

ORIGINAL PAPER

Ines Günther-Leopold · Beat Wernli · Zlatko Kopajtic
Detlef Günther**Measurement of isotope ratios on transient signals by MC-ICP–MS**

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Abstract Precise and accurate isotope ratio measurements are an important task in many applications such as isotope-dilution mass spectrometry, bioavailability studies, or the determination of isotope variations in geological or nuclear samples. The technique of MC-ICP–MS has attracted much attention because it permits the precise measurement of isotope compositions for a wide range of elements combined with excellent detection limits due to high ionisation efficiencies. However, the results are based mainly on measurements using continuous sample introduction. In the present study the determination of isotope ratios on various transient signals with a time duration of 30 to 60 s has been achieved by coupling high-performance liquid chromatography to a multicollector inductively coupled plasma mass spectrometer. In order to investigate the origin of ratio drifts across the transient signals for this hyphenated technique, measurements with the same standard solutions were also carried out using a flow-injection device for sample introduction. As a result of this application it could be concluded that the main source of the bias in the measured isotope ratios is within the ICP–MS instead of fractionation effects on the chromatographic column material. Preliminary studies on short transient signals of gaseous samples (dry plasma) showed a reverse fractionation effect compared with wet plasma conditions (flow injection and HPLC).

Keywords Multicollector ICP–MS · Transient signals · Isotope ratios · Hyphenated techniques

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I. Günther-Leopold (✉) · B. Wernli · Z. Kopajtic
Laboratory for Materials Behaviour, Paul Scherrer Institute,
5232 Villigen PSI, Switzerland
e-mail: guenther@psi.ch

D. Günther
Laboratory of Inorganic Chemistry – Elemental and Trace Analysis,
ETH Hönggerberg, 8093 Zürich, Switzerland

Introduction

The determination of elemental species is one of the most important fields in analytical and environmental chemistry today. This is because the toxicity, the bioavailability, and the environmental mobility of an element strongly depend on its chemical form. By coupling a chromatographic separation system with an element-specific detector, for example inductively coupled plasma mass spectrometry (ICP–MS), powerful and sensitive detection of elemental species in an online procedure is available. However, online coupling between a chromatographic separation system and a mass spectrometer is not only carried out for speciation but also for separation of the sample matrix from the analyte elements, sample preconcentration, and separation of interfering elements.

Because quantification of elements separated on chromatographic systems is mostly carried out by the method of isotope dilution [1] or the isotopic composition of the elements itself is of interest [2], highly reliable data can only be achieved with a mass spectrometric technique which is able to detect the isotopes of one or more elements simultaneously, such as multicollector inductively coupled plasma mass spectrometry (MC-ICP–MS). All types of hyphenation between a chromatographic separation system like gas or liquid chromatography [3], methods like capillary electrophoresis [4], laser ablation [5], or thermal desorption [6] and an ICP mass spectrometer lead to transient signals often of very short duration (from less than 5 s for gas chromatography up to about 60 s for liquid chromatography). However, the best precision for the measurement of isotope ratios with any mass spectrometric system is obtained using steady-state signals of several minutes or even longer and not when using short transient signal acquisition. Thus, the simplification of the sample preparation procedure obtained by the online coupling of a separation technique may be offset by a reduction in precision resulting from measurements made on short transient signals.

The strength of MC-ICP–MS lies in the combination of a high efficiency ionisation source and an array of Fara-

day collectors for simultaneous measurement of different ion beams over a restricted mass range. Therefore, it enables the precise measurement of isotope compositions for a wide range of elements combined with excellent detection limits. Isotope ratio determinations by MC-ICP-MS can provide external precision as low as 0.002% RSD (2 sigma) [7, 8, 9] for different elements. However, these results are based entirely on measurements using continuous sample introduction.

A significant feature of plasma source mass spectrometry is the large instrumental mass bias reflecting the tendency of heavier ions to be extracted in preference to light ions. This effect is approximately an order of magnitude larger than the mass discrimination observed during TIMS measurements [10]. This phenomenon is mainly ascribed to space-charge effects [11, 12, 13] in the plasma interface between sample and skimmer cone and in the focusing lens region. Irrespective of the space charge effect, the lighter isotopes should preferably be pumped down and, therefore, more light isotopes leave the central ion beam compared with the heavier isotopes. Using a hyphenated HPLC-MC-ICP-MS system these effects may be overlaid by "isotope fractionation" of the elements on the chromatographic resin of the HPLC system.

Major applications in the group "Isotope and Wet Analytical Chemistry" in the hot laboratory of the Paul Scherrer Institute are characterisation of spent nuclear fuel samples, especially determination of the isotopic composition of fission products and actinides and their elemental concentrations. The main objective of these post-irradiation examinations is to improve knowledge of the inventories of these elements within irradiated fuels, because these data are important for licensing and safety aspects, for increasing the fuel enrichment, and finally for the storage of the nuclear waste in a geological repository.

The burn-up of a nuclear fuel is one of the important properties that have to be determined in the framework of post-irradiation examinations. The burn-up of a fuel is proportional to the quotient of the number of fissions and the number of heavy metal atoms (U and Pu) that were present in the fuel before irradiation. Therefore, experimental determination of the burn-up is carried out by analysing the number of U and Pu atoms and the number of one fission product that can be used as burn-up monitor. The group of lanthanides is the major part of the stable and long-lived fission products of ^{235}U and ^{239}Pu irradiated in a light-water reactor. Since the fission yield of ^{148}Nd is well characterised and nearly independent of the neutron energy, the method mostly used for burn-up determination is based on this isotope. Consequently, the characterisation of the burn-up of a nuclear fuel includes the analysis of the isotopic composition of U, Pu, and Nd and the determination of the concentration of these elements by isotope-dilution analysis.

