

## **Precise Determination of Isotope Ratios in Nuclear Samples by CE-MC-ICP-MS**

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### **ABSTRACT**

The determination of the isotopic and elemental composition of nuclear samples is essential for the validation of neutronic codes and for the management of nuclear materials, particularly as the multi-recycling of Pu is considered in France. A capillary electrophoresis - multicollector inductively coupled plasma mass spectrometry (CE-MC-ICP-MS) method for the measurement of actinides (U, Pu, Am, Cm) and of lanthanide fission products (Nd, Sm, Eu, Gd) isotope ratios in spent nuclear fuel samples was developed. This method allowed the determination of isotope ratios for the elements of interest with relative standard deviations and relative errors in the per-mil (0.1%) range. The CE-MC-ICP-MS results were in accordance with the ones obtained by two-step chromatography followed by offline measurement with mass spectrometry with a reduction of sample quantities and of liquid waste by a factor of at least 100. The application of CE-MC-ICP-MS developments to the design and fabrication of analytical microsystems could provide new miniaturized tools for the determination of isotopic and elemental compositions of nuclear samples.

### **1 INTRODUCTION**

The multi-recycling of plutonium in French nuclear reactors is currently being considered. The development of scenarios towards the implementation of Pu multi-recycling relies on simulation and evolution codes for nuclear fuels. [1] Among the output of these codes, the isotopic and elemental composition of spent nuclear fuel is particularly important for its storage and reprocessing. These codes need to be qualified by comparison with experimental data. To this end, it is necessary to experimentally determine the isotopic and elemental composition of spent nuclear fuel samples. In this context, the required precision and trueness for the determination of the isotopic and elemental composition of spent nuclear fuel samples is in the per-mil (0.1%) range.

Spent nuclear fuels are composed of U, Pu, minor actinides (Am, Cm) and fission products (such as the lanthanides Nd, Sm, Eu, Gd). One example of required determination is the burn-up of spent nuclear fuel, which involves the determination of the concentration of  $^{148}\text{Nd}$ ,  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . [2] For the spent nuclear fuel examined in this study, solid spent nuclear fuel was

dissolved using boiling nitric acid in a hot cell of the ATALANTE facility in CEA Marcoule. [3] The spent nuclear fuel sample to be analyzed therefore contains U, Pu, minor actinides (Am, Cm) and fission products (including Nd, Sm, Eu, Gd) in a nitric acid matrix.

In order to perform the determination of the isotopic and elemental composition of spent nuclear fuel samples, thermal ionization mass spectrometry (TIMS) and/or multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) are often used in the nuclear domain because of their sensitivity and precision. These methods are however impaired by isobaric interferences such as the interference between  $^{241}\text{Am}$  and  $^{241}\text{Pu}$ . To overcome this limitation, one solution is chemical separation of the interfering species before analysis by mass spectrometry. The protocol used by CEA/LANIE employs gravitational chromatography and high-performance liquid chromatography before fraction collection and mass spectrometric analysis. [4] The uncertainty that can be attained with this protocol is in the per-mil range for major elements. Downsides of the use of chromatography are the sample quantity (in the  $\mu\text{g}$  range) and waste volume production (a few tens of mL). The diminution of these quantities is of great importance in the nuclear field in order to reduce the radioactive dose and nuclear liquid waste production.

A scale reduction is possible with the use of alternative separation methods. In this context, capillary electrophoresis (CE) is a particularly interesting choice because of the capillary dimensions. [5] Capillary volumes are usually in the  $\mu\text{L}$  range, sample quantities in the pg range and waste volume production in the  $\mu\text{L}$  range as well. The hyphenation of CE with ICP-MS (CE-ICP-MS) allows the online determination of isotope ratios by ICP-MS of the elements previously separated by CE.

The migration of elements in CE can be modified by complexation with ligands present in the CE electrolyte. It is possible to separate various elements with the selection of an appropriate complexing agent. CE-ICP-MS separations and analyses were described for lanthanides using HIBA [6–8], for actinides (Th, U, Np, Pu, Am) using acetic acid [9, 10], for U and Th using HMBA. [11] There is to our knowledge no study dealing with the analysis of both actinides and fission products in spent nuclear fuel samples by CE-ICP-MS.

