximately 30 μL and enables to quantify a typical absolute quantity of 150 ag for the lanthanides (between 63 ag for praseodymium and 231 ag for samarium), since the injection volume is some nanoliters. Moreover the analysis duration for the separation of the lanthanides by CE-ICP-SFMS is shorter than that by IC-ICP-MS, respectively 13 min by CE-ICP-SFMS and 30 min (till europium) by IC-ICP-MS [9]. This method can represent a valid alternative for the determination of lanthanides in nuclear spent fuel samples.

3.2.2. Determination of lanthanides in nuclear samples by CE-ICP-MS

The CE-ICP-MS method has been applied first to a simulated sample of nuclear spent fuel (Fig. 5A and B for CE-ICP-QMS and CE-ICP-SFMS, respectively). The standard addition method has been used to determine the concentration of lanthanides in the simulated sample of nuclear spent fuel. The

Table 7
Analytical figures of merit for the determination of lanthanides by CE-ICP-SFMS

Analytical figures of merit	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Analysis duration (min)	Thirteen minutes for the whole lanthanide series													
Detection limit (S/N = 3) (pg/mL)	4	3	3	10	11	4	9	3	6	3	6	5	8	4
Quantification limit (S/N = 10) (pg/mL)	13	10	8	33	36	12	28	9	18	10	18	14	27	13
Absolute quantity detectable (ag)	84	63	63	210	231	84	189	63	162	63	162	105	168	84

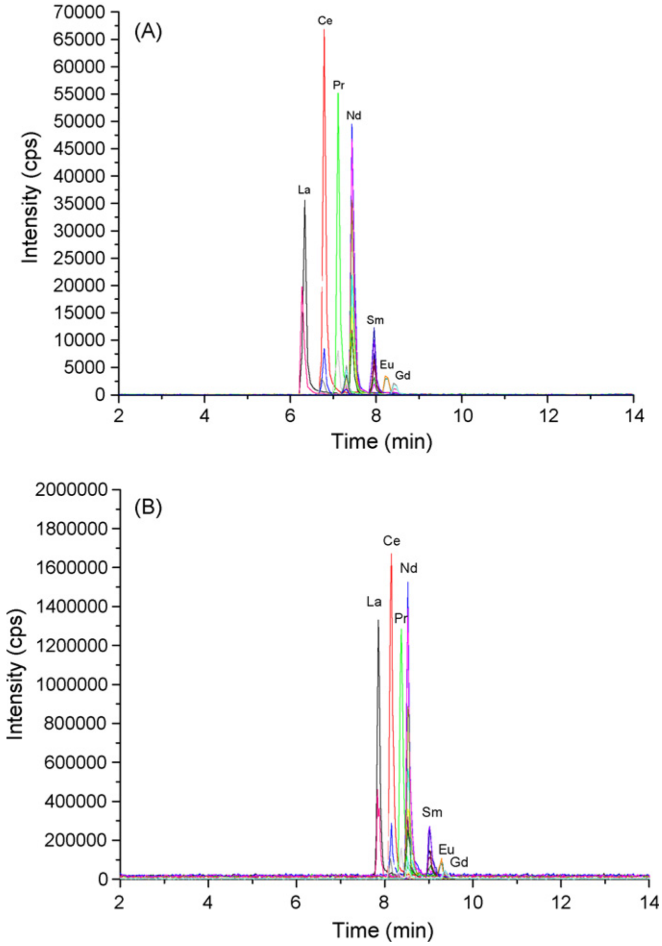

Fig. 5. Electropherogram obtained for the determination of lanthanides in a simulated sample of nuclear spent fuel. Ions detected by ICP-MS: La^+, Ce^+, Pr^+, Nd^+, Sm^+, Eu^+, Gd^+. (A) CE-ICP-QMS and (B) CE-ICP-SFMS. Experimental conditions—buffer: 0.8 mM picolinic acid, 10 mM HIBA, 25 mM formic acid, pH 4.7 adjusted by TRIS; make-up liquid: HNO_3 1%.

