

Determination of caesium and its isotopic composition in nuclear samples using isotope dilution-ion chromatography-inductively coupled plasma mass spectrometry

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As the natural isotopes of Ba give isobaric interferences on the radioactive isotopes of Cs at nominal masses of 134, 135 and 137, a chemical separation of Cs from Ba has been necessary for the determination of the isotopic composition of Cs by mass spectrometric techniques in highly active nuclear wastes (HAW), dissolved spent nuclear fuels or radioactively contaminated environmental samples. Ion chromatography (IC), which allows Cs and Ba to be chemically separated according to their different cationic charge, was coupled to an ICP-MS instrument and the chemical separation was performed on-line and followed directly by mass spectrometry. Three separation schemes were compared with respect to chromatographic resolution, accuracy and precision in irradiated spent fuel samples. The mass discrimination factors for the radioactive Cs isotopes were calculated by using a solution of natural Ba for the different chromatographic processes. They were found to be less than -2.5% . The results obtained by IC-ICP-MS were compared with those obtained by γ -spectrometry and with simulation calculations based on the KORIGEN code. The method using a CS5 cation-exchanger column and 1 M HNO₃ as eluent gave a detection limit of 16 pg g⁻¹ for total Cs with a precision of 2.5% at a concentration level of 100 ppb ($n=7$). Under the same chromatographic conditions, the accuracy of the ratio ¹³⁴Cs/¹³⁷Cs, calculated considering the γ -spectrometry measurements, was 2.5%.

Introduction

The determination of radioactive Cs isotopes (masses 134, 135, 137) by mass spectrometry suffers from isobaric interferences from natural Ba isotopes (134, 135 and 137 with 2.4, 6.6 and 11.2% natural abundance, respectively) which cannot be resolved even with modern high resolution mass spectrometers.^{1,2} Therefore, if Ba is not previously chemically separated, it can yield incorrect Cs isotopic composition in nuclear waste analysis, fuel inventory and environmental samples from contaminated zones, such as those collected after the Chernobyl accident.

The determination of ¹³⁷Cs is of great importance in environmental samples. Owing to its solubility and mobility this isotope can be used as a tracer for contamination studies. Since the Chernobyl accident the behavior of ¹³⁷Cs in the environment has been of great interest and has been studied in detail. Investigations dealing with the adsorption, mobility and concentration of ¹³⁷Cs in several areas close to that of the accident have been published.³ On the other hand, the origin of ¹³⁷Cs, due to its half-life of 30 years, detected in environmental samples cannot be directly attributed to reactor operations or to atmospheric weapon tests, but to ¹³⁴Cs having a half-life of 2 years. As an indicator of the source of radioactivity in the environment it may be possible to use the ratio of ¹³⁷Cs to ¹³⁵Cs. While ¹³⁵Cs is difficult to measure by radiochemical methods because of its long half-life and low-energy β -decay, modern ICP-MS instruments have detection limits of pg ml⁻¹ for ¹³⁵Cs.⁴ Moreover, a separation procedure to remove isobaric interferences from the natural ¹³⁵Ba is required for the quantification of ¹³⁵Cs.

As for nuclear fuels, a quantitative measurement of ratios of fission product pairs, e.g. ¹³⁴Cs/¹³⁷Cs, is a signature that

allows the identification of the cooling time of the irradiated spent fuel. Moreover, this ratio is dependent on the burn-up of the fuel and is one of the most important parameters to be evaluated for safeguards and forensic purposes and, therefore, needs to be measured with high precision isotopic analysis.

Normally, the burn-up of spent fuel is calculated from the ¹⁴⁸Nd concentration measured by TIMS (thermal ionization mass spectrometry) using isotope dilution analysis, but this method is time consuming since a chemical separation of Nd from the other fission products is needed before TIMS can be carried out.⁵ When a non-destructive analysis is applied, the burn-up is calculated from the activity of ¹³⁷Cs measured by γ -spectrometry. The burn-up values calculated by the two methods agree within a few per cent.⁶

For all the above-mentioned investigations a fast and reliable method for the determination of the isotopic composition and concentration of Cs is needed. A method of choice can be based on chromatographic separation coupled on-line to ICP-MS detection and the use of isotope dilution analysis for the quantification.^{7,8}