Typical isotope compositions for these elements within irradiated fuels are as follows: about 0.01% ^{234}U , 0.1–1% ^{235}U and ^{236}U (depending on the fuel type), >98% ^{238}U ; about 2% ^{238}Pu , 30–40% ^{239}Pu and ^{240}Pu , 10% ^{241}Pu and ^{242}Pu ; <1% ^{142}Nd , 20–30% ^{143}Nd and ^{144}Nd , 10–20% ^{145}Nd and ^{146}Nd , 10% ^{148}Nd , 5% ^{150}Nd .

The classical method for burn-up determination involves slow column techniques in order to isolate Nd, Pu, and U from interfering elements, resulting in a great risk for contamination of the sample and in a high radioactive dose rate for the operator, because the separations take several days.

In order to simplify the sample-preparation procedure (matrix separation, elimination of interfering elements) for these highly radioactive materials and to combine it with a mass spectrometric detector suitable for precise and accurate isotope ratio measurements, an online coupled HPLC-MC-ICP-MS system was installed.

The aim of the present work was to investigate the precision of isotope ratio measurements on transient signals typical of HPLC separations compared with continuous sample introduction. Because nuclear fuel samples do not have common isotope compositions with "stable" isotope ratios, an internal mass-bias correction cannot be applied. Therefore, it is necessary to test whether the chromatographic system leads to a significant isotope fractionation. In order to differentiate between fractionation effects occurring in the chromatographic system and/or in the ICP-MS transient signals after HPLC separations were compared with transient signals of the same standard solutions measured with an online coupled flow injection MC-ICP-MS system. For comparison of fractionation effects under wet (HPLC, flow injection) and dry plasma conditions, a preliminary study of short transient signals from gaseous samples was also carried out to explore the major source and occurrence of such effects.

Experimental

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 (ThermoFinnigan, Germany). The CS5A column is a mixed-bed ion-exchange column that has both anion- and cation-exchange capacity. The flow rate of the HPLC system was 0.25 mL min^{-1} .

Because the MC-ICP-MS at our laboratory is mainly used for the characterisation of nuclear fuel samples the study was restricted to transient signals of uranium (main component of nuclear fuels) and neodymium (burn-up monitor) standard solutions. Chromatographic separations of uranium and neodymium from the interfering elements samarium and cerium were performed according to the methods described in Röllin et al. [14]. Uranium was eluted with 1 mol L^{-1} HCl, whereas the elements of the lanthanide group were separated with a linear gradient of α -hydroxyisobutyric acid (HIBA).

The coupling of the HPLC to the MC-ICP-MS was achieved by passing the effluent from the chromatographic column to a four-way valve. All sample components separated on the chromatographic column can be either sent directly to the MC-ICP-MS for the analysis of the isotopic composition or to waste in order to keep the sample loading into the mass spectrometer as low as possible. The sample introduction system of the MC-ICP-MS consists of a PFA microconcentric nebuliser and a tandem spray chamber. The Neptune is a magnetic sector field mass spectrometer using up to nine Faraday cups (50 V dynamic range, attached to $10^{11}\text{-}\Omega$ resistors) for simultaneous detection and provides high mass-resolution capabilities. The central counter is switchable between a Faraday cup and a discrete dynode ion counter with a high-abundance sensitivity filter on the low-mass side. The baseline for the Faraday cups was measured with the amplifier gate valve closed (electronic noise) because this was the only option in the software version 2.04

Table 1 Operating conditions of the Neptune MC-ICP-MS

| | HPLC and flow injection | Experiments with gaseous samples |
|----------------------------------|-------------------------|----------------------------------|
| Forward power (W) | 1100 | 1300 |
| Torch shield | On | On |
| Gas flows (L min ⁻¹) | | |
| Cool | 15 | 15 |
| Auxiliary | 0.9 | 0.9 |
| Sample | 0.925 | 0.925 (Kr), 0.6 (Xe) |
| Resolution mode | low | low (Kr), high (Xe) |
| Collection mode | Static | Static |
| Integration time (s) | 0.131, 1.049, or 2.097 | 0.131, 1.049, or 2.097 |

used for all the measurements in this study. Since software release 2.5 two options:

- defocusing the ion beam, or
- measurement of the baseline on two predefined masses

have been available. The operating conditions of the Neptune are given in Table 1.

The internal mass bias-correction was carried out for Nd and U by normalising measured isotope ratios to $^{145}\text{Nd}/^{146}\text{Nd}=0.4826$ and $^{235}\text{U}/^{238}\text{U}=0.01014$ (NIST-SRM-010), 0.11360 (NIST-SRM-100), and 0.99970 (NIST-SRM-500), using an exponential law. The $^{145}\text{Nd}/^{146}\text{Nd}$ ratio was chosen because both of these isotopes are free from possible Sm interferences that may occur in the Nd/Sm mixture when separation of the elements by HPLC is incomplete.

For handling and analysis of highly toxic radioactive nuclear fuel samples parts of the HPLC (autosampler, injection valve, separation column, four-way valve) and the sample-introduction system of the MC-ICP-MS (peristaltic pump, nebuliser, spray chamber, torch-box) were encapsulated within a glove-box system in order to prevent radioactive contamination.

A comparative study for gaseous samples (dry plasma conditions) was performed by injecting 0.5 cm³ of a gas mixture (calibration gas for gas mass spectrometry) containing about 15% Xe, 2% O₂, 8% N₂, 1% Kr, 1% Ar, 0.5% CO₂ in He (Messer Griesheim, Germany) using a four-way stainless steel valve (Supelco, Switzerland) directly into the nebuliser gas flow of the MC-ICP-MS.

