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Characterization of Spent Nuclear Fuels by an Online Combination of Chromatographic and Mass Spectrometric Techniques

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The determination of the burn-up is one of the essential parts in post-irradiation examinations on nuclear fuel samples. In the frame of national and international research programs the analysis of the isotopic vectors of uranium, plutonium, neodymium and some other fission products and actinides was carried out in the Hot lab of the Paul Scherrer Institute in the last years by using high-performance liquid chromatography coupled online with an inductively coupled plasma quadrupole mass spectrometer. In the meantime a multicollector ICP-MS, suitable for high precision isotope ratio measurements, was installed within the Hot lab and has been used now in combination with a chromatographic separation system for the first time for burn-up determinations of nuclear fuel samples. The results of these investigations, a comparison of both methods with the classical technique for burn-up analyses (thermal ionization mass spectrometry), the advantages and limitations of the methods and the accuracy and precision of this type of analyses are presented in the paper.

KEYWORDS: nuclear fuels, burn-up, HPLC, ICP-MS, isotopic vectors, isotope dilution

1. Introduction

The objective of different international programs dealing with post-irradiation examinations (PIE) of nuclear fuels is to improve the knowledge of the inventories of actinides, fission and neutron activation products in MOX and/or UO_2 spent fuel elements. The prediction of the source term of these nuclides is of major importance in numerous nuclear fields, such as

- definition of basic licensing data for UO_2 and MOX fuel
- increase of fuel enrichment for power reactors with a possible reevaluation of criticality licenses
- 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 actinides, activation and fission products in spent fuel provides a relevant data base for the validation of the theoretical models and represents an experimental basis for the minimization of the uncertainty in the prediction models.

The burn-up of a nuclear fuel as one of the important parameters that has to be determined for PIE is proportional to the quotient of the number of fissions N_F and the number of heavy metal atoms N^0_M (uranium and plutonium) which were present in the fuel before irradiation. The burn-up is given in % FIMA (fissions per initial metal atoms)

$$\%FIMA = \frac{N_F}{N_M^0} \cdot 100 \qquad (1)$$

Therefore, the experimental determination of the burn-up in an irradiated nuclear fuel is carried out by analyzing the number of U and Pu atoms and the number of one fission product that can be used as burn-up monitor. The accepted and mostly used method for burn-up determination is based on ^{148}Nd as burn-up monitor since Nd has several advantages compared with other fission products.

- Nd is not volatile and does not move in the fuel rod. Therefore, local burn-up determinations are possible.
- Nd is not a component of the non-irradiated fuel material.
- ^{148}Nd is not radioactive. Consequently, the method is not influenced by a decay time.
- The fission yield of ^{148}Nd is nearly independent from the neutron energy and from the fissionable isotope.

Consequently, the characterization of the burn-up of a nuclear fuel includes the mass spectrometric analysis of the isotopic vectors of U, Pu and Nd and the determination of the concentration of these elements. The quantification is normally carried out by isotope dilution, which is known as the most precise quantification method for mass spectrometric analyses.

Since numerous isobaric overlaps restrict the direct determination of most actinides and fission products by mass spectrometry, conventional methods for burn-up determination require a careful and often time-consuming chemical separation of the analytes. U and Pu show isobaric interferences with each other and with other actinides (e.g. $^{238}U/^{238}Pu$, $^{241}Pu/^{241}Am$), whereas Nd is interfered by other lanthanides (^{142}Ce,

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^{147}Pm, ^{147}Sm, ^{148}Sm, ^{150}Sm).

In order to combine the chemical separation with the mass spectrometric detection into one analytical step a high-performance liquid chromatographic system (HPLC) was online connected to an inductively coupled plasma quadrupole mass spectrometer (Q-ICP-MS) within the Hot lab of the Paul Scherrer Institute (PSI). This hyphenated technique was used within the last years routinely for burn-up determinations of MOX and UO_2 fuel samples in our lab.