For the past five years the chemical separation and quantification of fission products (lanthanides) and actinides have been routinely performed in our laboratory using ion chromatography (IC)-ICP-MS for the characterization of samples of nuclear origin.⁹⁻¹¹ This paper deals with the application of different chromatographic separation schemes to the determination of the isotopic composition of radioactive Cs, considering the possibility of exploiting the different methods developed for the on-line chromatographic separation of fission products (lanthanides) or of the actinides. The results for the Cs concentration and ¹³⁴Cs/¹³⁷Cs activity ratio using the different methods are compared. The chromatographic separation presented in this paper was applied to the determi-

nation of the isotopic composition and concentration of Cs using isotope dilution analysis; the $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratio was calculated and also ^{137}Cs was quantified. The burn-ups of the samples were determined and compared with those obtained by TIMS (based on ^{148}Nd concentration) and γ -spectrometry (based on ^{137}Cs concentration).

Experimental

Instrumentation

An Elan 5000 quadrupole ICP-MS instrument (Perkin-Elmer SCIEX, Thornhill, Ontario, Canada), equipped with a Pt sampler, a Pt skimmer cone and a ceramic injector tube in the torch, was used. The instrument was installed in a glove-box in order to handle radioactive samples. The details of its installation have been given previously.^{9,11} A chromatographic system was coupled on-line to the ICP-MS instrument. A 4500I high-pressure chromatographic pump (Dionex, Sunnyvale, CA, USA) was used.

The ICP-MS instrument (coil, torch, nebulizer, spray chamber, injector, cone), one six-way injection valve and the analytical column are inside the glove-box. The skimmer is located at the interface and the mass spectrometer as well as the chromatographic pump and eluents outside the glove-box. An injection valve along with the analytical columns to be used when working with inactive samples for calibration before applying the method to active samples are also installed outside the glove-box. In this case, the eluent from the analytical column from outside enters the glove-box by a small tube through a filter and is connected directly to the nebulizer of the ICP-MS instrument. Radioactive samples are introduced into the glove-box before being analyzed and are injected into the chromatographic system (injection valve and analytical columns) located inside the glove-box. For a schematic diagram of this installation the reader is referred to ref. 9 and 12.

Reagents and materials

The chromatographic separations of Cs and Ba were performed using three different separation schemes: the first was based on the use of mixed bed columns (cationic and anionic exchangers) of CG5 and CS5 (Dionex) and 1 M nitric acid (Suprapur, Merck, Darmstadt, Germany) as eluent. The second separation scheme consisted of the use of CG10 and CS10 (cation-exchange columns from Dionex) and 0.6 M nitric acid–40 mM 2,3-diaminopropionic acid monohydrochloride (DAP from Dionex) as eluent. In the third separation, CG3 and CS3 (cation-exchange columns, Dionex) and nitric acid as eluent were tested.

The CS10 column consists of a support material composed of a highly cross-linked ethylvinylbenzene–divinylbenzene copolymer with a particle size of 8 μm . The covalent bond of the latex beads to the support material provides a high mechanical and chemical stability for this stationary phase. This cationic exchanger is recommended for the simultaneous determination of alkali and alkaline-earth metals under isocratic conditions.¹³

The CS3 column is filled with a resin consisting of a weakly sulfonated polystyrene–divinylbenzene substrate with a particle size of 10 μm . Fully aminated latex beads with a much smaller diameter of about 50 nm are agglomerated on its surface by both electrostatic and van der Waals interactions. The anion-exchange substrate thus produced is covered by a second layer of latex beads which carry the actual exchange function in the form of sulfonate groups. The sulfonated latex beads have a diameter of about 250 nm and a degree of cross-linking of 5%. Such a separator column is preferred when extremely high concentration differences require maximum resolution between the individual components.

The CS5 column consists of a support material composed of a highly cross-linked ethylvinylbenzene–divinylbenzene copolymer with a particle size of 9 μm . The column is a high resolution ion-exchange column that has both anion- and cation-exchange capacity (sulfonic acid and quaternary ammonium as functional groups).

Standard solutions of natural Cs and Ba (1000 mg l⁻¹) were purchased from Spex (Grasbrunn, Germany) and working solutions containing both elements in different ratios were prepared by diluting by mass in polyethylene bottles previously pre-cleaned. Suprapure grade nitric acid and Elgastat UHQPS ultrapure water (Elga, High Wycombe, Buckinghamshire, UK) were used for all dilutions.