The objective of this study was the demonstration of the capability of CE-MC-ICP-MS to determine isotope ratios in a spent nuclear fuel sample with a per-mil level of uncertainty. To this end, the CE separation and ICP-MS analysis of both actinides (U, Pu, Am, Cm) and lanthanide fission products (Nd, Sm, Eu, Gd) was developed and applied to a spent MOX fuel sample. The study was focused on the choice of the complexing agent for the CE separation of both actinides and lanthanide fission products in the spent nuclear fuel sample and on the demonstration of the feasibility of the measurement of isotope ratios of elements contained in a spent nuclear fuel sample by CE-MC-ICP-MS.

## **2 CAPILLARY ELECTROPHORESIS SEPARATION DEVELOPMENT**

The capillary electrophoresis step aims at separating isobaric interferences for all elements of interest. In order to avoid all interferences between the elements analyzed in this study (U, Pu, Am, Cm, Nd, Sm, Eu, Gd), it was necessary to isolate those elements and obtain resolved CE peaks. As Pu, Am and Cm are radioactive elements that require specific handling precautions, the method was first developed without these elements in a conventional laboratory before testing the method with radioactive elements in a second phase. Developments in the conventional laboratory are presented in the following section.

## 2.1 Development of the CE separation with a synthetic sample

For these first developments, Pu, Am and Cm are not included in the sample to avoid manipulations in the glovebox. The synthetic sample analyzed in the present section is composed of the 14 natural lanthanides, of uranium and thorium at a concentration of approximately  $1 \mu\text{g}\cdot\text{g}^{-1}$  in the separation electrolyte. All lanthanides were included in the sample for exhaustivity but only Nd, Sm, Eu and Gd are discussed in this study as they are particularly important for the evaluation of neutronic codes. [12]

To optimize the separation, it is first necessary to select the CE electrolyte. The separation electrolyte often contains a complexing agent to modify analytes' electrophoretic mobilities. HMBA and HIBA are especially interesting as complexing agents because of their capacity to separate trivalent lanthanides and trivalent actinides. [13, 14] HMBA and HIBA are both  $\alpha$ -hydroxycarboxylic acids ( $\alpha$ -HCA) and will be denoted as such in the rest of the study.

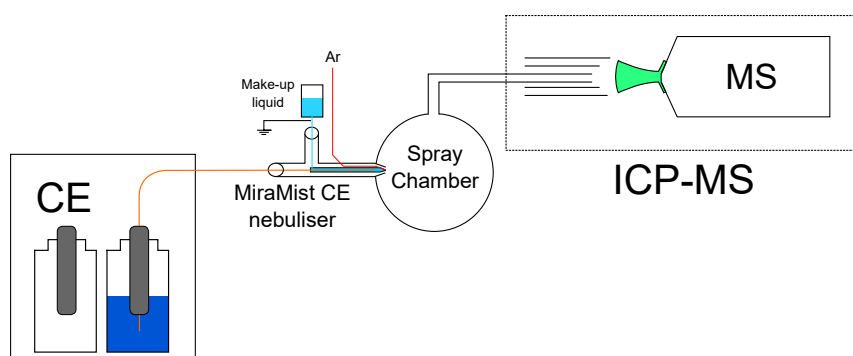


Figure 1: Instrumental setup used for the capillary electrophoresis - quadrupole ICP-MS (CE-Q-ICP-MS) hyphenation

It was thus decided to verify the ability of HMBA and HIBA to perform the CE separation of the elements of the synthetic sample and to select an appropriate  $\alpha$ -HCA concentration to perform the separation of all elements of interest in the spent MOX fuel sample. The effect of the HIBA and HMBA concentration on the migration of the elements of interest was studied between 5 and 500  $\text{mmol}\cdot\text{L}^{-1}$  at a pH of 3. The pH of 3 was selected to limit the hydrolysis of actinide elements. [15] For the optimization of the CE step, a commercial CE instrument was hyphenated to a XSeries II (Thermo Fisher Scientific) quadrupole ICP-MS. This commercial CE instrument allows the application of high-voltage as well as pneumatic pressure ( $\Delta P$ ) on the inlet vial. The instrumental setup used for the CE-Q-ICP-MS is presented in Figure 1. The CE-ICP-MS hyphenation presented in Figure 1 is achieved by a MiraMist CE nebulizer. This nebulizer ensures both nebulization of the sample and closure of the CE electric circuit with the use of a make-up liquid. After droplet selection in the spray chamber, the sample is atomized and ionized in the ICP and introduced in the mass spectrometer. Using this setup, the species separated during the CE step are analyzed online by ICP-MS.

