

CHARACTERISATION OF SPENT NUCLEAR FUELS BY AN ON-LINE COUPLED HPLC-ICP-MS SYSTEM

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The determination of burn-up is one of the essential components of post-irradiation examination of nuclear fuel samples. In the framework of the ARIANE programme (Actinides Research in a Nuclear Element), at PSI the analysis of the isotopic vectors of uranium, plutonium, neodymium and some other fission and spallation products was carried out for the first time in the Hot Lab using high-performance liquid chromatography (HPLC), coupled on-line with an inductively coupled plasma mass spectrometer (ICP-MS). The results of these investigations, a comparison with the classical technique for burn-up determination, the advantages and limitations of the new method, the accuracy and precision of these types of analyses, the applicability of the technique to other samples and separation problems, and conclusions for further analyses of nuclear fuel samples, are here presented.

1 INTRODUCTION

The main objective of the various international programmes dealing with post-irradiation examination of nuclear fuels is to improve the knowledge of the inventories of actinides and fission products in MOX and/or UO₂ spent fuel elements. The prediction of the source term of actinides, fission and activation products is of major importance in numerous nuclear fields, such as:

- the definition of basic licensing data for UO₂ and MOX fuel;
- the increase of fuel enrichment for power reactors, with a possible re-evaluation of criticality licenses; and
- the improvement of waste source-term codes for high burn-up fuel conditions, and for MOX fuel recycling scenarios.

The mass spectrometric determination of trace amounts of spallation and fission products in spent nuclear fuels and targets provides a relevant database for the validation of theoretical models, and represents an experimental basis for the minimisation of the uncertainty in prediction models.

The burn-up of a nuclear fuel, as one of the important parameters to be determined in this kind of programme, is proportional to the quotient of the number of fissions N_F and the number of heavy-metal atoms N_M^0 (uranium and plutonium) which were present in the fuel before irradiation. The burn-up is given in % FIMA (Fissions per Initial Metal Atoms) as

$$\% FIMA = \frac{N_F}{N_M^0} \cdot 100$$

The experimental determination of the burn-up in an irradiated nuclear fuel is accomplished by analysing the number of U and Pu atoms, and the number of one-fission products which can be used as burn-up monitors. The accepted, and widely used, method for burn-up determination is based on ¹⁴⁸Nd as burn-up monitor. The element Nd has several advantages compared with other fission products:

- Nd is not volatile, and does not move in the fuel rod, so local burn-up determinations are also possible;
- Nd is not a component of the non-irradiated fuel material;
- ¹⁴⁸Nd is not radioactive and, consequently, the method is not influenced by a decay time; and
- the fission yield of ¹⁴⁸Nd is almost independent of the neutron energy and the fissionable isotope.

Consequently, the characterisation of the burn-up includes the analysis of the isotopic vectors of U, Pu, and Nd, and the determination of the concentrations of these elements by isotopic dilution analysis, the most precise quantification method in mass spectrometric analyses.

Numerous isobaric overlaps restrict the direct determination of fission products such as Nd by mass spectrometry. U and Pu also show isobaric interferences with each other, or with other actinides (e.g. ²³⁸U and ²³⁸Pu, ²⁴¹Am and ²⁴¹Pu). Therefore, an extensive chemical separation for all these elements is required. Since the concentrations of these elements are determined by isotopic dilution analysis, the separation has to be done twice: once for the unspiked sample and once for the spiked sample.

2 EXPERIMENTAL

2.1 HPLC-ICP-MS system

2.1.1 Apparatus

High-performance liquid chromatography (HPLC) and ion chromatographic (IC) techniques have been used for different applications as routine methods in analytical laboratories over many years. One reason for the wide-spread use of these methods is that they are applicable to organic as well as to inorganic compounds.

The inductively coupled plasma (ICP) has been used for more than 20 years as the excitation source for optical emission spectrometry. The possibility to use a mass spectrometric detector to analyse the ions produced in an argon plasma was first described by Houk

et al. [1]. ICP-MS systems have been used since the middle of the eighties in many laboratories for different analytical applications. In principle, gaseous, liquid and solid samples may be analysed with this technique. Nevertheless, the most widely used application is the analysis of liquid samples. The nebulizer produces a fine aerosol of the liquid sample, which is then transported with an argon gas stream to the spray chamber where the droplets are separated according to their size. Only those with a diameter less than $8\ \mu\text{m}$ are transported with the gas stream to the argon plasma, where the actual ionisation of the sample takes place. The ions pass through two apertures (the sample and skimmer cones), with different orifice diameters, are focused with a set of ion lenses, and then separated according to their mass-to-charge-ratio in a quadrupole mass filter. The detection of the separated ions is carried out with an electron multiplier in a sequential mode.