Results and discussion

Wet plasma conditions (HPLC and flow injection)

Measurement of the Nd isotopic composition on transient signals

A typical transient signal for separation of the interfering elements samarium and neodymium is shown in Fig. 1. The transient signals for both elements last for about 60 s depending on the retention time on the chromatographic column. The transient signal of the interfering element cerium is not shown in Fig. 1, because the retention time is between 15 and 17 min.

Because the signal intensity varies substantially across the transient, the achievable precision for each data point in time will also vary. Therefore, the calculation of internal precision over the transient signal is meaningless. For this reason the external reproducibility of the isotope ratios from several replicate sample injections was determined as an indicator of the analytical performance of the HPLC-MC-ICP-MS system. Ratios for a single replicate

were determined by first integrating the signal intensity for the entire transient signals for each isotope and then calculating ratios using the integrated data. A comparison of individual injections on the HPLC system and repeated analyses of the same solutions by continuous sample introduction (steady-state signals) is shown in Fig. 2. The integration time was changed from 0.1 s to 2 s for both introduction methods (Table 1). The measurement time for continuous sample introduction was about 2 min, which corresponds to a sample consumption of about 120 μL (microconcentric nebulizer, self aspirating). The sample volume for each individual HPLC injection was 25 μL , because of the size of the injection loop. Because the experiments with continuous sample introduction and HPLC injection were carried out with identical Nd concentrations (50 ng Nd/g solution) the absolute amount of Nd for the online HPLC-MC-ICP-MS analyses is about a factor of five lower than for continuous nebulisation.

The external reproducibility of the mean value (indicated by the error bars) of the mass bias-corrected ratios after HPLC injections (Fig. 2, open triangles, mean value) is about a factor of five worse than for continuous sample introduction (filled triangles, mean value) whereas the external reproducibility for the uncorrected ratios is of the same order of magnitude for both sample introduction methods, as indicated by the error bars of the mean values (open and filled squares, mean values). Generally, for all the measurements carried out so far with uranium and neodymium the degradation of the external reproducibility for transient signals is less than a factor of ten compared with steady-state signals.

These results are consistent with a similar study for GC-MC-ICP-MS published by Krupp et al. [15, 16]. The external precision determined for continuous flow was two-to tenfold better than the relative standard deviation for GC coupling to MC-ICP-MS with 3 s transient signals for Pb.

Evans et al. [6] reported the determination of Hg isotope ratios in different coal and fly ash samples by preconcentration on to gold traps followed by thermal desorption into different MC-ICP-MS systems. In contrast with the results presented here the external reproducibility of these transient signals of about 30 s duration was similar to that from continuous sample introduction. Although a clear explanation for this finding cannot be given, it is possible that it could be influenced by the different plasma condi-

Fig. 1 Separation of a multi-element standard solution containing 50 ng g^{-1} Sm and Nd by HPLC–MC–ICP–MS (integration time 1 s; mobile phase gradient of α -hydroxyisobutyric acid in MilliQ-water)

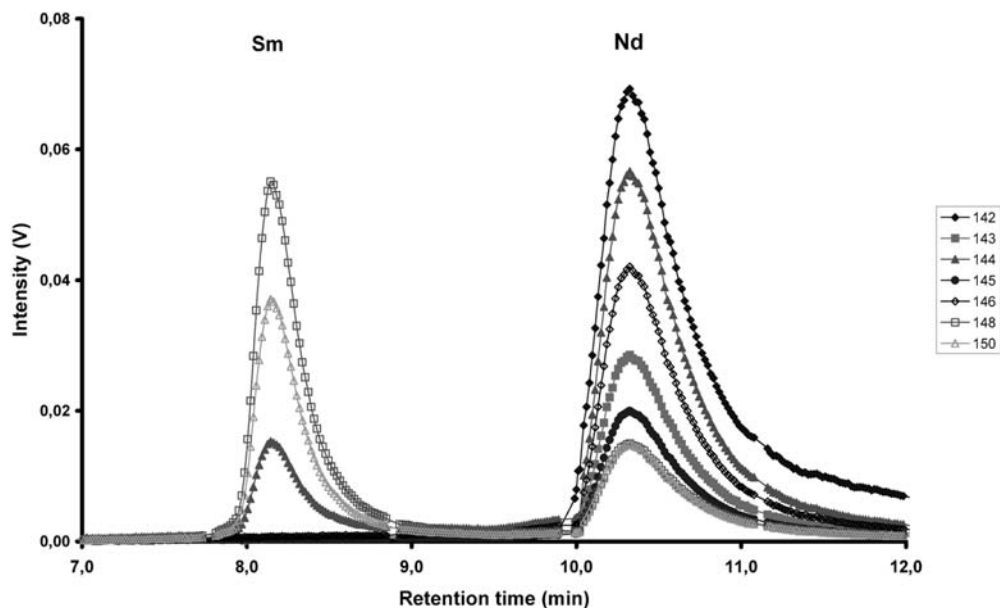
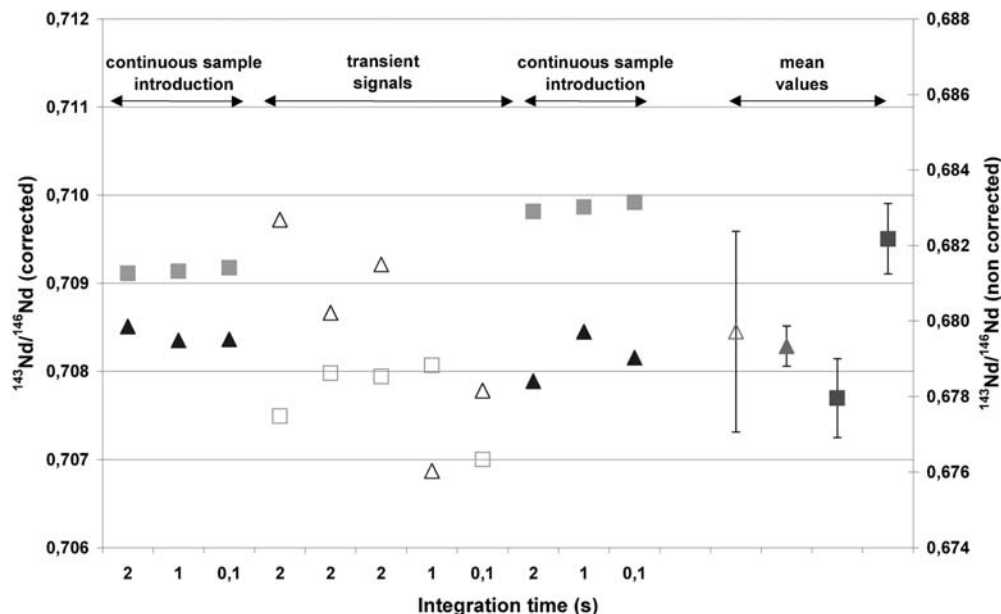