Experiments were conducted for concentrations of 5, 20, 50, 100, 200, 350 and 500  $\text{mmol}\cdot\text{L}^{-1}$  at pH 3 for HIBA and for HMBA. Electrophoretic mobilities of analytes were calculated using Eq. (1) where  $L$  is the capillary length,  $U$  the applied voltage and  $t_m$  the migration time of the analyte.

$$\mu_{ep} = \frac{L^2}{U \times t_m} - \mu_{eo} \quad (1)$$

The electroosmotic mobility, characteristic of the electroosmotic flow present in the capillary when the voltage is applied was calculated using Eq. (2) where  $t_{eo}$  is the migration time of an electrically neutral species.

$$\mu_{eo} = \frac{L^2}{U \times t_{eo}} \quad (2)$$

In this study, ICP-MS was used as the CE detector. For the measurement of the electroosmotic mobility with the ICP-MS, a complex of gallium and N-N'-N''-triacyclononanetriacetic acid (NOTA) was used.

In order to choose the optimal  $\alpha$ -HCA concentration, two criteria were chosen. The first was the electrophoretic mobility of uranium which had to be positive in order to obtain U migration without applying pressure on the inlet vial. The second was the Nd/Sm resolution which had to be maximized, as it was hypothesized that Am and Cm would migrate between Nd and Sm, similarly to what was observed in HPLC using HMBA in the mobile phase. [16]

It was found that the Nd/Sm resolution increases as the  $\alpha$ -HCA concentration increases, as presented in Figure 2.

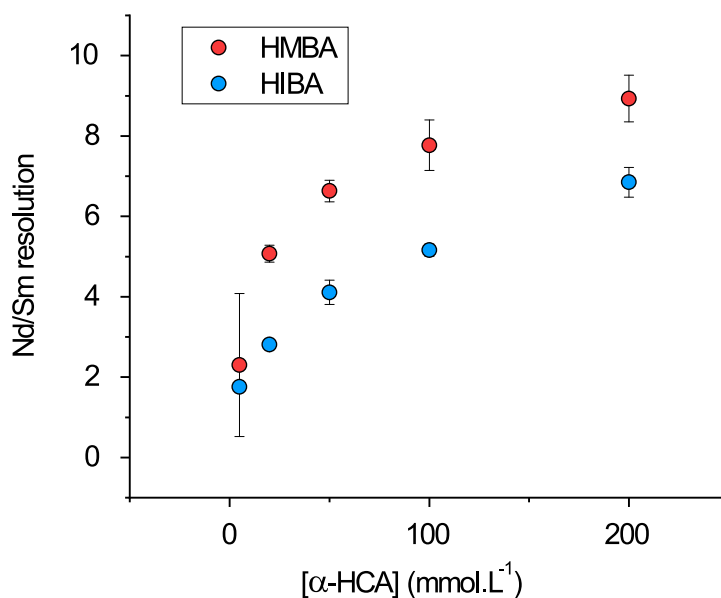


Figure 2: Nd/Sm resolution as a function of the  $\alpha$ -HCA concentration

For all concentrations studied, the Nd/Sm resolution was superior for HMBA over HIBA, as visible in Figure 2. This finding was consistent with studies from the literature in which HMBA was more selective than HIBA for the separation of light lanthanides. [17, 18] The limiting criterium was therefore the electrophoretic mobility of uranium ; the selected concentration was the one for which the  $\alpha$ -HCA concentration is the highest and for which the electrophoretic mobility of uranium is still positive. The electrophoretic mobility of uranium was found to be zero at a HMBA concentration of approximately 150 mmol.L<sup>-1</sup>. A HMBA concentration of 120 mmol.L<sup>-1</sup> was chosen in order for the electrophoretic mobility of uranium to be slightly positive.

The electrophoregram obtained by CE-Q-ICP-MS for a HMBA concentration of 120 mmol.L<sup>-1</sup> with the synthetic sample is presented in Figure 3.