A standard solution of natural Cs was used for spiking the irradiated spent fuels in the glove-box.

Experimental procedures

Caesium–barium separation scheme. The working solutions containing Cs and Ba in several ratios were injected (200 μl) through a four-way injection valve onto the analytical column where elution took place when the eluent, supplied by a high-pressure pump, reached the column. The effluent from the analytical column was directed to the nebulizer of the ICP-MS instrument by a tube that was as short as possible in order to minimize peak broadening.

For the three different chromatographic systems, the precision of the determination of Cs was calculated.

Sample preparation. Fuel pellets (*ca.* 30 g) of irradiated UO₂ and mixed oxide (MOX) fuels were dissolved in 7 M HNO₃ in a hot-cell facility by reflux and diluted with 4 M HNO₃. A second dilution by mass was performed using 1 M HNO₃ and 5 ml of these solutions containing about 100 μg of fuel per gram of solution were transferred into a glove-box for further dilution and spiking.

Quantification procedures. The sample, spiked samples and spike (for the analysis of irradiated fuels the use of natural Cs as a spike is possible due to its favorable natural abundance) were injected consecutively into the chromatographic system. The mass discrimination factor was determined by using the natural Ba standard solution and dead time correction was not applied because care was taken to avoid excessively high intensity for the ions measured. Integration of the chromatographic peaks was performed using the software GRAMS/386 (Galactic Industries, Salem, NC, USA).

The calculation of the burn-up (BU) was performed using the following equation:

$$\text{BU (at.-%)} = \frac{(^{137}\text{Cs}/Y)}{(^{137}\text{Cs}/Y) + \text{U} + \text{Pu}} \times 100$$

where ^{137}Cs is expressed in at. g⁻¹, Y is the fission yield for Cs and U and Pu are expressed in at. g⁻¹. The burn-up, in at.-%, is expressed as the number of heavy atoms that have fissioned per total heavy atom content.

It is important to note that Y changes depending on the composition of the spent fuel (uranium oxide or mixed oxide), the initial enrichment and the burn-up of the sample. The exact calculation of Y must take into account the change in the concentrations of ^{235}U and ^{239}Pu in the fuel during irradiation in the reactor. A Y value of 6.4% for ^{137}Cs ⁶ is considered as a standard value for all burn-up calculations in this work. The ^{137}Cs concentration measured by γ -spectrometry or IC-ICP-MS at the moment of the analysis is lower than that at the end of the irradiation (half-life of ^{137}Cs , 30.17 years); therefore, if this concentration is used the BU value calculated will be biased. The real BU value corresponds to that calculated from the ^{137}Cs concentration at the end of the irradiation. Consequently, all concentrations determined by γ -spectrometry or ICP-MS have to be corrected for

the time elapsing between the end of the irradiation and the chemical analysis before applying the general equation to calculate the burn-up.

Results and discussion

The most common method of determining Cs is γ -spectrometry. The measurements can be carried out both on entire fuel pellets to determine ^{137}Cs activity and on aliquots of fuel solutions to determine the activities of ^{134}Cs and ^{137}Cs . As already mentioned, an alternative method is that based on the use of ICP-MS provided that a previous chromatographic separation is performed. Ion-exchange chromatography is a separation method based on an ion-exchange process occurring between the mobile phase containing the ions to be separated and functional groups bonded to the support material.^{14,15} The choice of a suitable stationary phase and the chromatographic conditions determines the quality of the analysis. The degree of chemical separation obtained is given by the separation factor, which can be defined as the concentration ratio for two components after separation divided by the same ratio in the original sample. Based on previous work,^{9,10} where the

isotopic composition of fission products (including Cs) and actinides was determined by IC-ICP-MS, a comparative study of $^{134}\text{Cs}/^{137}\text{Cs}$ determination using three different chromatographic ion-exchange columns was performed. Three sulfonic acid-based resins (two cationic exchangers and one mixed bed exchanger) were tested to separate Cs and Ba and the results, in terms of resolution, sensitivity, precision and accuracy, were compared.