In combining an HPLC with an ICP-MS, the mass spectrometer becomes the element-sensitive detector of the separation system. In principle, it is possible that the effluent of the separation column first passes the flow cell of a UV or conductivity detector, and afterwards the ICP-MS. For the determination of the isotopic vectors of ionic compounds, as is necessary for burn-up analysis in irradiated fuel samples, there is no benefit from such a combination. The large distance between the separation column and the ICP-MS detector would lead to peak-broadening, and a significant deterioration of the peak resolution. Therefore, the effluent of the chromatographic column is sent directly via a post-column valve to the nebulizer of the ICP-MS system.

For all separations, a Dionex DX300 HPLC system was used, with IonPac CG5 or CG10 (4 x 50 mm) as guard, and IonPac CS5 or CS10 (4 x 250 mm) as analytical column, respectively. The injection valve and the chromatographic columns are installed in a $1\ \text{m}^3$ glove-box. The flow rate of the HPLC is 1 ml/min; the injection valve is equipped with a 1 ml sample loop.

The ICP-MS system actually used is a PQ2+ from VG Elemental (Winsford, UK). The torch box, with the sample introduction system consisting of a Meinhard type nebulizer, the spray chamber and a quartz torch, is located in a $2\ \text{m}^3$ glove-box, together with the interface chamber of the mass spectrometer.

The coupling of the HPLC to the ICP-MS is achieved by passing the effluent of the chromatographic column to a 4-way, post-column valve, and connecting this to the nebulizer of the ICP-MS system and to waste. All components which were separated in the chromatographic system may be sent directly to the ICP-MS, where they are analysed for their elemental composition, or they may be sent to waste. Figure 1 shows schematically the on-line, coupled HPLC-ICP-MS device installed in the Hot Lab.

2.1.2 Measurement conditions

Before analysing the first fuel samples, a broad, experimental programme was started with standard solutions, to investigate the best measurement parameters for accurate analysis of the isotopic vectors. The influence on the results of the measurement time, the points per peak, the amount of the added spike, and of mass discrimination effects, was determined.

