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Measurement of plutonium isotope ratios in nuclear fuel samples by HPLC-MC-ICP-MS

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Abstract

Radioactive isotopes are traditionally quantified by means of radioactivity counting techniques (α, β, γ). However, these methods often require extensive matrix separation and sample purification before the identification of specific isotopes and their relative abundance is possible as it is necessary in the frame of post-irradiation examinations on nuclear fuel samples.

The technique of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) is attracting much attention because it permits the precise measurement of the isotope compositions for a wide range of elements combined with excellent limits of detection due to high ionization efficiencies. The present paper describes one of the first applications of an online high-performance liquid chromatographic separation system coupled to a MC-ICP-MS in order to overcome isobaric interferences for the determination of the plutonium isotope composition and concentrations in irradiated nuclear fuels.

The described chromatographic separation is sufficient to prevent any isobaric interference between ^{238}Pu present at trace concentrations and ^{238}U present as the main component of the fuel samples. The external reproducibility of the uncorrected plutonium isotope ratios was determined to be between 0.04 and 0.2% (2 s) resulting in a precision in the ‰ range for the isotopic vectors of the irradiated fuel samples.

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1. Introduction

The main objective of post-irradiation examination programs on nuclear fuels is to improve the knowledge of the inventories of actinides, fission and neutron activation products within irradiated fuels. The prediction of the source term of these nuclides is of major importance for fuel licensing, safety studies, increasing the fuel enrichment for power reactors and for the storage of nuclear waste in geological repositories. In order to determine the isotope composition of actinides and fission products, which depends on the actual burn-up of the nuclear fuel, precise and accurate isotope ratio measurements are necessary.

Plutonium was the second transuranium element of the actinide series that was discovered. Plutonium may be formed as a by-product of the processes in conventional light water reactors when UO_2 fuel is used. Otherwise, it can already be a component of the non-irradiated fuel when a mixed oxide fuel (MOX) is applied. The formation of plutonium is based on neutron capture by ^{238}U in particular. At least 17 plutonium isotopes with different half-life are known. The most important isotope is ^{239}Pu, which has a half-life of 24,100 years. After reprocessing, the fissile isotopes of plutonium (^{239}Pu and ^{241}Pu) can be used in combination with depleted or natural uranium as MOX in a nuclear reactor; where the other isotopes are capable of absorbing neutrons and becoming fissile. Therefore, the characterization of the isotope composition of plutonium in UO_2 and MOX fuel is an essential part of the burn-up determination in irradiated nuclear fuels.

Classical radioanalytical methods are often unsuitable for plutonium determinations since ^{239}Pu and ^{240}Pu are not distinguishable due to their similar α energies. Furthermore,

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liquid scintillation spectrometry has proved to be useful for the analysis of the soft beta-emitter ^{241}Pu [1]. However, the complete isotope composition of plutonium cannot be determined with these methods.

In principle, different inorganic mass spectrometric techniques like glow discharge (GDMS), spark source (SSMS), resonance ionization (RIMS), accelerator (AMS), laser ionization (LIMS), thermal ionization mass spectrometry (TIMS) or ICP-MS can be used for isotope ratio measurements. A critical discussion of these techniques and a comparison of the achievable precisions are presented in [2,3]. In comparison with radioanalytical techniques commonly used for nuclear applications, ICP-MS offers very low detection limits, is also applicable for long-lived radionuclides, provides information on the isotope composition of fission products and actinides, and is capable of measuring stable as well as radioactive nuclides with similar sensitivity. Therefore, ICP-MS is meanwhile an accepted technique for routine measurements in the nuclear industry. For example, the American Society for Testing and Materials (ASTM) has already developed and published ICP-MS atom counting standard methods for the determination of many long-lived actinides and their daughter products [4].

For the control of environmental or occupational exposure the concentrations of plutonium and other actinides, e.g. in human urine samples have been measured by quadrupole (Q-ICP-MS) or sector field ICP-MS [5]. Since sector field mass spectrometers produce flat-topped peaks, such instruments are better suited for isotope ratio determinations. However, highly reliable data for plutonium isotope ratios can only be achieved using a mass spectrometric technique able to detect the corresponding isotopes simultaneously, such as TIMS or MC-ICP-MS.