Fig. 2 Comparison of uncorrected (*squares*) and mass bias-corrected (*triangles*) $^{143}\text{Nd}/^{146}\text{Nd}$ isotope ratios for continuous (*filled symbols*) and HPLC (*open symbols*) sample introduction for 50 ng g^{-1} Nd in a multi-element standard solution. Determination of the external reproducibility (error bars of the mean values are 1 sigma). The integration time for the signals was changed according to Table 1 from 0.1 to 2 s



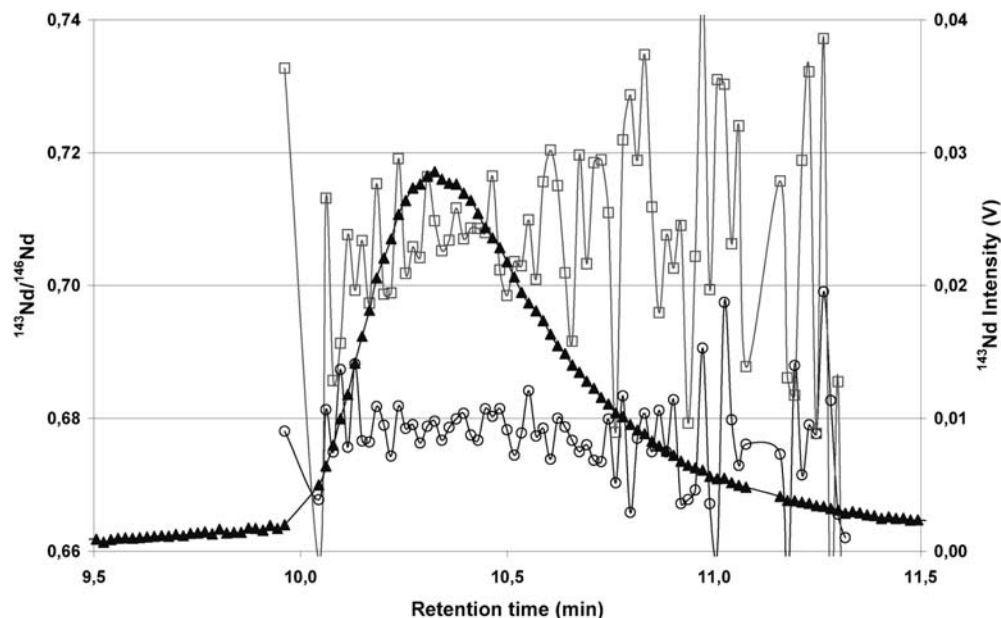
tions. Using thermal desorption for sample introduction of Hg a dry plasma was maintained, because the internal standard for correction of the mass fractionation (TI) was simultaneously introduced via a desolvating nebuliser [6]. For determination of Pb by GC–MC–ICP–MS [15] a TI standard solution was continuously aspirated into the plasma via a T-piece using a conventional Meinhard concentric nebuliser. Therefore, these measurements were carried out under wet plasma conditions as for the HPLC–MC–ICP–MS hyphenation described in the present paper.

A clear shift in the uncorrected isotope ratios is apparent in Fig. 2 when changing the sample introduction from continuous flow (filled squares) to HPLC injection (open squares) and vice versa. This can be explained in terms of matrix dependency of the mass discrimination. The matrix

for continuous sample introduction is about 5% HNO_3 , whereas the matrix for the neodymium separation by HPLC is a gradient of α -hydroxyisobutyric acid. However, due to the internal mass bias-correction by using the $^{145}\text{Nd}/^{146}\text{Nd}$ ratio for both approaches, the matrix dependency is compensated for the corrected ratios and the mean values for continuous sample introduction and HPLC injection coincide within the error bars.

Whenever no invariant or known isotope ratio for internal mass bias-correction can be used (as for nuclear fuels, because the isotopic composition of the elements depends on the respective burn-up) a bracketing procedure between samples and standard materials or a double-spike approach have to be applied. Because of the illustrated matrix dependency it is essential to inject the standards

Fig. 3 Uncorrected (circles) and mass bias-corrected (squares) $^{143}\text{Nd}/^{146}\text{Nd}$ isotope ratios across the transient signal of 50 ng g^{-1} Nd separated by HPLC. The elution of Nd from the chromatographic column is illustrated by the ^{143}Nd intensity (filled triangles). Integration time 1 s



also via the HPLC system and it is recommended not to switch between transient signals from the HPLC for samples and continuous sample introduction for standards.