Since the activity of the samples to be analyzed is high, the possibility to determine $^{134}\text{Cs}/^{137}\text{Cs}$ using the same separation scheme as used routinely to determine the isotopic composition of lanthanides in highly active nuclear wastes (HAW) (CG5 and CS5 columns with oxalic acid as eluent) was also tested. Moreover, to minimize the handling of the sample and the analysis time, the CG10 and CS10 columns with 0.6 M HNO_3 -40 mM DAP as eluent (a separation that is routinely used to determine Np concentration and isotopic composition of Am and Cm) were also tested. The third separation scheme consisted of CG3 and CS3 columns with nitric acid as eluent.

The first step was to compare the two pure cationic exchangers: the CS3 column with the CS5 column using nitric acid as eluent. For this purpose, a solution containing 100 ppb of natural Cs and Ba was injected ten times onto each column and the precision of the determination of Cs was calculated. The selection of CS5 using 1 M HNO_3 to continue the study with irradiated spent fuels instead of CS3, under the same elution conditions, was based on the better precision obtained (2.5% for CS5 versus 9% for CS3). The elution patterns obtained are illustrated in Fig. 1. The mass discrimination factor for Cs was evaluated using the Ba isotopes.¹⁶ In Table 1 the values obtained for the two chromatographic processes using the CS3 and CS5 columns are reported. The relative systematic error in the isotope ratios was found to be proportional to the mass difference between the two isotopes considered. The plot of the relative systematic error versus the mass difference showed a linear correlation of slope -2.1 and -2.4% when using the CS3 and CS5 columns, respectively.

The elution pattern obtained on the CS5 column was then compared with the elution mode on the CS10 column. As for the CS5 column, two different eluents were used: oxalic acid, which is employed for the separation of lanthanides, and nitric acid.

In Fig. 2 the Cs and Ba elution profiles are compared when three different conditions are employed. For Ba, only the masses of the isotopes interfering with Cs are reported. As can be seen, a good separation is obtained in all three cases. When oxalic acid is used, the elution pattern is inverted and the Cs elutes with a very broad peak after 400 s. The figures of merit of the three methods are summarized in Table 2. The precisions of the isotope ratios, based on peak area measure-

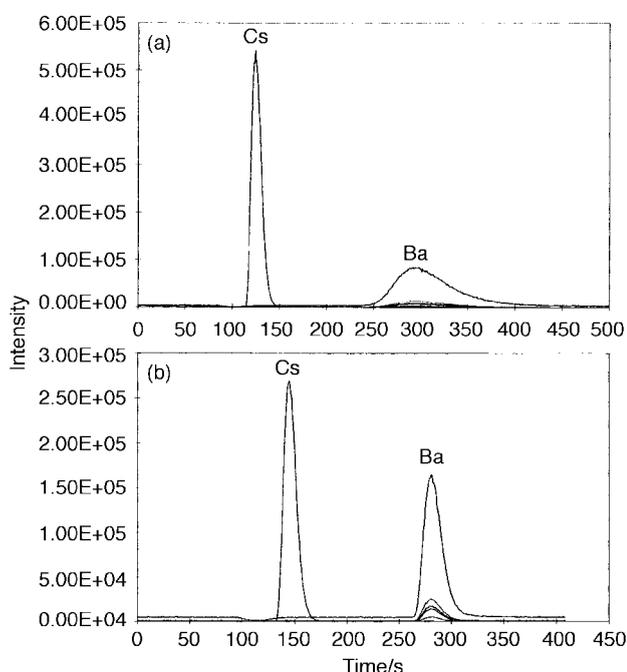


Fig. 1 Separation obtained using two pure cationic exchangers. (a) CS3, 1 M nitric acid. (b) CS5, 1 M nitric acid.

Table 1 Mass discrimination factors obtained by two different chromatographic processes by injecting 200 μl of a solution of 50 ppb of natural Ba in 1 M nitric acid