results by CE-ICP-QMS and by CE-ICP-SFMS are compared with the reference values (Table 8). Good agreement is obtained. It demonstrates that the CE-ICP-MS method can be used to determine lanthanides in nuclear spent fuel samples. The CE-ICP-SFMS method has been then applied to a nuclear sample from PUREX process (Fig. 6). All the isobaric interferences of this nuclear sample from PUREX process are resolved. The standard addition method has been used to determine the concentration of lanthanides in the nuclear sample from PUREX process. The results obtained by CE-ICP-SFMS are compared with the values obtained by ICP-SFMS in Table 9. Good agreement is obtained between the CE-ICP-SFMS and the ICP-SFMS

Table 9
Comparison of the results obtained by CE-ICP-SFMS with the values obtained by ICP-SFMS for the determination of lanthanides in a nuclear sample from PUREX process

Isotope	Results	
	CE-ICP-SFMS (μg/mL)	ICP-SFMS (μg/mL)
^{139}La	259.2 ± 15.8	251.1 ± 10.1
^{140}Ce	240.3 ± 14.6	249.2 ± 10.0
^{141}Pr	215.0 ± 13.1	224.6 ± 9.0
^{142}Ce	3.9 ± 0.6	226.5 ± 9.1
^{142}Nd	222.4 ± 13.5	
^{143}Nd	106.3 ± 6.5	114.2 ± 4.6
^{144}Nd	317.2 ± 18.7	329.8 ± 13.2
^{145}Nd	113.2 ± 6.8	124.0 ± 5.0
^{146}Nd	144.1 ± 8.5	159.0 ± 6.4
^{147}Sm	36.8 ± 2.4	35.5 ± 1.8
^{148}Nd	27.5 ± 1.8	125.9 ± 5.1
^{148}Sm	106.3 ± 6.5	
^{150}Nd	14.5 ± 1.3	106.5 ± 4.4
^{150}Sm	84.0 ± 5.1	
^{151}Eu	14.9 ± 1.9	15.6 ± 0.9
^{152}Sm	14.0 ± 1.9	16.3 ± 1.0
^{153}Eu	22.0 ± 1.4	23.0 ± 1.3
^{154}Sm	14.5 ± 1.9	16.3 ± 1.0
^{155}Gd	4.0 ± 0.7	4.9 ± 0.4
^{156}Gd	47.8 ± 3.4	49.5 ± 2.5
^{157}Gd	3.8 ± 0.6	3.6 ± 0.3
^{158}Gd	12.4 ± 1.0	10.5 ± 0.7
^{159}Tb	3.5 ± 0.7	2.4 ± 0.4
^{160}Gd	5.1 ± 0.8	5.0 ± 0.6
^{161}Dy	2.4 ± 0.4	1.8 ± 0.3
^{162}Dy	3.3 ± 0.5	2.3 ± 0.3
^{163}Dy	3.0 ± 0.5	Not measured
^{164}Dy	3.8 ± 0.5	Not measured
^{165}Ho	4.1 ± 0.6	Not measured
^{166}Er	2.7 ± 0.5	Not measured
^{167}Er	2.2 ± 0.4	Not measured
^{168}Er	2.5 ± 0.5	Not measured
^{169}Tm	2.2 ± 0.4	Not measured
^{171}Yb	1.0 ± 0.2	Not measured
^{172}Yb	1.3 ± 0.3	Not measured
^{173}Yb	1.0 ± 0.2	Not measured
^{174}Yb	2.3 ± 0.4	Not measured
^{175}Lu	0.9 ± 0.2	Not measured
^{176}Yb	1.0 ± 0.2	Not measured

Table 8
Comparison of the results obtained by CE-ICP-QMS and CE-ICP-SFMS with the reference values for the determination of lanthanides in a simulated sample of spent fuel

Element	Results		
	CE-ICP-QMS (μg/mL)	CE-ICP-SFMS (μg/mL)	Reference values (μg/mL)
Lanthanum	1203 ± 88	1054 ± 94	1171 ± 81
Cerium	2168 ± 126	2051 ± 118	2118 ± 114
Praseodymium	1103 ± 61	977 ± 63	1030 ± 53
Neodymium	3940 ± 206	3895 ± 217	3964 ± 195
Samarium	980 ± 60	956 ± 62	916 ± 46
Europium	183 ± 20	181 ± 16	180 ± 10
Gadolinium	211 ± 19	170 ± 15	185 ± 11