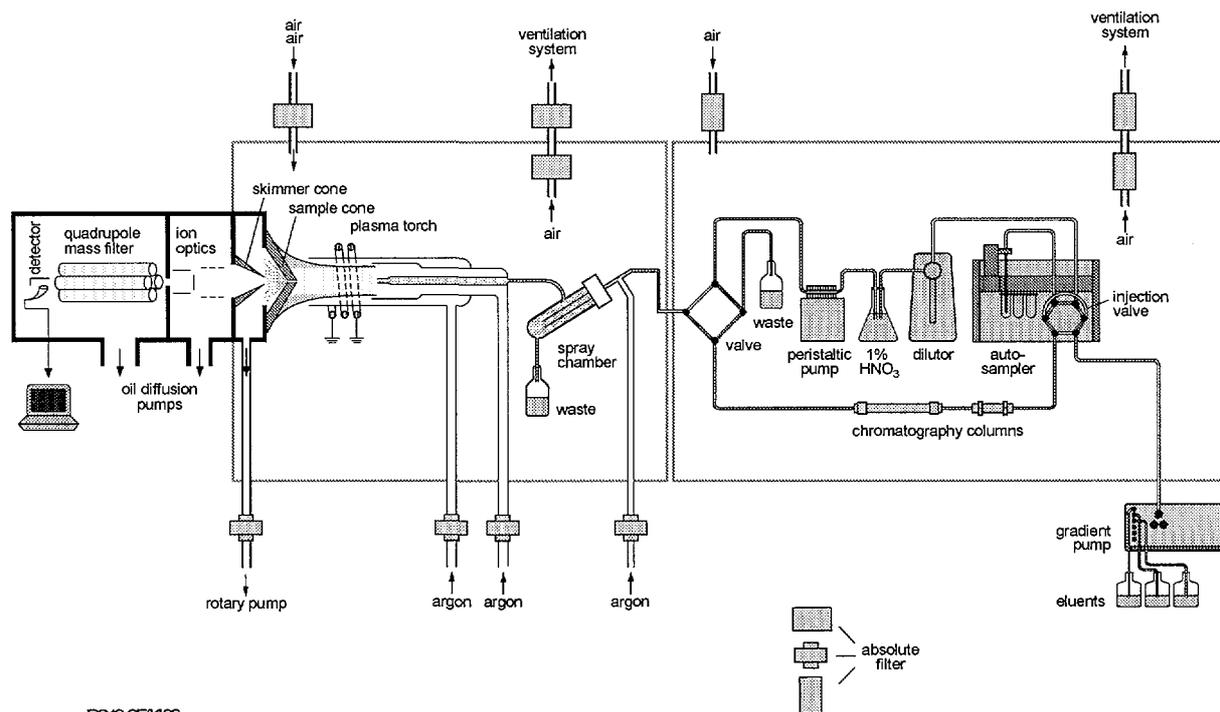


Fig. 1: Schematic view of the HPLC-ICP-MS system

Mass fractionation represents a limitation to the accuracy of isotopic ratio measurements in all mass spectrometric methods. In order to correct for this, standard materials, with known isotopic composition of the element to be determined, are analysed before and after each sample measurement. Additionally, 1% HNO₃ as a blank solution is also measured between standards and samples to avoid memory effects in the separation system. The normal sequence of a measurement procedure for one element is: blank - standard (3 injections) - blank - unspiked sample (5 injections) - blank - standard (2 injections) - blank - spiked sample (5 injections). All of the separations described in this report can be carried out for this sample sequence in one day. Table 1 lists the instrumental parameters and measurement conditions which were found to guarantee the best performance.

Table 1: Instrumental parameters and measurement conditions

<i>Instrumental parameters</i>	
RF power	1350 W
coolant gas flow	15 l/min
auxiliary gas flow	0.8 - 1 l/min
nebulizer gas flow	0.9 l/min
sample uptake rate	1 ml/min
HPLC sample loop	1 ml
HPLC flow rate	1 ml/min
<i>Measurement conditions</i>	
measuring mode	peak-jumping
points per peak	1
dwel time per point	20.48 ms

2.2 Sample preparation

Both UO₂ and MOX fuel samples, irradiated to various burn-up levels, and under various operation conditions, were analysed in the framework of the ARIANE programme in different laboratories. The samples were dissolved in 8 M HNO₃ under reflux for about 6 hours. The further dilution steps were carried out with 1 M HNO₃ up to a concentration of about 0.5 mg fuel/g solution. Aliquots of this stock solution were mixed with the enriched isotopic spikes (for burn-up determination: ²³³U, ²⁴⁴Pu, ¹⁵⁰Nd), and diluted with 1% HNO₃ to about 10 ml solution. A second set of aliquots was directly diluted to about 10 ml solution without any spiking, in order to determine the isotopic vectors in the original fuel samples. Pu can be found in fuel solutions in different oxidation states, of which the most stable is Pu⁴⁺. Because the chromatographic separation of Pu and U is based on PuO₂²⁺, 250 µl 6 M HClO₄ were added to the aliquots for U and Pu determination in order to completely oxidize the Pu to PuO₂²⁺. 1 ml of the unspiked and the spiked samples

was injected 5 times into the HPLC-ICP-MS system for the determination of the isotopic composition of the different elements.

3 RESULTS AND DISCUSSION

3.1 Burn-up determination

3.1.1 Classical technique

In the classical technique for burn-up determination, the elemental separations for U, Pu and Nd are carried out in small ion exchange columns, with collection of the different fractions. The separation procedure is very time-consuming, and needs at least two days per element. Additionally, the handling of radioactive samples under such conditions leads to a high dose for the operator.

The isotopic composition of the separated elements is usually analysed with thermal ionisation mass spectrometry (TIMS). In principle, this technique is a single-element method, i.e. only one element can be analysed in any one measurement procedure. The advantages of TIMS are: 1) a very stable ionisation process, leading to minor instabilities of the signal; and 2) the presence of a series of detectors, at least in modern instruments. Therefore, each isotope of the element to be analysed is detected with a separate Faraday cup detector. This kind of simultaneous detection, together with the stable ionisation process, leads to the excellent precision of the results for which TIMS is renowned. A disadvantage is the poor ionisation efficiency for some elements of the periodic table, and the time-consuming sample preparation process. Consequently, precise determination of the isotopic composition using TIMS is restricted to just a few elements.

In the Hot Lab we have a 20-year-old TIMS system, with only one Faraday cup and one ion counter as detectors. Consequently, the measurement of the different isotopes is sequential, not simultaneous, as in modern instruments. The analytical results are not as precise as for newer systems, as will be shown in Section 3.1.2.1. Therefore, for the first time, the classical TIMS technique was replaced in the ARIANE programme by HPLC-ICP-MS for burn-up determination in the Hot Lab. Nevertheless, a cross-check between TIMS and HPLC-ICP-MS results is possible. The comparison of the results of the isotopic ratio measurements will be presented in Section 3.1.2.1.