However, the analytical figures of merit of a quadrupole based mass spectrometer measuring the different isotopes sequentially were shown to be not comparable to the performance of the classical technique (thermal ionization mass spectrometry, TIMS). Therefore, end of 2001 a multicollector ICP mass spectrometer (MC-ICP-MS) measuring up to nine isotopes simultaneously was installed within our lab and has been used in combination with a HPLC separation system for first burn-up determinations. The general advantages and limitations of both techniques as well as first comparative results will be discussed.

2. Experimental

2.1 Sample Preparation

Irradiated MOX and UO_2 fuel samples from light water reactors were dissolved using a HNO_3/HF (Merck, Suprapur) mixture in a high pressure digestion equipment at 150 °C for three hours. Mother solutions were prepared by dilution with 1 M HNO_3 up to a concentration of about 0.5 mg fuel per ml solution.

For isotope dilution aliquots of the mother solutions were mixed with enriched isotopic spike standards (^{233}U (IRMM-040a), ^{242}Pu (IRMM-049c) or ^{244}Pu (IRMM-042a), ^{150}Nd (ORNL)) and diluted with 1 % HNO_3. A further set of aliquots was directly diluted with 1 % HNO_3 without spike addition. Pu can be found in fuel solutions in different oxidation stages, of which the most stable is Pu^{4+}. Because the chromatographic separation of Pu and U is based on PuO_2^{2+} $HClO_4$ was added to all aliquots in order to oxidise the Pu to PuO_2^{2+}.

Aliquots of the spiked and unspiked sample solutions were injected three to five times into the HPLC-ICP-MS (quadrupole or multicollector) systems for the determination of the isotopic composition of the different elements.

2.2 Correction of Mass Bias Effects

Mass discrimination represents a limitation to the accuracy of isotope ratio measurements in all mass spectrometric methods. Ions entering the ICP-MS experience so called mass bias effects, and this bias favors the transmission of the heavier isotope into the mass spectrometer. In order to correct for these effects standard materials with a known isotopic composition were analyzed together with the samples.

For the characterization of U, Pu and Nd the following standard materials were used:

- IRMM-073, NBS-U010 and NBS-U100 uranium standards
- NBS948 plutonium sulfate
- Nd La Jolla reference material

2.3 Instrumentation

2.3.1 HPLC

A DX300 HPLC system (Dionex, Switzerland) equipped with an IonPac CG5 or CG10 (4 mm x 50 mm) as guard and IonPac CS5 resp. CS10 (4 mm x 250 mm) as analytical column was used in combination with the Q-ICP-MS. The flow rate of this HPLC is 1 ml/min and the injection valve is equipped with a 1 ml sample loop.

For online coupling to the MC-ICP-MS a modern DX-600 GS50 HPLC system (Dionex, Switzerland) equipped with a CG5A (2 mm x 50 mm) as guard and a CS5A (2 mm x 250 mm) as analytical column was installed. Because of the smaller column dimensions the flow rate of this system is restricted to 0.25 ml/min and the injection valve has a sample loop of only 0.025 ml.

The chromatographic separations of U, Pu and Nd were performed according to the methods described earlier[1]. U was eluted with 1 M HCl, Pu with 0.4 M HNO_3 and Nd was separated from other lanthanides with a linear gradient of α-hydroxyisobutyric acid (HIBA).

The coupling of the HPLC systems to the corresponding ICP-MS is achieved by passing the effluent of the chromatographic column to a 4-way valve. All sample components separated on the chromatographic column can be either sent directly to the ICP-MS for analysis or to waste in order to keep the sample loading into the mass spectrometer to a minimum.

2.3.2 ICP-MS

Inductively coupled plasmas are used since more than 25 years as excitation source for the optical emission spectrometry. The possibility to analyse the ions that are produced in an argon plasma by a mass spectrometric detector was first described in the eighties [2].