CS3/1 M nitric acid—					
Isotope ratio	Experimental value (RSD%, $n=4$)	Theoretical ratio ¹⁷	(Experimental theoretical)/theoretical (%)	Mass difference	Corrected ratio
134/138	0.030967 (2.02)	0.033752	-8.25	4	0.034408
135/138	0.085048 (2.50)	0.091911	-7.46	3	0.090657
136/138	0.104039 (2.70)	0.109484	-4.90	2	0.109515
137/138	0.152893 (1.50)	0.156206	-2.12	1	0.156206
CS5/1 M nitric acid—					
Isotope ratio	Experimental value (RSD%, $n=4$)	Theoretical ratio ¹⁷	(Experimental theoretical)/theoretical (%)	Mass difference	Corrected ratio
134/138	0.030751 (0.90)	0.033752	-8.89	4	0.034060
135/138	0.085550 (0.92)	0.091911	-6.92	3	0.092188
136/138	0.105124 (1.38)	0.109484	-3.98	2	0.110425
137/138	0.153347 (0.94)	0.156206	-1.83	1	0.157118

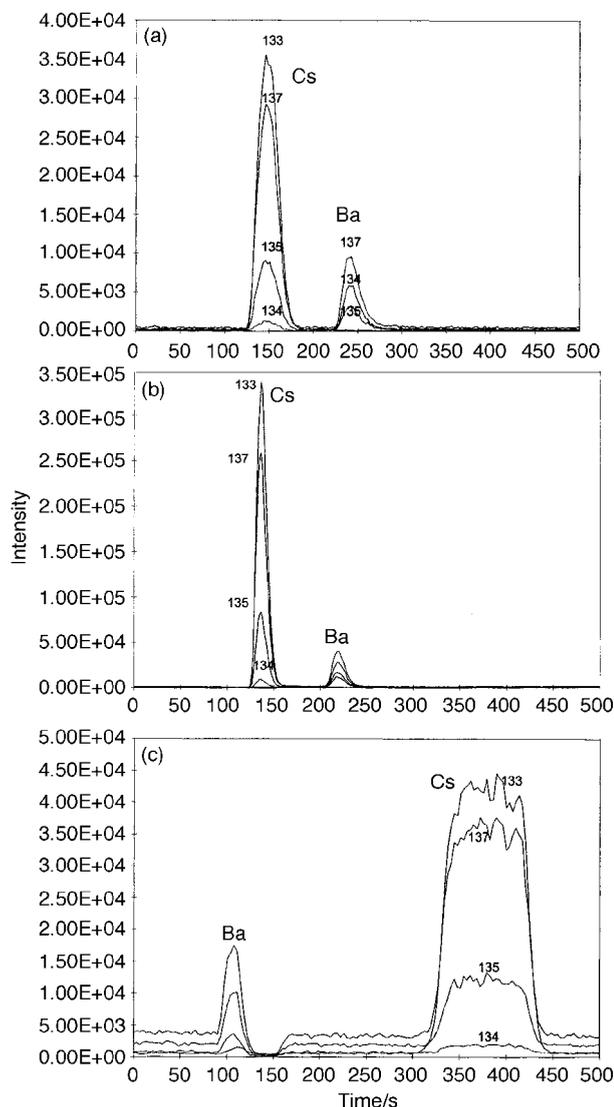


Fig. 2 Comparison of the use of the CS10 and CS5 columns for the separation. (a) CS10, DAP–nitric acid; (b) CS5, nitric acid; (c) CS5, oxalic acid.

ments, obtained with the three different separations are compared and for the ratio 134/137 the accuracy is obtained by considering the ratios obtained by γ -spectrometry (0.03435). As for the accuracy of the ratios 133/135 and 135/137, the results obtained by analyzing spent fuel solutions by IC-ICP-MS were compared with the values obtained by KORIGEN code calculations. By using the CS5 column with 1 M HNO₃, a typical accuracy of 5% was obtained. From these data it can be concluded that the use of CS5 with 1 M HNO₃ gives the best separation as regards precision and accuracy. The separation with CS5 using 1 M HNO₃ as eluent gives a precision of 2.5% calculated from seven consecutive

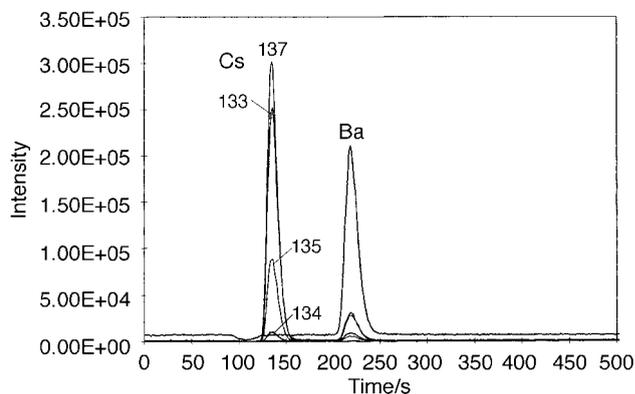


Fig. 3 Separation profile obtained for a solution of a spent nuclear fuel.