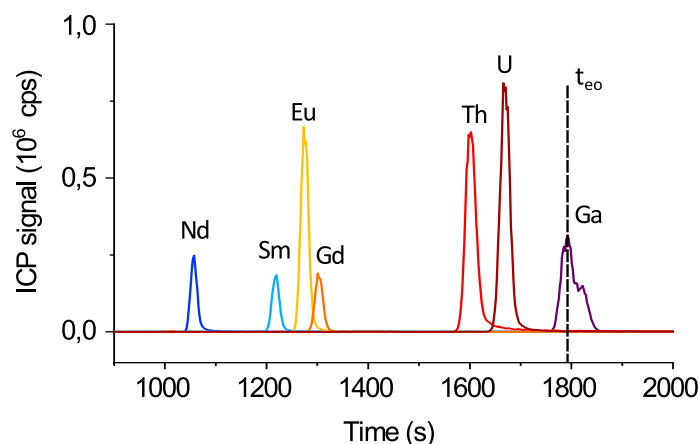


Figure 3: CE-Q-ICPMS electropherogram of the synthetic sample with a 120 mmol.L<sup>-1</sup> HMBA electrolyte at a pH of 3, U=25 kV and  $\Delta P=50$  mbar

It is visible in the electropherogram presented in Figure 3 that Nd, Sm and Eu are baseline separated. Nd and Sm were particularly well separated with more than 100 seconds of baseline between the Nd and Sm peaks. The Eu/Gd pair was the most difficult to separate ; there was an overlap between the two peaks. The resolution between the Eu and Gd peaks can however be increased if desired with, for example, a diminution of the pressure ( $\Delta P$ ) applied on the inlet vial during the separation. In this case, the downside of increased Eu/Gd resolution is increased analysis times. It is noteworthy that the separation can be tailored to the analyst's needs ; if Eu/Gd separation is more important for a specific application, the use of HIBA or of another  $\alpha$ -HCA concentration is recommended. This demonstrates the versatility of the use of  $\alpha$ -HCA in CE separations.

The results obtained with HMBA as the separation electrolyte using a synthetic sample demonstrate that the one step separation of lanthanide fission products is possible and that the online measurement of isotope ratios, free from isobaric interferences for these elements can be achieved with CE-ICP-MS. Several aspects of the CE separation including the behaviour of elements such as Pu, Am and Cm need to be examined. This examination was done using a diluted spent MOX fuel solution and is discussed in the following section.

## 2.2 CE separation of a spent MOX fuel sample

The spent MOX fuel analyzed in this study was dissolved in boiling nitric acid and diluted before shipment to our laboratory. [3] Due to the nature of the sample, the CE separation and MS analysis had to be performed in a glovebox. A custom setup was previously developed to allow the integration of the CE separation in a glovebox. [9] With this setup, high-voltage and pressure ( $\Delta P$ ) are applicable as with a conventional CE instrument.

Prior to CE separation, an additional oxidation step had to be performed when analyzing Pu-containing samples. Whereas lanthanide fission products, Am and Cm are predominantly in the +III oxidation state in moderate redox conditions, plutonium has a remarkably complex redox chemistry. [15, 19] Four different oxidation states (+III, +IV, +V and +VI) can coexist in moderate redox conditions. [20]

As trivalent actinides have similar physico-chemical properties, Pu(III) was not selected as an appropriate oxidation state for the CE separation to avoid isobaric interference on <sup>241</sup>Am(III). Pu(IV) is known to be subject to hydrolysis and polymerization starting from pH values as low as 0. [15] For this reason, Pu(IV) was deemed inappropriate for the CE separation.

It was therefore decided to oxidize the spent MOX fuel sample in order to obtain Pu(V) or Pu(VI). Plutonium oxidation was performed using concentrated perchloric acid as described in the literature. [15, 21] A dry residue is obtained at the end of the oxidation step. The dry residue was dissolved in HMBA  $120 \text{ mmol.L}^{-1}$  at a pH of 3 before separation and analysis by CE-Q-ICP-MS.

The electropherogram obtained for the separation and analysis of the spent MOX fuel sample by CE-Q-ICP-MS with an electrolyte of HMBA  $120 \text{ mmol.L}^{-1}$  at a pH of 3 is presented in Figure 4.