In a **Q-ICP-MS** the ions entering the mass spectrometer are separated according to their mass-to-charge ratio in a quadrupole mass filter and the detection of the ions is carried out with an electron multiplier in a fast but **sequential** mode. Since the entire mass range can be measured with a Q-ICP-MS in less than one second, these instruments are suitable for multielemental analyses. However, the precision of isotope ratio measurements is not comparable to the classical TIMS technique, because of the sequential detection mode.

In a **MC-ICP-MS** the ions are normally separated in a magnetic sector field and the detection is carried out by a set of 9 to 12 Faraday cups that allow the

simultaneous detection of different isotopes over a restricted mass range of about 15 %. Therefore, isotope ratio measurements of MC-ICP-MS can provide precision as low as 0.002 % RSD for different elements[3-4]. These results are in the range of or even superior to TIMS, which has been the preferred method so far for highly precise isotope ratio measurements for elements with relatively low first ionization potentials, such as U, Pu and Nd.

The Hot lab of the PSI is equipped with a PQ2+ Q-ICP-MS (ThermoElemental, UK) and a Neptune MC-ICP-MS (ThermoFinnigan, Germany) with nine Faraday cups.

For handling and analyzing highly toxic radioactive nuclear fuel samples parts of the respective HPLC system as well as the sample introduction part of the ICP mass spectrometers are encapsulated within glove-boxes.

3. Results and Discussion

3.1 Determination of U and Pu

Due to isobaric overlaps between U and Pu a separation of these two elements is necessary for burn-up determinations. 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 on both chromatographic systems (2 mm and 4 mm column diameter) to prevent any isobaric interference between ^{238}Pu, which is present at trace concentrations and ^{238}U as the main component of UO_2 and MOX fuel.

In principle, both elements could be determined in one chromatographic run. However, the concentration of U is much higher than the Pu concentration in fuel samples. Therefore, two different dilutions of the samples have to be analysed: a higher concentrated fuel solution for the Pu determination and a more diluted sample for U. Furthermore, using MC-ICP-MS it is not possible to analyze the entire mass range from ^{233}U to ^{242}Pu or even ^{244}Pu within one single measurement procedure. Two different Faraday cup configurations have to be determined: one from mass 233 to 239 for the U measurements and one from mass 238 to 242 or 244 for Pu analyses.

Figure 1 shows the chromatographic separation of U and Pu in an unspiked UO_2 fuel sample. The measurements were performed on the HPLC-MC-ICP-MS system.