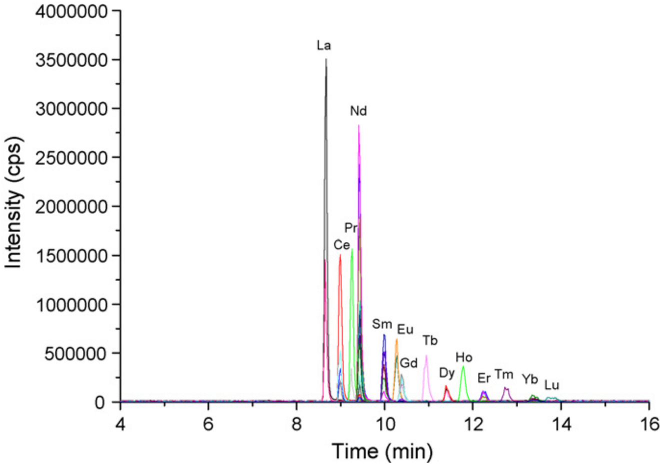

Fig. 6. Electropherogram obtained for the determination of lanthanides by CE-ICP-SFMS in a nuclear sample from PUREX process. Ions detected by ICP-MS: $^{139}La^+$, $^{140,142}Ce^+$, $^{141}Pr^+$, $^{142,143,144,145,146,148,150}Nd^+$, $^{144,147,148,149,150,152,154}Sm^+$, $^{151,153}Eu^+$, $^{154,155,156,157,158,160}Gd^+$, $^{159}Tb^+$, $^{160,161,162,163,164}Dy^+$, $^{165}Ho^+$, $^{164,166,167,168,170}Er^+$, $^{169}Tm^+$, $^{170,171,172,173,174,176}Yb^+$, $^{175,176}Lu^+$. Experimental conditions—buffer: 0.8 mM picolinic acid, 10 mM HIBA, 25 mM formic acid, pH 4.7 adjusted by TRIS; make-up liquid: HNO_3 1%.

values. However the CE-ICP-SFMS method enables to have a more complete inventory of lanthanides than by ICP-SFMS. Indeed we have access to all the lanthanide isotopes by CE-ICP-SFMS because the isobaric interferences between cerium and neodymium at mass 142 and between neodymium and samarium at masses 148 and 150 are resolved.

4. Conclusion

Simple and rapid CE-ICP-MS methods for the determination of fission products (caesium and the whole lanthanide series) have been developed. These CE-ICP-MS methods present a lot of advantages compared with other analytical techniques used for the determination of fission products, such as α, β and γ-spectrometry as well as mass spectrometry or mass spectrometry hyphenated to a chromatographic method. Analyses are performed in a short time: fission products are determined in some minutes by CE-ICP-MS (6 min for caesium, 13 min for lanthanides). Contrary to the mass spectrometry, which suffers from the presence of numerous isobaric interferences, CE-ICP-MS overcomes all the isobaric interferences (^{135}Cs–^{135}Ba, ^{137}Cs–^{137}Ba, ^{142}Ce–^{142}Nd, ^{144}Nd–^{144}Sm, ...). Consequently both content and isotopic composition is determined at a very low detection limits (ng/mL for CE-ICP-QMS and pg/mL for CE-ICP-SFMS). Moreover a low microliter range sample volume (typically 30 μL) is needed for the analyses by CE-ICP-MS contrary to the coupling with a chromatographic system, which needs several hundred microliters (200–250 μL) of sample.

The CE-ICP-MS methods have been applied with success to the determination of fission products in different nuclear samples such as nuclear samples from PUREX process and leachates of MOX fuels. Isotopic ratios such as $^{134}Cs/^{137}Cs$ and $^{135}Cs/^{137}Cs$ and isotopes of interest for the characterisation of the nuclear fuel such as ^{148}Nd can be then determined.

As a conclusion, these CE-ICP-MS methods represent a valid alternative to currently available techniques to perform the inventory of fission products in nuclear fuels. We can also remark that the determination of lanthanides by CE-ICP-MS can be also applied in some other scientific and technological fields such as metallurgy, environmental sciences and geology [28–36].

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