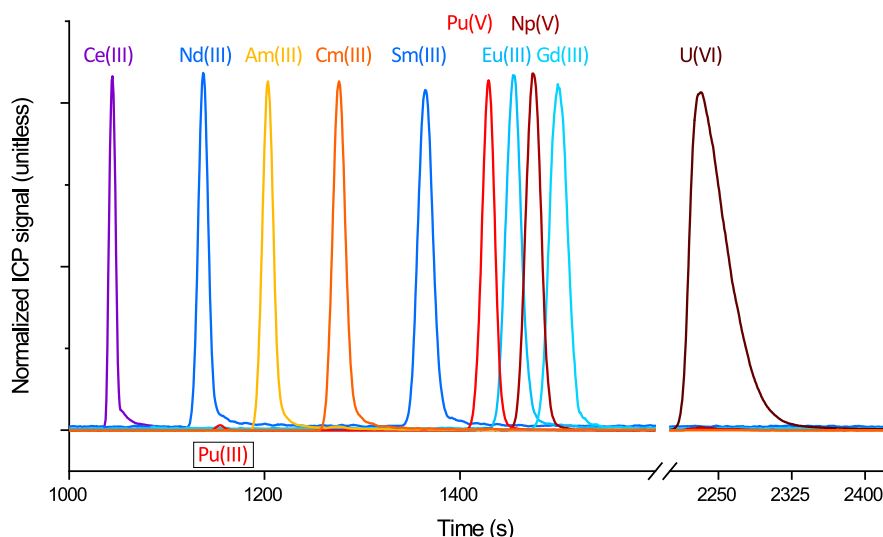


Figure 4: CE-Q-ICPMS electropherogram of the spent MOX fuel sample with a  $120 \text{ mmol.L}^{-1}$  HMBA electrolyte at a pH of 3,  $U=25 \text{ kV}$  and  $\Delta P=75 \text{ mbar}$

The CE-Q-ICP-MS electropherogram presented in Figure 4 was normalized to facilitate the visualization of all the separated elements. For lanthanide fission products, Nd, Sm and Eu are separated with 169 and 32 seconds of baseline separating the peaks, respectively. Eu and Gd are resolved with a baseline return between the two peaks. For actinides, Am(III) and Cm(III) are separated with 25 seconds of baseline separating the two peaks. The separation was improved in Figure 4 as compared to Figure 3 due to a change in CE setup and conditions.

For Pu, two peaks were observed. The first one migrated before Am(III) and was identified as Pu(III). Even if the amount of Pu(III) should be as low as possible to avoid isobaric interference on  $^{241}\text{Am(III)}$  and on  $^{242}\text{Am(III)}$ , HMBA was effective at separating Pu(III) and Am(III) with 15 seconds of baseline separating the two peaks. In fact, only 1.5 % of the observed Pu was in the +III state in the electropherogram of Figure 4. This demonstrates the requirement and the efficiency of the oxidation protocol. The second plutonium peak was identified as Pu(V). Pu(V) migrated before Np(V) with a baseline return between the Pu(V) and Np(V) peaks. Pu(V) was not separated from Eu(III) with the CE separation. This was not a problem for isotope ratio determination as there are no spectral interferences between Eu and Pu.

Uranium migrated at the end of the separation and was separated from other elements by more than 8 minutes of baseline. This duration can be decreased if necessary by applying more pressure on the inlet vial after the migration of Gd(III).

To summarize, the CE separation with HMBA  $120 \text{ mmol.L}^{-1}$  at a pH of 3 of lanthanide fission products (Nd, Sm, Eu, Gd) and actinides (U, Pu, Am, Cm) of a diluted spent MOX fuel

sample was demonstrated. This is, to our knowledge, the first occurrence of such a separation in the literature. The next part of this study deals with the application of this CE separation to the measurement of isotope ratios of a diluted spent MOX fuel sample using multicollector ICP-MS (MC-ICP-MS), one of the reference techniques for high-precision isotope ratio measurements.

### **3 ISOTOPE RATIO MEASUREMENTS IN A SPENT MOX FUEL SAMPLE WITH CE-MC-ICP-MS**

The CE separation developed in the first part of this study was applied to the determination of isotope ratios in a spent MOX fuel sample by capillary electrophoresis hyphenated to MC-ICP-MS.

While MC-ICP-MS allows to constrain the uncertainty on isotope ratios at the per-mil level, the measurement procedure has to be carefully optimized to obtain precise and true isotope ratios. The following section deals with the optimization of the measurement procedure for CE-MC-ICP-MS analysis of the spent MOX fuel sample.

#### **3.1 Optimization of the measurement procedure for CE-MC-ICP-MS**

The instrument used in this study is a NeptunePlus MC-ICP-MS (Thermo Scientific). The multi-collector array is composed of nine detectors, one fixed at the central position and eight motorized detectors. [22] The collector array can monitor at most nine different  $m/z$  simultaneously. The mass on the central detector is controlled by the magnetic field value. For a specific magnetic field value, collectors then need to be aligned to the ion beams in order to measure isotope ratios.

As the migration of lanthanide fission products and actinides was concomitant with the developed CE separation, two CE injections were necessary for the MC-ICP-MS to measure all isotope ratios. One CE injection was dedicated to isotope ratio measurements of lanthanide fission products and the other to isotope ratio measurements of actinides. Three cup configurations were designed, two for lanthanide fission products in the mass range 139-160 and one for actinides in the mass range 234-248.