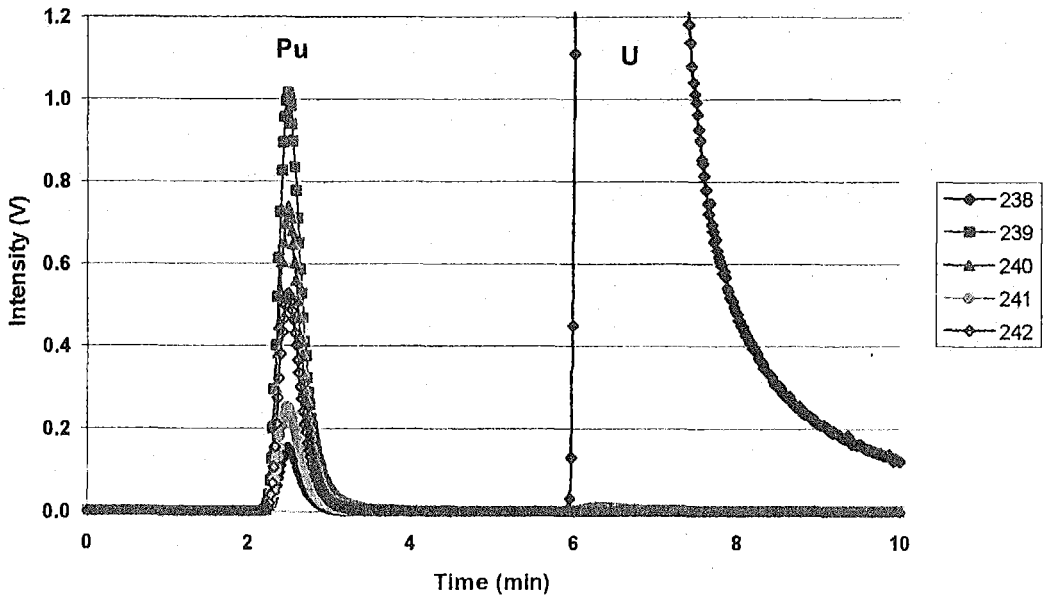

Fig. 1 Separation of Pu and U in an UO_2 fuel sample (1 s integration time of the MC-ICP-MS, HPLC injection volume: 25 μl, concentration of the analyzed solution: 15 μg fuel/ml solution)

3.2 Determination of Nd

In aqueous solutions, the group of lanthanides is 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 HIBA or oxalic acid. Lanthanides that form the most stable complexes with HIBA, such as lutetium, will elute first from the separation column.

U and Pu as the main matrix elements can be eluted with HCl resp. HNO_3 before the separation of the lanthanides. This is very important because the high concentration of these elements may decrease the sensitivity of ICP-MS for trace elements like Nd.

Figure 2 shows a typical chromatographic separation of Nd and the interfering element Sm in an unspiked MOX fuel sample. These measurements were performed on the HPLC-Q-ICP-MS system.

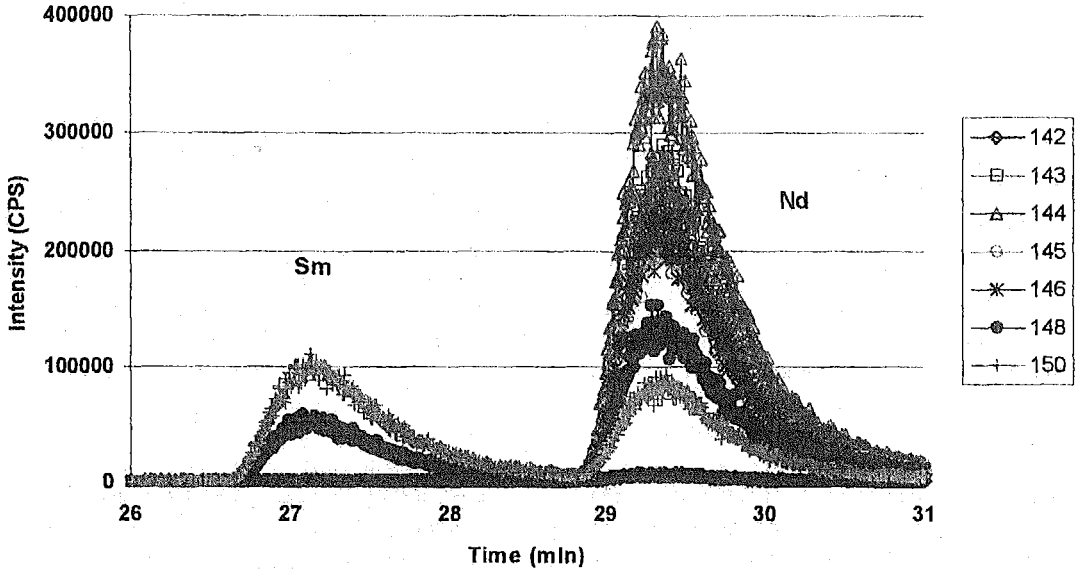

Fig. 2 Separation of Sm and Nd in a MOX fuel sample (10 ms dwell time per mass of the Q-ICP-MS, HPLC injection volume: 1 ml, concentration of the analyzed solution: 20 μg fuel/ml solution)

3.3 Precision and Accuracy of the Isotope Ratio Measurements

Typical relative standard deviations (RSD, in %) for the determination of isotopic vectors for the investigated elements U, Pu and Nd are listed in Table 1 for both techniques.