Since numerous isobaric overlaps restrict the direct determination of most actinides and fission products by quadrupole and even high-resolution sector field ICP-MS and mathematical correction procedures cannot be applied owing to the unknown isotope composition of the elements, conventional ICP-MS or TIMS methods for plutonium 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). The classical method for plutonium measurements in nuclear fuel samples involves slow column techniques for matrix separation and elimination of these interfering elements [6]. In order to simplify the sample preparation procedure for the highly radioactive materials and to combine it with a mass spectrometric detector suitable for precise isotope ratio measurements, an online-coupled HPLC-MC-ICP-MS system was used for this study. A similar analytical approach for the analysis of neptunium, plutonium and fission products like cesium in fuel pellets was described by online coupling of an ion chromatography with a quadrupole ICP-MS [7–9]. The aim of the present study was to investigate the capabilities of a MC-ICP-MS in combination with online chromatographic sample preparation for actinides in nuclear fuel samples. The general feasibility of isotope ratio measurements on transient signals using the HPLC-MC-ICP-MS technique and the technical details of the system are described elsewhere [10].

Isotope dilution mass spectrometry (IDMS) was used in order to quantify the plutonium concentrations in the HPLC separated fuel samples. Among other advantages, IDMS is quite insensible to loss of sample during matrix separation on the chromatographic column.

2. Experimental

2.1. Sample preparation

Irradiated fuel samples from light water reactors (UO_2 and MOX) were dissolved using a HNO_3/HCl (Merck, Suprapur) mixture in a high pressure digestion equipment (Berghof, Germany) at 170 °C for 3 h. Stock solutions were prepared by dilution with 1 M HNO_3 up to a concentration of about 0.5 mg fuel/g solution.

For isotope dilution analyses, aliquots of the mother solutions were mixed with the spike isotopic reference material IRMM-049c (Geel, Belgium; ^{242}Pu enrichment: 94.29%) and diluted with 1% HNO_3. A further set of aliquots was directly diluted with 1% HNO_3 without spike addition.

2.2. Instrumentation

A HPLC system (DX-600 GS50, Dionex, Switzerland) equipped with a CG5A guard and a CS5A analytical column (2 mm × 250 mm) and a 25 μl injection loop was coupled to the Neptune MC-ICP-MS (ThermoElectron, Germany). The CG5A and CS5A columns are filled with a mixed bed high-resolution ion exchange resin with both anion and cation exchange capacity. The flow rate of the HPLC system was 0.25 ml min^{-1}. For handling and analyzing highly toxic radioactive nuclear fuel samples parts of the HPLC system as well as the sample introduction system of the MC-ICP-MS were placed into a glove–box system.

The chromatographic separations of U and Pu were performed according to the methods described earlier [11]. The solution chemistry of Pu is complicated because four oxidation states can be present at the same time in fuel solutions; the most stable are Pu^{IV} and Pu^{VI}. Because the chromatographic separation of Pu and U used in that study is based on PuO_2^{2+}, perchloric acid was added to all aliquots in order to oxidize the Pu. In a first step Pu was eluted from the chromatographic column as PuO_2^{2+} with 0.4 M HNO_3. In aqueous solutions U is present as the uranyl cation (UO_2^{2+}) and forms strong complexes with chloride ions. Therefore, it was eluted with 1 M HCl from the chromatographic resin. The chromatographic conditions for the separation of the two elements are summarized in Table 1.

The coupling of the HPLC to the MC-ICP-MS was achieved by passing the effluent from the chromatographic

Table 1
Chromatographic conditions for the separation of uranium and plutonium (flow rate: 0.25 ml min^{-1})

Time (min)	Water (%)	1 M HNO_3 (%)	1 M HCl (%)
0	60	40	0
1.5	60	40	0
1.6	0	0	100
10	0	0	100

column to a four-way valve [10]. The sample introduction system of the Neptune consists of a PFA microconcentric nebulizer and a tandem spray chamber. The baseline for the Faraday cups was measured with a defocused ion beam and an opened amplifier gate valve. The isotope ratio measurements on the transient signals of Pu were performed in the static, low-resolution mode with an integration time of 1.049 s per data point.

2.3. Mass discrimination

Since no invariant or known isotope ratio for internal mass bias correction can be used (because the isotope composition of plutonium depends on the respective burn-up of the fuel and is therefore unknown) a bracketing procedure between samples and a standard material was applied for mass bias correction. Within this study, the NIST-SRM-948 plutonium sulfate was used as reference material. Since the mass discrimination is matrix dependent the standard material was also injected via the HPLC into the MC-ICP-MS.