#### **3.2 Isotope ratio measurements by CE-MC-ICP-MS**

This part of the study deals with the determination of isotope ratios in diluted spent nuclear fuel solutions by MC-ICP-MS after separation by CE. Isotope ratio measurements were performed on the spent MOX fuel sample using the custom CE setup and the oxidation procedure described in section 2.2. A custom two-inlet spray chamber was used, one inlet being dedicated to the MiraMist CE nebulizer and the second inlet being dedicated to mass-bias standard injection. Mass bias is a phenomenon inherent to the ICP-MS technique that induces a systematic error on isotope ratios ; it therefore needs to be corrected. [23] This setup was designed for the introduction of a mass-bias standard before and after the CE separation, for sample bracketing.

Isotope ratios were calculated on the Nd, Sm, Eu and Gd peaks for lanthanide fission products and on the U, Pu, Am and Cm peaks for actinides. As these peaks were transient signals, specific calculation methods had to be applied. The Linear Regression Slope (LRS) method was chosen on the basis of previous studies. [9, 11, 24] The LRS method allowed the determination of isotope ratios for Nd, Sm, Eu, Gd and for U, Pu, Am and Cm. The relative standard deviations were calculated for five CE-MC-ICP-MS separations and analyses, for lanthanides fission products and for actinides. The relative error between the average values

obtained in this study and reference values obtained by two step chromatography followed by mass spectrometry analysis was also calculated. [4]

The relative standard deviations were inferior to 0.5% for plutonium ratios, for the  $^{243}\text{Am}/^{241}\text{Am}$  ratio and for  $^{245}\text{Cm}/^{244}\text{Cm}$  ratio. For lanthanide fission products, relative standard deviations were inferior to 0.7% for all isotope ratios studied. Relative errors between the values of this study and the reference values were inferior to 1% for all lanthanide fission products and all actinides except uranium. For uranium, memory effects were observed which resulted in increased standard deviations and relative errors. The origin of the memory effects has been found since.

The results obtained in the present study demonstrate the feasibility of CE-MC-ICP-MS measurement of isotope ratios in spent MOX fuel samples. Relative standard deviations and relative errors were in the per-mil range, in the same order as the values obtained by conventional methods.

#### 4 CONCLUSION

In this study, a CE-MC-ICP-MS method for the determination of isotope ratios in spent nuclear fuels samples was designed and applied to a spent MOX fuel sample. This method aimed at determining the isotopic composition of the dissolved spent nuclear fuel sample with reduced sample quantities and liquid waste production as compared to classical methods. [4]

First, the separation by capillary electrophoresis of Nd, Sm, Eu, Gd, U, Pu, Am, and Cm in a diluted spent MOX fuel sample was developed. The optimization on a synthetic sample containing lanthanides, uranium and thorium led to the selection of HMBA  $120\text{ mmol.L}^{-1}$  at a pH of 3 as the separation electrolyte. This choice was confirmed with the analysis of a spent MOX fuel sample by CE-Q-ICP-MS. It was found that Am, Cm and Pu were separated by CE using HMBA  $120\text{ mmol.L}^{-1}$  at a pH of 3. Finally, isotope ratios of Am, Cm, U, Pu, Nd, Sm, Eu and Gd were measured in two CE runs using the developed capillary electrophoresis - multicollector inductively coupled plasma mass spectrometry (CE-MC-ICP-MS) method.

Relative standard deviations and relative errors were in the per-mil range as with conventional studies while sample quantities were reduced from the  $\mu\text{g}$  to the ng or pg and liquid waste production from the tens of mL to the  $\mu\text{L}$  range. This scale reduction is particularly valuable for the analysis of spent nuclear fuel samples as it reduces the radioactive dose and the production of liquid waste. CE-MC-ICP-MS can also be applied to the measurement of elemental concentrations in nuclear samples with the use of the isotope dilution method. [25]

The use of capillary electrophoresis hyphenated to MC-ICP-MS is also promising for other applications where the sample is either hazardous or precious. Furthermore, the scale reduction for the determination of isotope ratios (and elemental concentrations) in diluted spent nuclear fuel samples initiated with the present CE-MC-ICP-MS method can be continued with the use of analytical microsystems in order to facilitate the integration of the CE setup in the glovebox and to ease the operator's manipulations.

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