Theoretically, external normalization to an isotope ratio of an admixed element would also be possible. This is a well-known procedure for the analysis of elements like Pb (admixing of Tl) [15] or Cu (admixing of Ni) [17]. However, in irradiated nuclear fuels most of the elements of the periodic table are already contained within the samples as fission and spallation products of unknown isotopic composition. Furthermore, for online-coupled HPLC-ICP-MS systems it would be necessary to add an element in the same mass range as the element to be analysed that shows similar chromatographic behaviour and elutes from the column material under identical conditions as the element to be determined. This would be only possible for HPLC separations under isocratic conditions (e.g. Cs/Ba or Rb/Sr can be separated using 1 mol L^{-1} HNO_3 without any gradient) and is no alternative for the presented separations of U and Nd.

Figure 3 shows the uncorrected and corrected $^{143}\text{Nd}/^{146}\text{Nd}$ isotope ratio against time and intensity of the neodymium transient signal for the same chromatographic separation as shown in Fig. 1. According to counting statistics the isotope ratios around the peak top (highest signal-to-noise-ratio) show the lowest point-to-point fluctuations. Generally, the lower the intensities on both edges of the transient peak the higher the variations of the isotope ratio. Due to the internal mass bias-correction with a second isotope ratio ($^{145}\text{Nd}/^{146}\text{Nd}$) the fluctuations of the corrected $^{143}\text{Nd}/^{146}\text{Nd}$ ratio are strengthened compared to the uncorrected ratio. However, no systematic trend for “isotope fractionation” on the chromatographic column can be observed for neodymium in that low concentration range with signal intensities lower than 100 mV for each isotope.

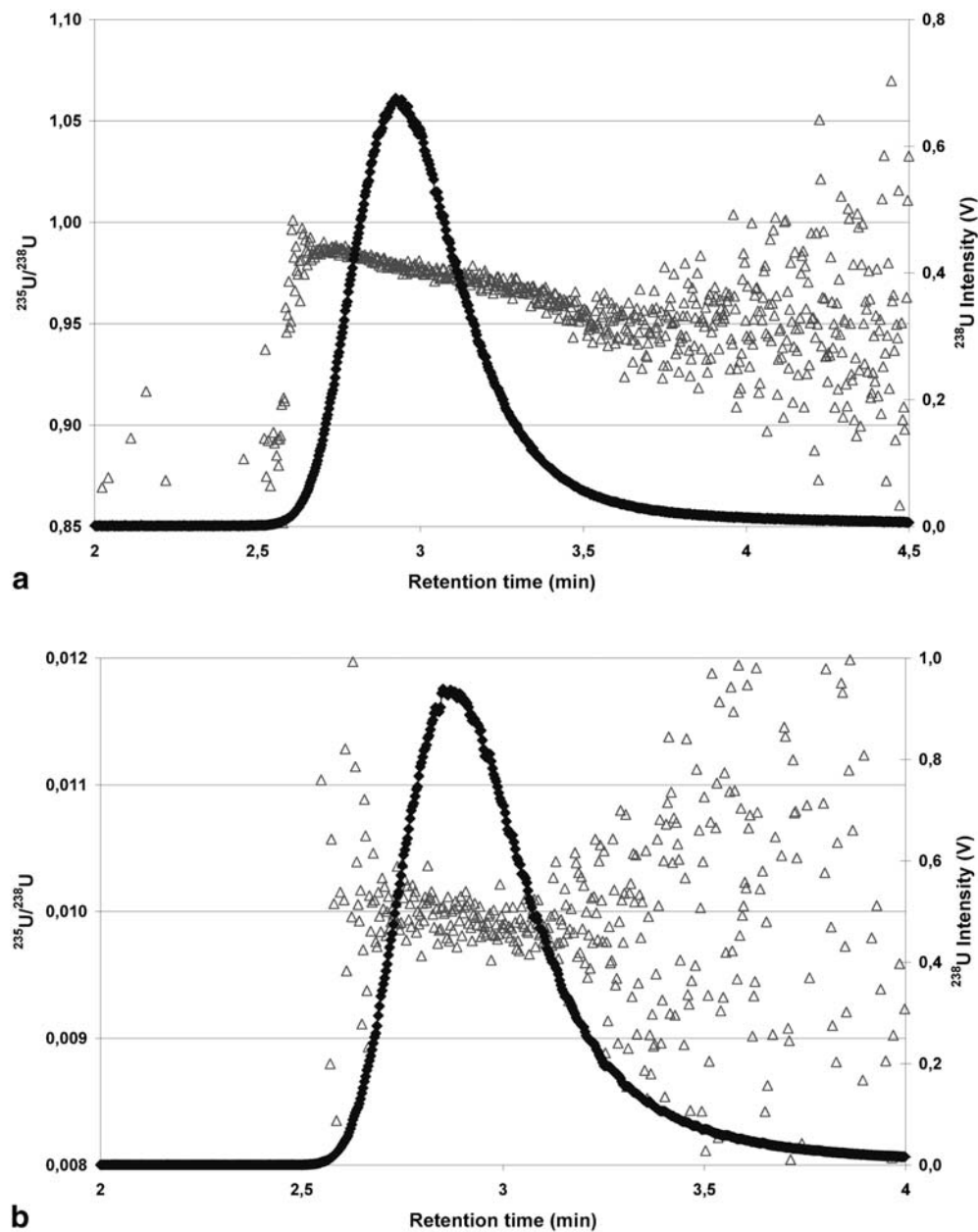
Measurement of the U isotopic composition on transient signals

A more extensive study was carried out for uranium. The elemental concentrations and the isotopic composition of the standard solutions were changed over a broad range. Typical transient signals for uranium standards (NIST-SRM-500 and -010) are shown in Fig. 4. The chromatographic method was developed for nuclear samples, in which separation of the interfering elements uranium and plutonium is necessary [14]. Since no plutonium is present in the NIST uranium standard materials only one peak with a signal length of about 60 s elutes from the chromatographic column. Figure 4a shows the uncorrected $^{235}\text{U}/^{238}\text{U}$ isotope ratio as a function of retention time for a 100 ng g^{-1} NIST-SRM U-500 standard solution. This isotope ratio is characterised by a nearly linear decrease across the entire transient (slope -0.038 ± 0.001). In order to keep the concentration of the uranium standard solution constant but to reduce the isotope ratio by a factor of about one hundred, 100 ng g^{-1} NIST-SRM U-010 standard solutions were also analysed. The results of these measurements are illustrated in Fig. 4b. In contrast with the U-500 standard the $^{235}\text{U}/^{238}\text{U}$ ratio is nearly constant for the entire transient signal (slope -0.0003 ± 0.0001).