3. Results and discussion

A typical separation of the interfering elements plutonium and uranium in an irradiated nuclear fuel sample (UO_2 fuel) is shown in Fig. 1. The transient signal for plutonium lasts for about 0.6 min and 1 min for uranium, respectively (peak width at 10% peak height). The separation is sufficient to prevent any isobaric interference between ^{238}Pu present at trace concentrations and ^{238}U present as the main component of the fuel samples. In principle, both elements could be determined within one chromatographic run. However, in nuclear fuel samples the concentration of uranium is much higher (by a factor of about 15 up to 100 depending on the fuel type) than the concentration of plutonium. Therefore, the dynamic range of the Faraday cups (0.01–50 V) is limiting the analysis of both elements within one run. To overcome this limitation, two different dilutions of the same samples were analyzed whenever the isotope composition of both elements were of interest.

Since americium basically forms trivalent ions when the dissolution of fuel samples is carried out with nitric acid, Am^{3+} could only interfere on mass 241 with the oxidation state Pu^{3+} (if present in the sample) but not with $PuO_2{}^{2+}$ [12,13]. Therefore, an interference-free determination of the plutonium isotope composition is possible with the described separation method.

Fig. 2a shows a typical chromatographic peak of plutonium in an irradiated MOX fuel sample together with the plutonium isotope ratios across the transient signal in Fig. 2b. The isotope ratios shown (filled symbols) are not mass bias corrected. Mass bias correction using the exponential law was finally carried out for the mean value of the isotope ratios after five individual injections and not for each data point within one chromatographic run. The mass discrimination factor for plutonium determined by the NIST-SRM-948 plutonium sulfate reference material was stable in the range of 0.7–0.9% amu^{-1} over a measurement period of about 4 months. The chromatographic separation conditions were kept constant within this time period, whereas the plasma conditions of the MC-ICP-MS varied due to different tuning parameters.

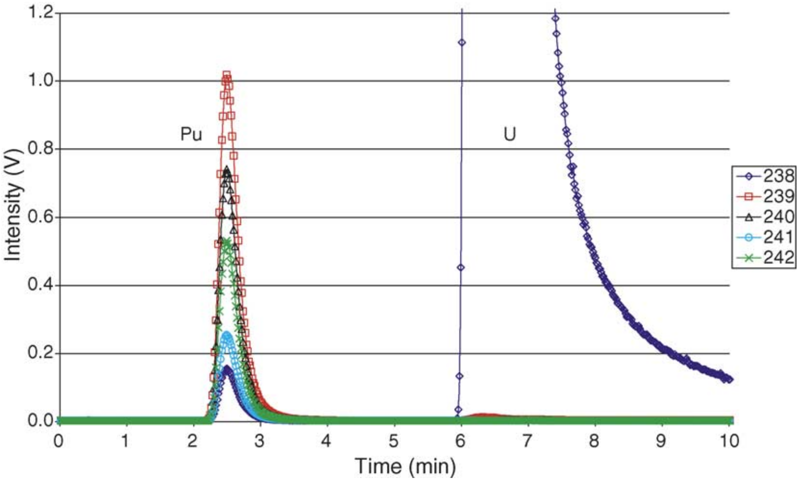

Fig. 1. Separation of Pu and U in an irradiated UO_2 fuel sample (integration time of the MC-ICP-MS detectors: 1 s, HPLC injection volume: 25 μl, concentration of the analyzed solution: 15 μg fuel/ml solution; intensity of $^{238}U > 50$ V).