injections of 100 ppb and a detection limit of 16 pg g⁻¹, calculated as 3 σ of the blank. Solutions containing different Cs/Ba concentration ratios were prepared and injected. Over the concentration range 0–100 ppb of Cs a calibration graph with $r^2=0.9998$ was obtained. Once the separation has been achieved, isotope dilution analysis can be applied for a precise and accurate quantification. This method can be applied to elements with several isotopes when enriched spikes are available. Mono-isotopic elements are quantified with other methods of analysis (*e.g.* by using internal standards as reference, external calibration or standard additions to the sample) that have to be chosen depending on the sample to be analyzed and the precision and accuracy required for the analysis. The determination of Cs in HAW can be performed by isotope dilution analysis since these samples contain several Cs isotopes with no natural existence (134, 135 and 137, which are built up during the irradiation) using natural Cs (100% abundance for 133 isotope) as spike.

The optimized separation procedure was applied to solutions of spent fuels and spent fuel leachates. In Fig. 3 a typical separation profile is shown.

The ¹³⁴Cs/¹³⁷Cs activity ratio in irradiated spent fuel samples with different burn-ups was determined. In Fig. 4 the correlation between the ¹³⁴Cs/¹³⁷Cs activity ratio, obtained by the three different methods, *viz.*, γ -spectrometry, IC-ICP-MS and by calculation with the KORIGEN code,¹⁸ and the nominal burn-up values of the fuels is presented. The evolution in fuel composition can be calculated from reactor physics equations, using appropriate computer codes such as KORIGEN. This is a zero-dimension code which simulates the irradiation history of the fuel. The calculations are coupled with burn-up dependent cross-section libraries resembling, as closely as possible, a reactor–fuel combination. As expected the ¹³⁴Cs/¹³⁷Cs activity ratio increases with burn-up. In Fig. 5 a comparison of the ¹³⁴Cs/¹³⁷Cs activity ratio obtained in several highly active samples by γ -spectrometry, IC-ICP-MS and by calculations with the KORIGEN code is presented. The solid line represents the theoretical values obtained by KORIGEN and the experimental data [γ -spectrometry (indicated by Gamma

Table 2 Figures of merit for the separation of Cs from Ba according to three different chromatographic experimental conditions ($n=7$) when analyzing a spent fuel. Comparison of the precision of the isotope ratios obtained by IC-ICP-MS. The accuracy of the ratio ¹³⁴Cs/¹³⁷Cs is defined considering the value obtained by γ -spectrometry

Isotope ratio	CS5, 1 M nitric acid			CS5, oxalic acid			CS10, DAP–nitric acid		
	Corrected value	RSD (%) $n=7$	(ICP-MS– γ)/ γ (%)	Corrected value	RSD (%) $n=7$	(ICP-MS– γ)/ γ (%)	Corrected value	RSD (%) $n=7$	(ICP-MS– γ)/ γ (%)
133/137	0.85841	0.15		0.84952	3.25		0.85206	1.50	
134/137	0.03522	1.27	2.54	0.03651	13.00	6.30	0.03732	5.00	8.70
135/137	0.30482	0.65		0.30693	7.40		0.31085	3.45	

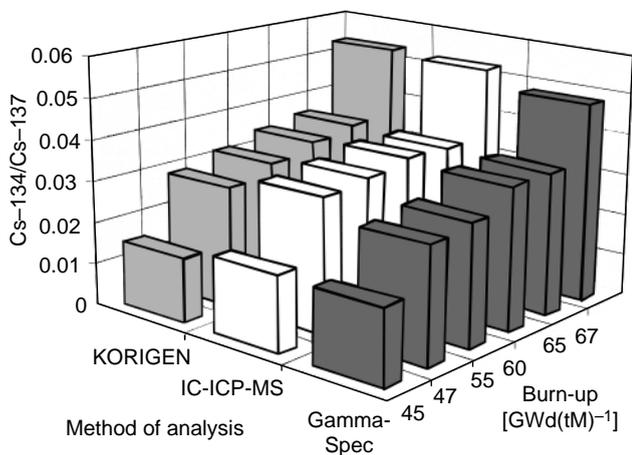


Fig. 4 Correlation between $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratio and nominal burn-up of the fuel.