In principal, there are two possible explanations of ratio instabilities:

1. the influence of the chromatographic system, i.e. “isotope fractionation” on the chromatographic resin (different retention behaviour of light and heavy isotopes); or
2. stabilisation effects of the plasma or the mass spectrometer (effects of variable analyte density in the plasma, space charge effects, different volatilisation efficiencies, etc.).

Fig. 4 Uncorrected $^{235}\text{U}/^{238}\text{U}$ isotope ratios (*open triangles*) across the transient signal of (a) a 100 ng g^{-1} NBS-SRM U-500 standard solution, and (b) a 100 ng g^{-1} NBS-SRM U-010 standard solution separated by HPLC. The elution of U from the chromatographic column is illustrated by the ^{238}U intensity (*filled diamonds*) versus retention time. Integration time 0.1 s



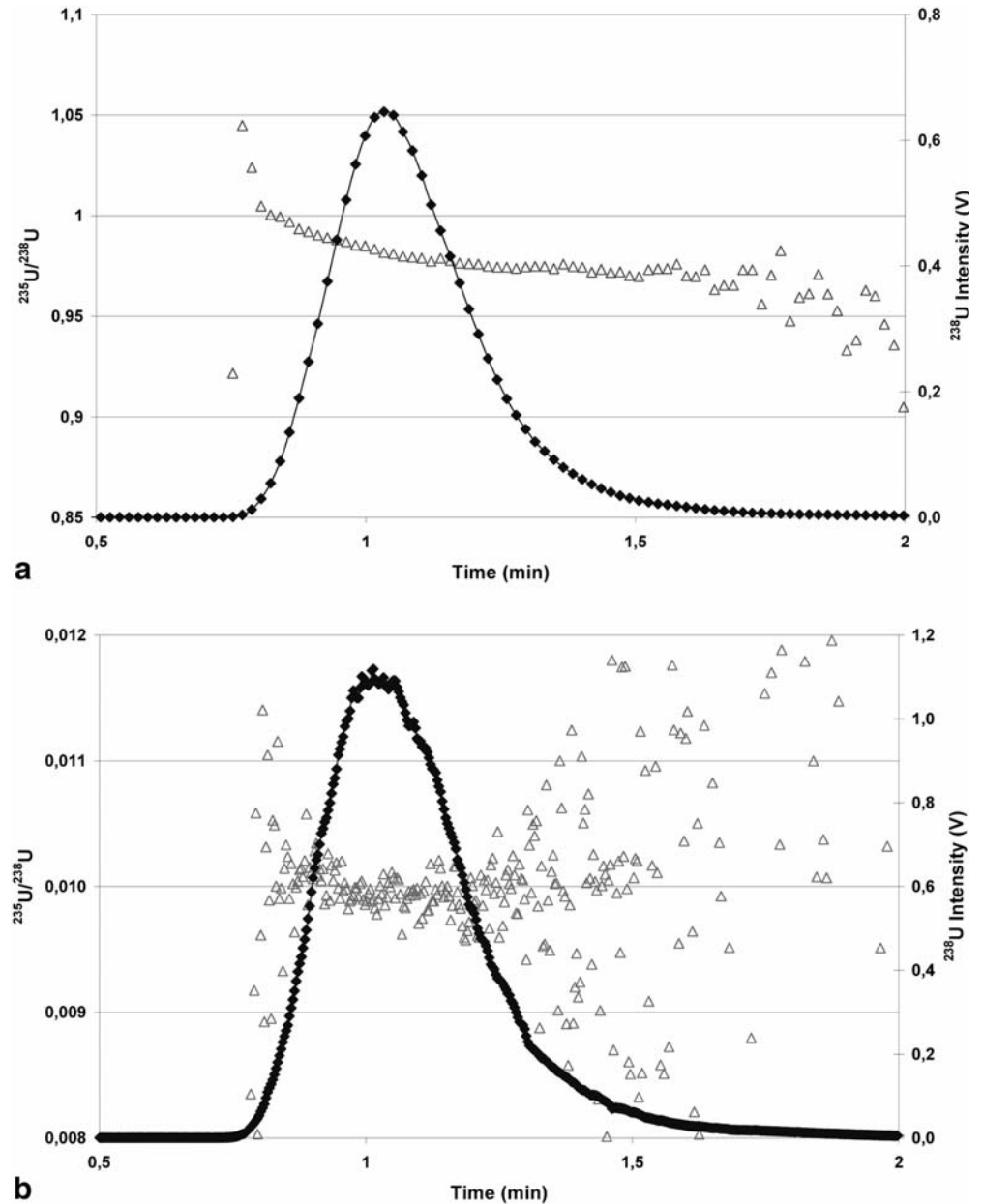
In order to get some indications for one of these hypotheses a comparative study between transient signals from an HPLC system and transient signals for the same standard solutions after flow injection (no chromatographic column) was carried out. The intention of using standard solutions instead of real samples was to create a very simple experimental system where only effects of the chromatographic column material and signal intensities can be investigated and complex matrix effects can be excluded.