Table 1 Precision of isotope ratio measurements for HPLC-Q-ICP-MS and HPLC-MC-ICP-MS determined for U, Pu and Nd

Isotope abundance (At. %)	HPLC-Q-ICP-MS	HPLC-MC-ICP-MS
< 0.1	2 – 10 % RSD	about 1 % RSD
0.1 – 1	2 – 5 % RSD	< 1 % RSD
1 – 10	1 – 2 % RSD	< 0.1 %
> 10	< 1 % RSD	< 0.05 % RSD

In order to evaluate the accuracy of an analytical method it is necessary to measure certified reference standards with the same procedure as the samples and to compare the results with the published reference values. The comparison between the reference values for isotope ratios of U and Nd and the measured results for MC-ICP-MS and HPLC-MC-ICP-MS is shown in Table 2.

The data in Table 2 clearly indicate the high accuracy for MC-ICP-MS and even for the online coupled HPLC-MC-ICP-MS where the deviation from the corresponding reference value for U and Nd is only slightly higher.

Table 2 Accuracy of isotope ratio measurements for Nd (LaJolla) and U (NBS-U500) reference materials (the number in brackets corresponds to the absolute standard deviation (1 s); the accuracy is calculated as the deviation from the reference value)

Ratio	Reference value	MC-ICP-MS	HPLC-MC-ICP-MS
$^{143}Nd/^{144}Nd$	0.511858(4)	0.511844(9)	0.511921(38)
accuracy		- 0.003 %	0.012 %
$^{234}U/^{238}U$	0.010422(4)	0.010443(2)	0.010462(66)
accuracy		+ 0.2 %	+ 0.4 %

3.4 Comparison with TIMS

A general advantage of the classical TIMS technique compared to plasma based methods is the very stable ionization process leading to minor instabilities of the signal. Since TIMS is

characterized by bad ionization efficiency for elements with a higher ionization potential, the method is restricted in its applications to only a few elements of the periodic table. Mass bias effects are approximately an order of magnitude larger in ICP-MS systems than the mass discrimination observed during TIMS measurements[5]. However, since these effects can be properly corrected by using reference materials this is not a drawback of ICP-MS methods.

Major advantages of online coupled HPLC-ICP-MS techniques are the simplified sample preparation procedure, which is very important especially for radioactive samples with a high dose rate, the speed of the analysis and the better ionization efficiency for elements with high ionization potentials. At least the quadrupole and sectorfield ICP-MS systems are real multielemental techniques compared to TIMS (or MC-ICP-MS) were only a restricted mass range can be detected simultaneously.

The precision and accuracy demonstrated for the MC-ICP-MS technique so far is absolutely comparable to the classical TIMS method. However, most of these data are based on measurements using steady-state signals of several minutes or even longer. Since the online combination of a chromatographic separation system like HPLC with an ICP-MS leads to transient signals with a signal length of only about 30 to 60 seconds, the precision of the isotope ratio measurements is slightly reduced by less than one order of magnitude[6]. However, the analytical performance of an online coupled HPLC-MC-ICP-MS system is still comparable with the classical TIMS technique.

4. Conclusion

With the online combination of a 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 analytical procedure.

The comparison of the results from Q-ICP-MS and MC-ICP-MS after HPLC separation shows a significant improvement in the analytical precision of the transient data with multicollector detection.

Whereas the analytical performance of a HPLC-Q-ICP-MS system is reduced for isotope ratio measurements because of the sequential detection mode, the HPLC-MC-ICP-MS allows the simultaneous
detection of up to nine isotopes and provides therefore highly precise isotope ratio data.