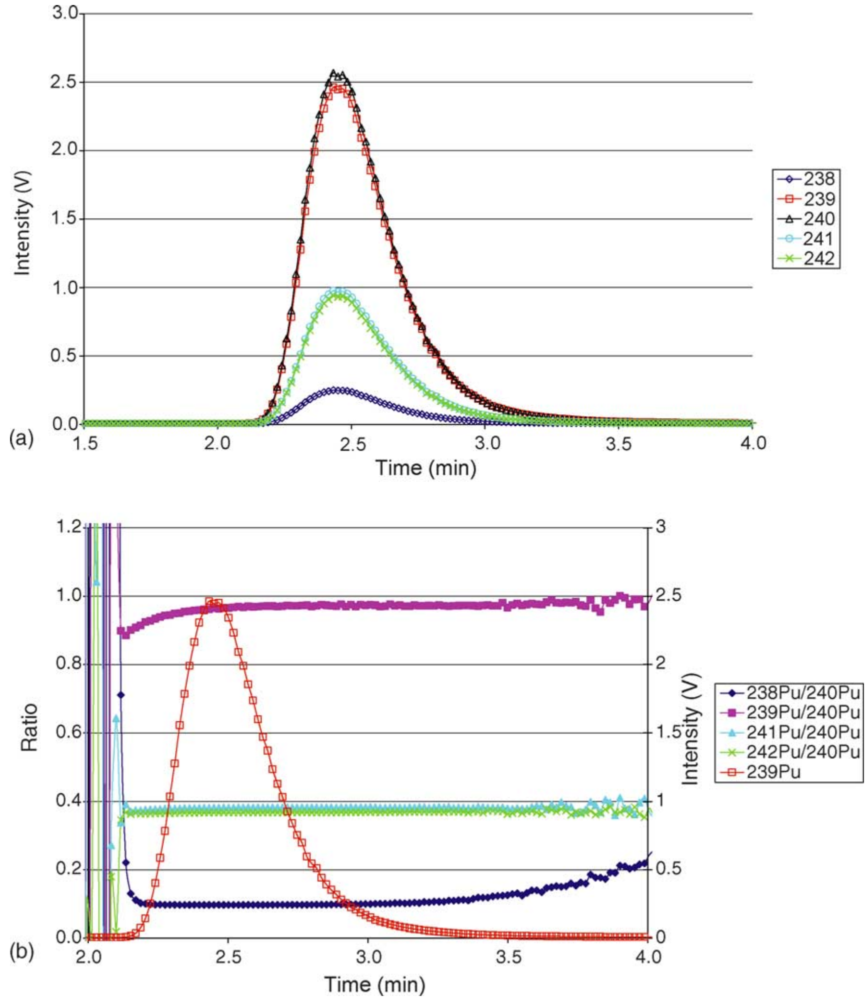

Fig. 2. Behavior of signal intensities and isotope ratios across the transient signal of a HPLC separated plutonium peak. (a) Plutonium peak of an irradiated MOX fuel sample (analytical conditions as in Fig. 1). The intensities of all detectable plutonium isotopes (^{238}Pu–^{242}Pu) are shown as a function of the retention time. (b) Non-corrected plutonium isotope ratios (filled symbols) across the transient signal shown in Fig. 2a. The elution of plutonium from the chromatographic column is illustrated by the ^{239}Pu intensity (open squares) vs. retention time.

Except the ^{239}Pu/^{240}Pu ratio (filled squares) all other isotopes show a stable isotope ratio (Fig. 2b) already after the first data points of the transient peak until the intensity reaches background level again. The increase in the ^{238}Pu/^{240}Pu ratio (filled rhombus) after about 3.3 min is caused by the beginning of the uranium elution from the chromatographic column. However, the fact that the ^{239}Pu/^{240}Pu isotope ratio does not reach a stable plateau before the maximum signal intensity of the plutonium peak cannot be explained by an interference effect or isotope fractionation. The behavior of the ^{239}Pu/^{240}Pu isotope ratio in the present study is different from the isotope ratio drift observed for HPLC-MC-ICP-MS measurements on uranium standard solutions discussed in [10]. If the absolute intensity of the transient signals would play an important role for the ratio drift as concluded in the previous paper all shown ratios should be biased to a similar extent, because the intensity of ^{239}Pu and ^{240}Pu is nearly identical (see Fig. 2a). Since this behavior is reproducible for all plutonium measurements carried out under almost identical operating conditions and a similar effect was observed for the ^{143}Nd/^{144}Nd ratio for neodymium measurements on transient signals as well as for other elements analyzed so far it can be postulated that this slight increase in the ratio depends on a slow amplifier response on one Faraday cup (^{239}Pu and ^{143}Nd were both measured on the L2 cup) in comparison to the other amplifiers.

A similar effect has already been reported by Hirata et al. [14]. The author described the influence of a slow response on Faraday preamplifiers when measuring copper and iron isotope ratios by laser ablation MC-ICP-MS. Although the structure of the transient signals for laser ablation (sharp signal increase followed by a signal plateau and a sharp signal decrease) and for chromatography (Gaussian profile) are different, both sample introduction techniques are characterized by a significant intensity change over time. For laser ablation this intensity change can be expressed in V s^{-1} [14], whereas for the presented HPLC peaks V min^{-1} is more appropriate. Since for HPLC separated peaks an intensity change occurs

Table 2
Isotopic composition of two irradiated fuel samples with a similar burn-up level (about 6% fissions per initial metal atom (FIMA))

	^{238}Pu (at.%)	1 s	^{239}Pu (at.%)	1 s	^{240}Pu (at.%)	1 s	^{241}Pu (at.%)	1 s	^{242}Pu (at.%)	1 s
UO_2	3.267	0.033	48.302	0.016	27.463	0.002	10.444	0.012	10.525	0.002
MOX	3.667	0.037	34.648	0.039	35.716	0.031	13.192	0.013	12.776	0.018

during the total analysis time an influence of the individual amplifier response time on isotope ratio measurements needs further investigations.