Comparison of the $^{235}\text{U}/^{238}\text{U}$ isotope ratios for transient signals of 100 ng g^{-1} NIST-SRM U-500 and U-010 standards after flow injection (Figs. 5a and 5b) with the corresponding transient signals from HPLC injections (Figs. 4a and 4b) shows exactly the same signal structure – a nearly linear decrease of the ratio over time for the U-500 standard (slope -0.033 ± 0.003 for flow injection vs. $-0.038 \pm$

0.001 for HPLC) and an almost constant ratio for U-010 (slope -0.0007 ± 0.0001 for flow injection vs. -0.0003 ± 0.0001 for HPLC).

The similar behaviour of the uranium isotope ratio transient signals with (HPLC) or without (flow injection) column separation excludes the possibility that “isotope fractionation” on the chromatographic resin is responsible for the significant ratio drift over time, as seen for the U-500 standard in the investigated concentration range. Before a final conclusion can be drawn about whether the signal structures of the ratios are based on stabilization/volatilisation effects inside the plasma (these effects would favour the transmission of lighter isotopes into the mass spectrometer) and whether these effects are combined with space-charge effects in the region of the skimmer cone, which would favour the transmission of the heavier

Fig. 5 Uncorrected $^{235}\text{U}/^{238}\text{U}$ isotope ratios (*open triangles*) across the transient signal of: (a) a 100 ng g^{-1} NBS-SRM U-500 standard solution (integration time 1 s), and (b) a 100 ng g^{-1} NBS-SRM U-010 standard solution (integration time 0.1 s) with flow injection as sample introduction method. The profile of the transient signal of U is illustrated by the ^{238}U intensity (*filled diamonds*) versus time



isotopes, more detailed and systematic investigations are necessary. Encinar et al. [18] evaluated a quadrupole-based ICP-MS, a double-focusing single-collector ICP-MS, and a single-focusing multicollector ICP-MS for lead isotope ratio measurements on steady-state signals and discovered that the mass-bias factors for the three instruments were very similar, whereas the ion lens and the mass spectrometer configurations were very different. This indicates that the main source of mass bias is in the plasma or the extraction interface.

A similar study of isotope fractionation when a laser-ablation sampling system was coupled with MC-ICP-MS suggested that the dominant source of isotope fractionation for larger particle sizes was the inability of the ICP to completely vaporise, atomise, and ionise all particles, rather than laser-induced isotopic fractionation at the sam-

pling site, which can occur when the laser energy is insufficient for ablation [17].

In principle it cannot be excluded that “isotope fractionation” occurs on the chromatographic resin used to a much lesser extent than observed in this study. However, these smaller fractionation effects (probably in the range of few ppm) are only detectable by using a fraction collector in order to split the chromatographic peak into several sub-samples and analysing the isotope composition of these fractions by continuous sample introduction MC-ICP-MS with the highest achievable precision.

Dry plasma conditions (gaseous samples)

For comparison of isotope ratios on transient signals without any chromatographic separation under wet (flow in-

Fig. 6 Uncorrected $^{132}\text{Xe}/^{136}\text{Xe}$ isotope ratios (*open triangles*) across the transient signal for injection of 0.075 cm^3 Xe into the nebulizer gas stream (*filled diamonds* illustrate the signal intensity of ^{132}Xe). Integration time 1 s

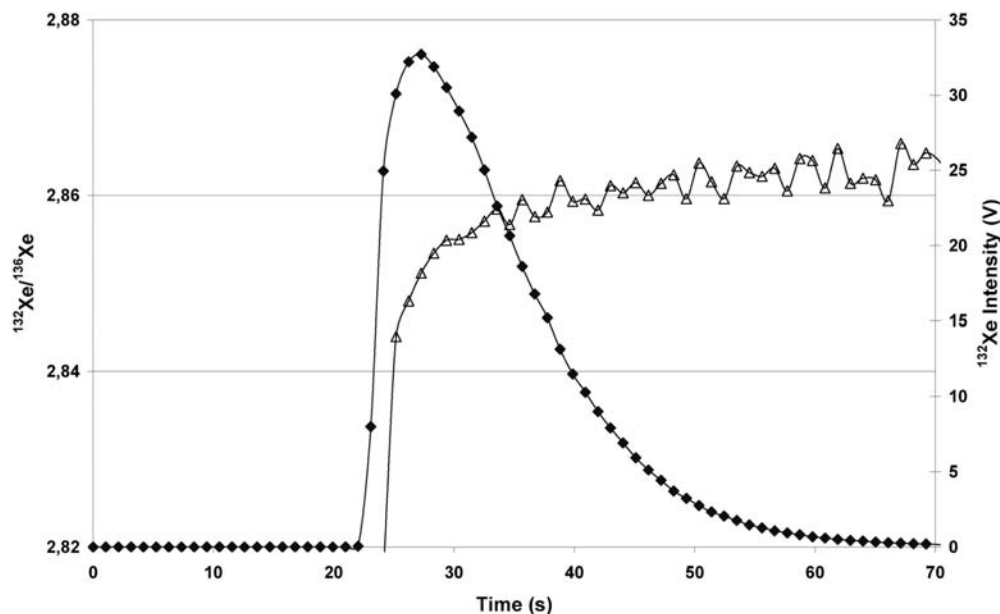
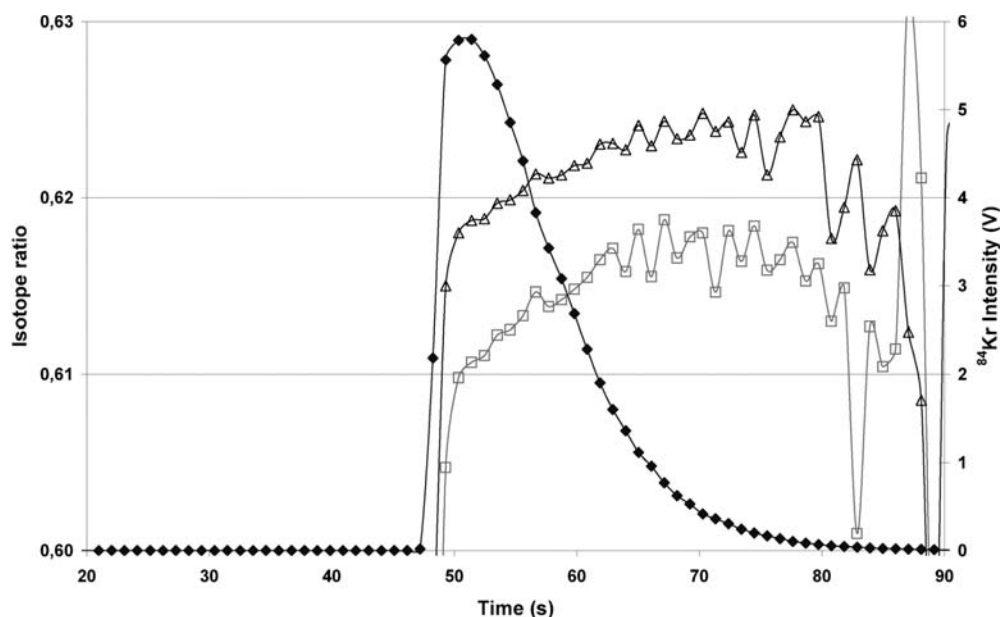