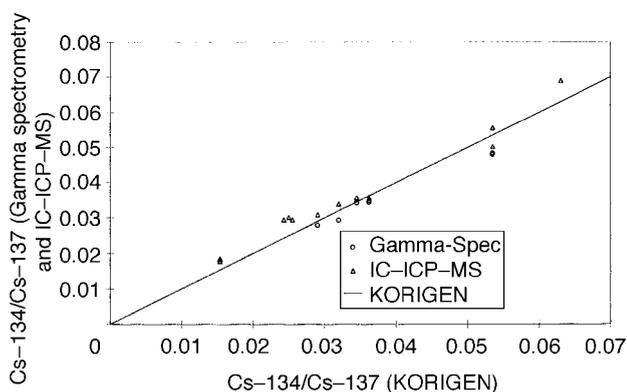


Fig. 5 Comparison of the values of the $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratio obtained by γ -spectrometry, IC-ICP-MS and KORIGEN code.

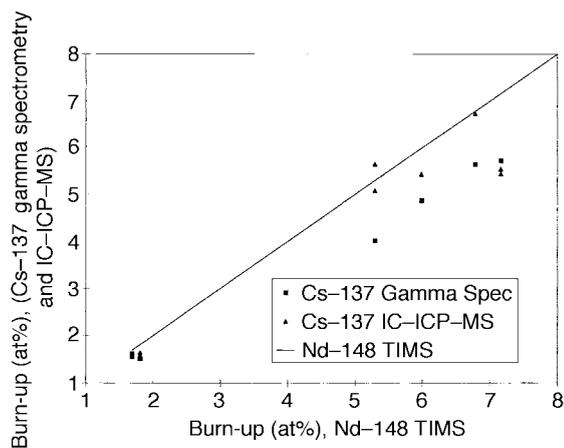


Fig. 6 Comparison of burn-up values obtained by ^{137}Cs and ^{148}Nd .

spectrometry) and IC-ICP-MS] fit well with the theoretical values. Moreover, the two experimental data series (obtained by G—where G indicates γ -spectrometry—and IC-ICP-MS) agree well with each other, since the slope of the linear regression obtained considering all data together has a value of 0.9975.

For all the samples analyzed the isotopic composition of Cs was calculated and the burn-up value using the ^{137}Cs concentration was obtained from both experimental techniques: γ -spectrometry and IC-ICP-MS. In Fig. 6 the burn-up ratios obtained are reported along with the burn-up value based on

^{148}Nd obtained by TIMS. It can be observed that the values obtained for ^{137}Cs by IC-ICP-MS are closer to those obtained by γ -spectrometry. The accuracy between the burn-up obtained by the ^{148}Nd concentration by TIMS and that obtained by IC-ICP-MS (based on ^{137}Cs concentration) is within 5% except for one sample for which it is 7%. The BU data obtained by γ -spectrometry when compared with those obtained by TIMS agree within 10%. As can be seen, the accuracy of the method based on IC-ICP-MS measurements is better than that based on γ -spectrometry. However, the discrepancy between the BU values obtained from ^{137}Cs by IC-ICP-MS and those from ^{148}Nd is not dependent on the instrumental technique, but can be attributed to the use of the same value of the fission yield of ^{137}Cs (6.4%) for all the samples analyzed, in spite of their different characteristics in terms of change in composition and final burn-up achieved.

Conclusions

The method based on the coupling of a chromatographic separation to ICP-MS detection can be applied to the determination of radioactive Cs in samples of nuclear origin. Only a small volume of sample (200 μl) is injected onto the chromatographic column and the separation is achieved in 500 s. By this method the burn-up of a nuclear fuel can be determined, avoiding prolonged handling of active samples. The burn-up values obtained from ^{137}Cs by IC-ICP-MS and ^{148}Nd agree typically within 5%. The method described can also be applied to radioactively contaminated environmental samples in order to detect the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio, as ICP-MS is capable of detecting very low levels of the ^{135}Cs isotope.

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