3.1.2 HPLC-ICP-MS system

3.1.2.1 Advantages and limitations

The important advantages of the HPLC-ICP-MS system compared with the classical TIMS technique are the fast and simplified sample preparation procedure, and the speed of the isotopic analysis itself. The complete on-line separation and analysis of all lanthanide elements needs only about 30 min per sample (spiked or unspiked) with the HPLC-ICP-MS, compared with about two days per element, and per sample, with TIMS. Even with 5 or 10 repeated HPLC injections per sample, in order to improve the reproducibility of the

results, there is still a reduction by a factor of about 6 in time for each individual element. Considering that ICP-MS is a multi-elemental detector, which can analyse the isotopic composition of more elements during one chromatographic separation than with TIMS, the time saving for sample preparation and measurement is, in fact, considerably higher. The simplified sample preparation procedure reduces the risk of contaminating the sample, and lowers the dose for the operator.

The limitations of the HPLC-ICP-MS method are the higher instabilities of the ionisation process in the plasma compared to thermal ionisation, and the sequential measurement technique, because quadrupole ICP-MS systems are equipped with only one detector. This means every isotope of each element which has to be analysed is detected sequentially, and not simultaneously, as is possible in modern multi-collector instruments. These two reasons lead to a significantly lower precision of the HPLC-ICP-MS results than for modern TIMS, as was demonstrated in the "Round Robin Test" described below.

Since U is the main component of the nuclear fuel, the accuracy and precision of the burn-up determination is mainly influenced by the accurate analysis of the U concentration. The quantification of U is carried out using isotopic dilution analysis for the classical TIMS, as well as for the ICP-MS-based technique. In order to compare the abilities of the two mass spectrometric methods to determine the isotopic composition of U correctly, a broad experimental programme was undertaken. A ^{233}U isotopic spike solution was mixed with the certified uranium EC-110 standard material in different ratios. These solutions were analysed with the TIMS system in the Hot Lab (sequential detection), with the on-line coupled HPLC-ICP-MS, and with a modern, multiple-collector TIMS at the Department of Earth Sciences, ETH Zürich, which is able to detect all U isotopes simultaneously. The results of this "Round Robin Test" are shown for one of the mixed samples in Table 2.

The results clearly indicate that the reproducibility of the TIMS measurements is superior, especially for the new system at the ETH Zürich, and for the isotopes with a low abundance (^{234}U , ^{235}U and ^{236}U), in comparison with the HPLC-ICP-MS data. The closest comparison between the measured and theoretical values is achieved using the multiple-collector TIMS (ETHZ).

3.1.2.2 Determination of Nd

As already pointed out, the burn-up analysis includes the determination of the isotopic vectors of U, Pu and Nd as the burn-up monitor.

In aqueous solutions, the lanthanides are present as strongly hydrated trivalent cations. Because their ionic properties are very similar, they cannot be separated easily by cation exchange. However, the selectivity of the separation can be increased with the use of appropriate chelating agents, such as α -hydroxyisobutyric acid (HIBA) [2] or oxalic acid [3]. Lanthanides form complexes with HIBA or oxalic acid, which lower the affinity of the element for the cation exchange resin. Therefore, lanthanides which form the most stable complexes with HIBA, such as lutetium, will elute first from the separation column. Using oxalic acid as chelating agent, the sequence of separation is directly opposed: i.e., lanthanum is eluting first from the column.

Uranium is present as uranyl cation (UO_2^{2+}) in aqueous solutions, and forms strong complexes with chloride ions. These complexes are not retained on a cation exchange resin, and therefore U can be eluted with hydrochloric acid before the separation of the lanthanides. This is very important because the high U concentration in fuel samples may decrease the sensitivity of ICP-MS for trace elements, such as Nd, due to so-called "matrix effects".

In order to avoid high concentrations of U in the ICP-MS during the analyses of Nd, which could lead to memory effects of U in the sample introduction systems, the U eluting from the HPLC column is sent via the post-column valve to waste.