Fig. 7 Uncorrected $^{82}\text{Kr}/^{86}\text{Kr}$ (*open squares*) and $^{83}\text{Kr}/^{86}\text{Kr}$ (*open triangles*) isotope ratios across the transient signal for injection of 0.005 cm^3 Kr into the nebuliser gas stream (*filled diamonds* illustrate the signal intensity of ^{84}Kr). Integration time 1 s



jection) and dry plasma conditions, replicate injections of a gas mixture containing the noble gases Kr and Xe into the nebuliser gas flow were carried out. For these transient signals only the signal structure and the external precision of the isotope ratio measurements were investigated. Information concerning the accuracy of the results or the mass bias level cannot be given, because a well characterised isotope ratio applicable for internal correction of the mass discrimination is not known for the gas mixture used.

The reason for this preliminary gas study was the intended characterisation of fission gas inclusions in burned nuclear fuel pellets by laser ablation MC-ICP-MS. The major fission gases within nuclear fuels are Xe and Kr and the aim of the study was to determine the general possi-

bility of analysing these two gases and to evaluate the limits of detection for MC-ICP-MS under dry plasma conditions.

Typical transient signals for Xe and Kr are shown in Figs. 6 and 7, in which the signals last for about 30 s. The external reproducibility over 15 injections for the uncorrected isotope ratios was determined to be less than 0.2% (2 sigma). A clear drift of all Xe and Kr ratios is obvious. This increase of the ratios is nearly the same order of magnitude for both gases (positive slopes 0.00020 ± 0.00004 for Kr and 0.00027 ± 0.00003 for Xe), an opposite trend in comparison with the decrease of the isotope ratios across the transient signal observed for the HPLC and flow injection experiments.

In contrast with liquids, enhanced fractionation during sample transport favouring the lighter, more volatile iso-

topes could be expected for gaseous samples. However, the measurements of both gases show a reverse fractionation effect in which heavy isotopes were preferentially transmitted into the mass spectrometer. This finding is consistent with results described for thermal desorption [6], in which the fractionation was explained by differential, mass-dependent adsorption of the isotopes on the gold traps. Because adsorption effects should not play a role within the sample introduction device used for the present study, a clear explanation of this phenomenon cannot be given at the moment.

Conclusion

By online hyphenation of HPLC with MC-ICP-MS it is possible to separate interfering elements and to determine precisely the isotope composition of these elements in a single analysis step. Compared with the results from continuous sample introduction the external precision of transient signals is reduced by less than one order of magnitude.

A comparative study of transient signals from HPLC and flow injections for the same standard solutions clearly indicates that the significant isotope ratio drifts observed for the HPLC-MC-ICP-MS system are not caused by isotope fractionation within the chromatographic column material (at the level of measurement precision possible with this system). This result is an indication that the main source of this bias is in the ICP-MS. A general observation for all HPLC and flow-injection measurements can be postulated – the isotope ratio drift across the transient is less pronounced for lower absolute intensity or a smaller ratio. For transient signals of gaseous samples a reverse fractionation effect was observed; further investigations are needed to validate this.

All isotope-ratio measurements have to be corrected for instrumental mass bias by normalisation to an invariant isotope ratio of the same element (internal correction) or, whenever the internal approach cannot be applied, to a well characterised isotope standard material (external correction). However, the external correction method requires that the mass discrimination on an element is identical for the sample and the standard, which is not necessarily the case. A large benefit of the hyphenated HPLC-MC-ICP-MS system, beside the high sample throughput compared to classical offline separation methods, is that all measurements of standards and real samples can be carried out with exactly the same matrix – the eluent of the HPLC system.

When the precision of the hyphenated HPLC-MC-ICP-MS method is compared with that of other ICP-based

techniques and TIMS, it can be clearly stated that this approach is more powerful than any quadrupole-based method, which detects the ions sequentially. The external precision of short transient signals is reduced by less than a factor of 10 compared with continuous sample introduction MC-ICP-MS or TIMS and is therefore very close to the performance of sector field instruments for continuous isotope-ratio measurements. However, due to the benefit of simplified sample preparation the HPLC-MC-ICP-MS method is superior to sector-field techniques whenever interfering elements have to be separated before isotope ratio measurements, especially for samples, e.g. radioactive materials, that require special precaution during handling.

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