As a consequence of the unstable isotope ratio profile for plutonium, only the data points from the second half of the chromatographic peak were used for the calculation of the plutonium isotope ratios for each injection.

Because the signal intensity varies substantially across the transient, the achievable precision of the isotope ratios for each data point is changing. Therefore, the calculation of internal precision over the transient signal represents less meaningful information. For this reason the external reproducibility of the isotope ratios from several replicate injections was determined as an indication for the precision of the results. The external reproducibility of the uncorrected plutonium isotope ratios for five consecutive injections of more than 20 plutonium samples analyzed by HPLC-MC-ICP-MS was determined to be between 0.04 and 0.2% (2 s). These data result in a precision in the ‰ range for the isotopic vectors of the irradiated fuel samples. Table 2 shows the isotopic composition (at.%) of Pu for a UO_2 and a MOX fuel sample. In comparison to previously measured HPLC-Q-ICP-MS analyses carried out on similar fuel samples the present achieved precision is improved by one order of magnitude.

The plutonium concentrations (mg Pu per g fuel solution) determined by isotope dilution analysis have typically a precision of 0.3–0.5% (2 s), since the error of these results is not only influenced by the precision of the isotopic composition of plutonium in the samples but also by the error of the spike standard composition (certificate), the error of the sample and spike weighing for isotope dilution and by the error of the concentration of the fuel solution. The total plutonium concentrations within the irradiated fuel samples varied between about 1.0 and 1.4% of the total uranium concentration in UO_2 fuel and between 5.7 and 7.9% in MOX fuel, respectively, depending on the actual burn-up value for the fuel rods.

In the present study, the plutonium concentrations of the samples are not a limiting factor for the analytical procedure. The plutonium isotopes built up in irradiated nuclear fuels to a significant extent (^{238}Pu–^{242}Pu) are present in comparably high amounts and even higher concentrated fuel solutions can be used when needed. Therefore, all plutonium isotopes are measured simultaneously on the Faraday cups, which is the ideal prerequisite for precise isotope ratio measurements. However, most of the plutonium isotope ratio measurements published in the literature have been carried out on environmental samples (water, soil, sediments, or biota). The measurement of the ^{239}Pu and ^{240}Pu isotopes in these samples can provide information on the source of environmental contamination (nuclear weapons fall-out or reactor discharge). Since plutonium is present in these samples only in trace concentrations, the signal levels of ^{239}Pu and ^{240}Pu are generally too small to be reliably measured on Faraday cups. Consequently, the majority of the published plutonium isotope ratio data has been measured using a peak jumping approach on quadrupole-based or sector field mass spectrometers. Becker [2] reported about the ^{240}Pu/^{239}Pu isotope ratio determination using a sector field ICP-MS and micronebulization with a precision of 2% at 100 fg ml^{-1}. Slightly better precisions can only be achieved at this low concentration levels using a double spike technique or a multiple ion counting approach on a MC-ICP-MS as described by Taylor et al. [15,16]. ^{240}Pu/^{239}Pu was reproducibly measured to within 1.4% (2 s) at 100 fg ml^{-1} and better than 0.3% at >3 pg ml^{-1}. This comparison shows that whenever plutonium concentrations are high enough, a real multicollector measurement of Faraday cups results in the best analytical performance. However, for trace concentrations of plutonium such as environmental contaminations multiple ion counting techniques available on modern MC-ICP-MS instruments or even sector field ICP-MS provide qualitatively good results.

4. Conclusion

With the online combination of a HPLC and an ICP-MS system it is possible to separate interfering elements like uranium and plutonium and to determine the isotope composition of these elements in a single analytical procedure. 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 12 isotopes (depending on the instrument) and provides therefore highly precise isotope ratio data. Nevertheless, due to the measurement on transient signals when coupling a chromatographic device with a MC-ICP-MS the analytical performance is reduced in comparison to continuous sample introduction. However, the simplicity of the sample preparation procedure makes such an online hyphenated technique attractive, especially for samples requiring special precaution during handling, e.g. radioactive materials.

An interference-free determination of high concentrations of plutonium in irradiated nuclear fuel samples without intensive and time-consuming sample preparation steps were investigated on real samples. The HPLC-MC-ICP-MS technique provides the requested analytical performance and is therefore a robust and high-throughput alternative to the

TIMS technique used so far in combination with offline column separations for plutonium determinations in the frame of burn-up studies.

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