Table 2: Determination of the isotopic composition of a U standard mixture; comparison between TIMS and HPLC-ICP-MS

	^{233}U (at.%)	^{234}U (at.%)	^{235}U (at.%)	^{236}U (at.%)	^{238}U (at.%)
Theoretical Value	35.1291	0.3289	0.2822	0.0174	64.2424
std.dev. (1 s)	0.6781	0.0063	0.0049	0.0003	1.1757
TIMS (ETHZ) *	35.0598	0.3279	0.2843	0.0175	64.3105
std.dev. (1 s)	0.0009	0.0001	0.0001	0.0001	0.0012
TIMS (PSI)	35.6831	0.3454	0.3613	0.0179	63.5924
std.dev. (1 s)	0.0833	0.0011	0.0015	0.0005	0.0823
HPLC-ICP-MS	35.4459	0.3359	0.2976	0.0169	63.9037
std.dev. (1 s)	0.0756	0.0368	0.0206	0.0130	0.0058

*data are kindly provided by Dr. F. Oberli, Department of Earth Sciences, ETH Zürich,

The eluent of the HPLC is afterwards directed to the ICP-MS before the first lanthanide element (i.e. Lu, if HIBA is used, as for our application) elutes from the column.

Figure 2 shows the separation of all lanthanides in a mixed, standard solution with a gradient of 0.04 to 0.26 M HIBA.

3.1.2.3 Determination of U and Pu

Due to isobaric overlaps between U and Pu, a separation of these two elements is also necessary for burn-up determination. Pu can be eluted as PuO_2^{2+} from the separation column with 0.4 M HNO_3 . Afterwards, 1 M HCl is used as mobile phase in order to elute U. This separation is efficient enough to prevent any isobaric interference between ^{238}Pu , which is present at trace concentrations, and ^{238}U , as the main component of the fuel. In principle, both elements can be determined in one chromatographic run.

However, in fuel samples, the concentration of U is much higher than that for Pu. Therefore, two different dilutions of the sample have to be analysed: a higher concentrated solution for Pu determination, and a more diluted sample for U. Figure 3 shows the chromatographic separation of U and Pu in a fuel sample.

3.1.3 Comparison between the classical technique and HPLC-ICP-MS for burn-up determination

Absolute values for the burn-up of nuclear fuel samples may not be presented in this report by agreement of the ARIANE participants. However, another criterion which makes it possible to compare the results of the different laboratories, and mass spectrometric techniques, is the determination of the so-called "mass balance". This is a suitable indicator of the accuracy of the results. The standard deviation of the burn-up, and of the elemental concentrations of U, Pu and Nd, are measures of the precision of the measurement techniques used. Specifically, the mass balance is equal to the sum of the measured actinides divided by the solid-fuel weight, corrected by a factor 0.8815 for the presence of oxygen. Ideally, the mass balance of a sample should be unity. A mass balance less than this means an underestimation of the concentration of the elements U, Pu, and Nd, and one greater than unity is synonymous with an overestimation. Since U is the main component of the nuclear fuel, the mass balance is mainly influenced by the correct determination of the U concentration.

Due to systematic optimisation of all factors influencing the accuracy of the HPLC-ICP-MS measurements (i.e., amount of spike, measurement time, mass discrimination effects), we were able to improve the mass balance for one of the ARIANE samples from about 0.905 in 1997 to 0.993 in 1999. This means an almost 100% recovery, and was achieved within the range of 0.98 to 1.02 for all fuel samples analysed to date.