Due to the high diversity of chromatographic resins and eluents 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. Online coupled HPLC-ICP-MS systems have a further benefit: the separation of the sample matrix from the analyte elements. Particularly for the determination of trace elements in a high concentrated matrix, the online separation of matrix elements may lead to significantly lower detection limits, because signal suppression due to high concentrated matrix elements is avoided.

Appendix: Review about PIE activities at PSI

Finally, Table 3 summarizes the PIE activities of the Paul Scherrer Institute. End of 1999 the international ARIANE program (organized by Belgonuclèaire) was finished, where ITU (Karlsruhe, D), SCK (Mol, B) and PSI took part as reference laboratories. Further ongoing and future projects for PIE and the corresponding fuel characteristics are also included in the table.

The aim of the **ARIANE** project was to provide improved knowledge of the inventories of actinides and fission products in UO_2 and MOX fuels irradiated at various burn-up levels for both PWRs and BWRs[7]. The ARIANE project has been launched end of 1994 with the participation of 15 organizations and was focused on two objectives:

- provide a large experimental data set regarding fuel selection for examination and the number of measured isotopes, some of them in very low concentrations,
- emphasize the accuracy of measurements by using various methods of analysis and by exchanging aliquots between laboratories for cross-checking.

PROTEUS is a zero-power research reactor operated at PSI in the Laboratory of Reactor Physics and Systems Behavior. The PROTEUS program is a joint effort by PSI and the Swiss Nuclear utilities with particular phases receiving additional support from other partners. The ongoing second phase of the LWR-PROTEUS experimental program is dedicated to the reactor physics investigation of well characterized highly burnt fuel samples from Swiss nuclear power plants by means of reactivity measurements and chemical assays. The chemical assays define the nuclide compositions of the samples and the measurements in the PROTEUS reactor provide information on the reactivity reduction with the fuel burn-up. The results will be used to validate theoretical methods for predicting composition and reactivity of fuel with burn-up, with special emphasis on the validation of high burn-up physics modeling[8].

Table 3 PIE activities at PSI

Program status/PSI method	Program name	Organization	Fuel type	Burn-up (GWd/t)	Reactor	Initial enrichment* (%)
Finished/ HPLC-Q-ICP-MS	ARIANE	Belgonucléaire	MOX	40-60	Beznau, CH (PWR)	5.9
			UO_2	32-60	Gösgen, CH (PWR)	3.4-4.1
			MOX UO_2	33-56	Dodewaard, NL (BWR)	6.4
Ongoing/ HPLC-MC-ICP-MS	PROTEUS, phase II	PSI	MOX UO_2	20-80	Gösgen, CH (PWR)	3.3-5.5 %
			MOX	50-75	Leibstadt, CH (BWR)	4.7 %
Future/ HPLC-MC-ICP-MS	MALIBU	Belgonucléaire	MOX UO_2	70	Gösgen, CH (PWR)	4.3-5.5%
			MOX UO_2	75	Grundremminge n, D (BWR)	3.75-5.5%

*Initial enrichment in % defined as $^{235}U/U$ for UO_2 fuel, Pu/U+Pu for MOX

The planned **MALIBU** project (also organized by Belgonucléaire) is an extension to the ARIANE program with a burn-up level of the UO_2 and MOX fuel samples of about 75 GWd/tM from BWRs and PWRs. Because of a shorter cooling time compared to the ARIANE program the accuracies for the measurement of short lived isotopes should be improved[9]. Supplementary to the ARIANE program a fourth reference laboratory (CEA, France) will take part in the MALIBU project.

During the ARIANE program the HPLC-Q-ICP-MS method was used for burn-up characterization within the Hot lab of PSI, whereas for the ongoing PROTEUS and future projects the new HPLC-MC-ICP-MS technique is applied for PIE measurements. This will allow a direct comparison of the accuracy of the data on real fuel samples for both techniques with the results of the classical TIMS technique that is used in other reference labs.

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