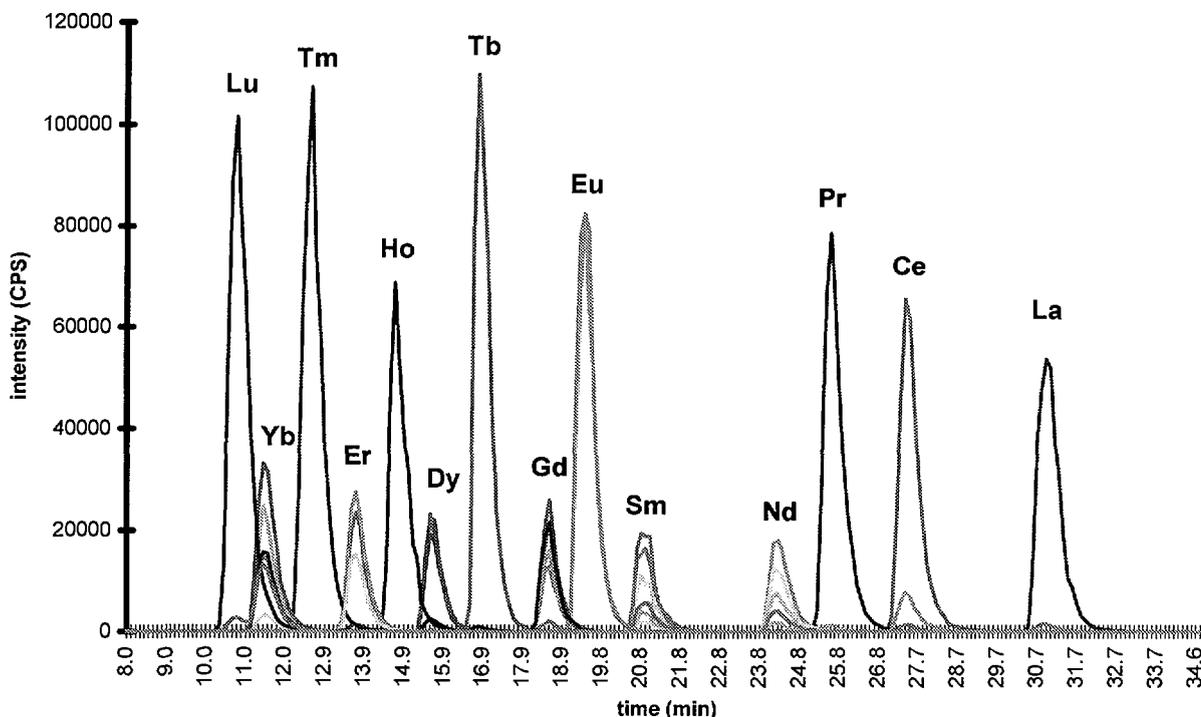


Fig. 2: Separation of the lanthanide elements in a standard solution with a linear gradient from 0.04 to 0.26 M HIBA (concentration of each element: 100 ng/g).

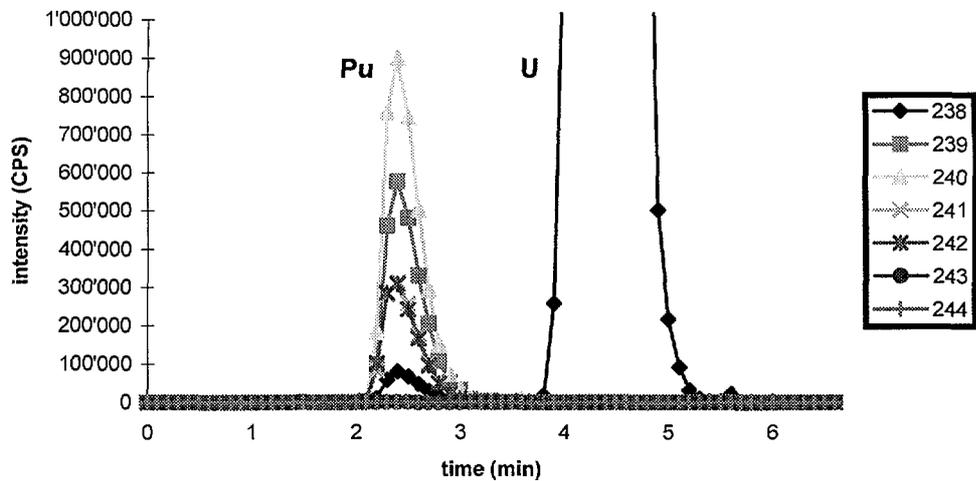


Fig. 3: Separation of Pu and U in a nuclear fuel sample with 0.4 M HNO₃ for the elution of Pu and 1 M HCl to elute U (the concentration of U in the sample is about 40 times higher than the Pu concentration); concentration of the analysed solution is 16 µg fuel/ml solution.

The SCK Laboratory in Belgium, which used TIMS as its analytical technique, achieved a mass balance in the range of 0.99 to 1.01 for all samples of the ARIANE programme.

These data show that a comparable accuracy can be obtained between the classical TIMS technique and the newly developed HPLC-ICP-MS system. However, considerable differences are found comparing the precision of the data. Typical standard deviations for burn-up and elemental concentrations determined by TIMS are in the range of 0.5 - 1% whereas, for the HPLC-ICP-MS data, the reproducibility is normally between 2 and 5%. These data confirm the results of the "Round Robin Test" on U standard mixtures, where a comparable accuracy for both techniques, and a reduced precision for ICP-MS, were found. Nevertheless, the "value" loss of precision in the ICP-MS approach compared with TIMS is more or less compensated by the considerable time-saving for the sample preparation and the analysis.

3.2 Determination of Am and Cm

The use of HPLC-ICP-MS to prevent isobaric overlaps between different elements is not restricted to the lanthanides, or to U and Pu. Due to the high diversity of chromatographic resins and mobile phases of the HPLC (inorganic acids, organic solvents and chelating agents), a separation method for most of the elements of the periodic table can be developed if the elements are present as ionic complexes. In the framework of the ARIANE programme, the actinides Am and Cm were also determined with this system, in addition to the burn-up elements U, Pu and Nd. Due to isobaric overlaps (²⁴¹Pu and ²⁴¹Am, ²⁴⁴Pu and ²⁴⁴Cm), it was necessary to separate the elements Am, Cm and Pu from each other. As described in Section 3.1.2.2, Pu can be eluted from the separation column with 0.4 M

HNO₃. In order to completely oxidize the Pu to PuO₂²⁺, either HClO₄ or KMnO₄ can be used as oxidizing agent.

In the dissolved fuel solution (prepared with 8 M HNO₃), Cm and Am will form principally Cm³⁺ and Am³⁺ ions. Because the ionic properties are very similar, as for the lanthanides, it is necessary to use a chelating agent. For this application, oxalic acid was considered to be the best choice. The HPLC separation for the Am and Cm isotopes in a fuel sample is shown in Fig. 4.

3.3 Determination of Rb, Sr, and Y

Fission products in the lower mass range between 80 and 90, such as Sr, are also important for the validation of theoretical models used for the calculation of the inventory of nuclear fuels. Because Rb and Y may possibly interfere with the Sr isotopes (⁸⁸Y and ⁸⁸Sr, ⁸⁷Rb and ⁸⁷Sr), it was necessary to develop a chromatographic separation for these elements. The three elements are different in their oxidation states; Rb⁺, Sr²⁺, and Y³⁺ are the most stable species in aqueous solution. Therefore, the chromatographic separation can be carried out very easily on a CS10 ion exchange column, with 1 M HNO₃ as mobile phase, under isocratic conditions.

For the same reason, the elements Cs and Ba (present as Cs⁺ and Ba²⁺ in aqueous solution), which also show isobaric overlaps, may also be completely separated under such chromatographic conditions.

Figure 5 shows the separation of Rb, Sr, and Y in a nuclear fuel sample with 1 M HNO₃. The complete analysis of the three elements can be carried out in about 8 minutes per sample.

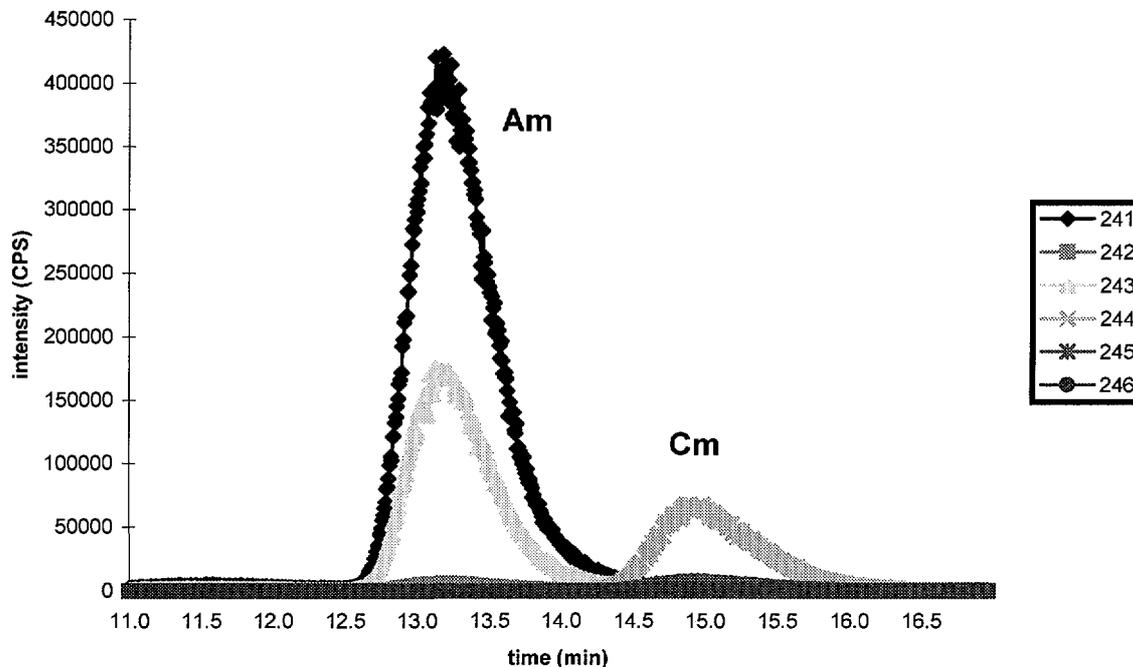


Fig 4: Separation of Am and Cm in a nuclear fuel sample with 0.1 M oxalic acid, 0.02 M LiOH (pH 4.6) under isocratic conditions. Pu was first eluted from the column with 0.4 M HNO₃, as described in Section 3.1.2.2; concentration of the analysed solution is 75 μ g fuel ml solution.

4 CONCLUSIONS AND OUTLOOK

With the on-line combination of an HPLC and an ICP-MS system, it is possible to separate interfering elements and to determine the isotopic composition of these elements, in a single analysis step. The quality of the chromatographic separation should be independent of the sample matrix. HPLC-ICP-MS systems are not only applicable to the characterisation of active samples, where the isotopic composition of most elements is unknown, but there are many applications in biological, clinical and toxicological research, and in the determination of the different valence states of an element (e.g. As(III)/As(V), Cr(III)/Cr(VI)). Besides the prevention of isobaric overlaps, and the characterisation of the binding behaviour or the valence of an element, on-line coupled HPLC-ICP-MS systems show an additional benefit: the separation of the sample matrix from the analyte elements. Particularly for the determination of trace elements in a high concentrated matrix, the on-line separation may lead to significantly lower limits of detection, because signal suppression due to the high concentrated matrix elements is avoided.

A comparative study between TIMS, as the classical technique for isotopic analysis, and HPLC-ICP-MS, showed that for U standard materials the loss of precision of ICP-MS compared with TIMS is compensated by the very reliable and efficient separation, and the short analysis time.

For each individual application, a compromise has to be found between the highly precise results produced by TIMS, at the expense of time-consuming sample preparation and measurement, and HPLC-ICP-MS,

with a reduced precision but with easy sample preparation and multi-elemental detection capability.

In order to combine the advantages of both mass spectrometric techniques, a new generation of instruments has been developed over the last two years. These so-called multiple-collector ICP-MS systems combine the ICP as ionisation source with the mass spectrometer and detector system used up to now for TIMS. The instruments are equipped with up to 12 Faraday cups as detectors, enabling the simultaneous measurement of all isotopes of an element [4]. This fact, together with the flat-peak shape of the isotope counting curves, are essential pre-requisites to achieving results of isotopic analysis which may even be comparable to the TIMS values.

The development of these instruments is a milestone for analytical chemistry, and will define a new level for isotopic analysis. Because the purchase of such a system is planned for the year 2000 in the Hot Lab, we have carried out test measurements with reference materials of different elements on all multiple-collector ICP-MS systems currently (commercially) available. The results look very promising in respect to the accuracy and precision of the data. The combination of such an instrument with a chromatographic separation system can be handled as easily as for the quadrupole ICP-MS, and will circumvent the necessity of a time-consuming sample preparation procedure, as is standard for TIMS. Therefore, we are very optimistic that we will soon be able to analyse the isotopic composition of different fuel components, or any other samples, with a precision and accuracy significantly higher than the data presented in this report, but with the same analysis effort.

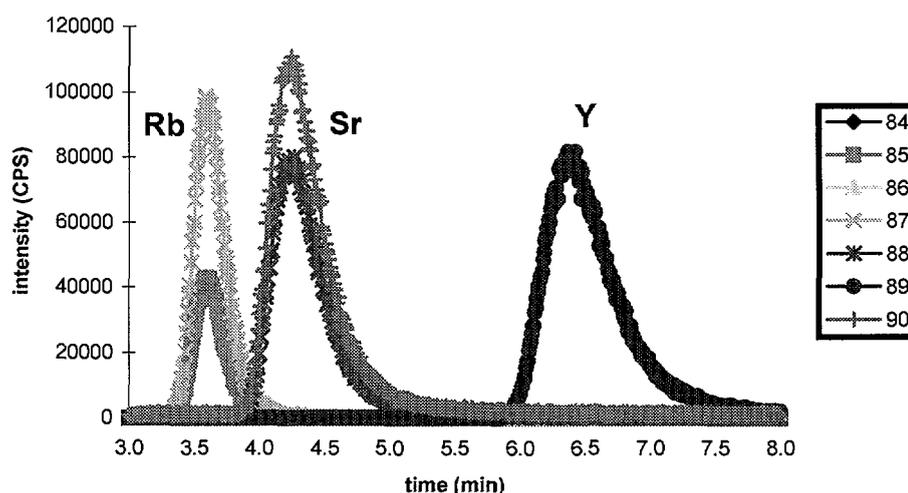


Fig 5: Separation of Rb, Sr, and Y in a nuclear fuel sample with 1 M HNO₃ under isocratic conditions; concentration of the analysed solution is 35 µg fuel/ml solution.

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