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Precise and accurate isotope ratio measurements by ICP-MS

Abstract The precise and accurate determination of isotope ratios by inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS (LA-ICP-MS) is important for quite different application fields (e.g. for isotope ratio measurements of stable isotopes in nature, especially for the investigation of isotope variation in nature or age dating, for determining isotope ratios of radiogenic elements in the nuclear industry, quality assurance of fuel material, for reprocessing plants, nuclear material accounting and radioactive waste control, for tracer experiments using stable isotopes or long-lived radionuclides in biological or medical studies). Thermal ionization mass spectrometry (TIMS), which used to be the dominant analytical technique for precise isotope ratio measurements, is being increasingly replaced for isotope ratio measurements by ICP-MS due to its excellent sensitivity, precision and good accuracy.

Instrumental progress in ICP-MS was achieved by the introduction of the collision cell interface in order to dissociate many disturbing argon-based molecular ions, thermalize the ions and neutralize the disturbing argon ions of plasma gas (Ar^+). The application of the collision cell in ICP-QMS results in a higher ion transmission, improved sensitivity and better precision of isotope ratio measurements compared to quadrupole ICP-MS without the collision cell [e.g., for $^{235}U/^{238}U$ ~1 (10 μg L^{-1} uranium) 0.07% relative standard deviation (RSD) vs. 0.2% RSD in short-term measurements (n = 5)]. A significant instrumental improvement for ICP-MS is the multicollector device (MC-ICP-MS) in order to obtain a better precision of isotope ratio measurements (with a precision of up to 0.002%, RSD).

CE- and HPLC-ICP-MS are used for the separation of isobaric interferences of long-lived radionuclides and stable isotopes by determination of spallation nuclide abundances in an irradiated tantalum target.

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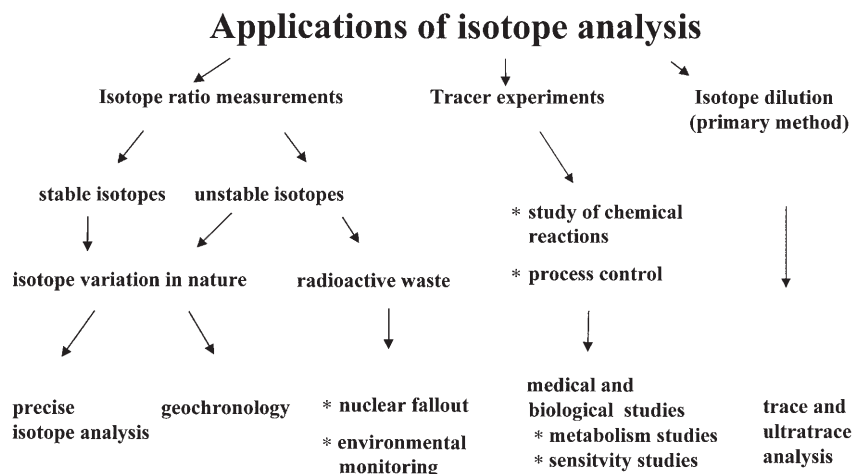
1 Introduction

Isotope ratio measurements are important in a number of different application fields, for example for the determination of stable isotopes and long-lived radionuclides by investigations of isotope variation in nature and geochronology [1–5], the quality assurance of fuel material, radioactive waste control or in environmental monitoring [6–10]. Furthermore, isotope ratio measurements are of interest for tracer experiments with the addition of high-enriched stable or unstable isotope spikes in biological and medical research [11–13], studies of chemical reactions, metabolism studies and in the isotope dilution technique as a primary method for the determination of element concentrations at the trace and ultratrace level [14]. Relevant fields of application in isotope ratio measurements are summarized in Fig. 1.

The main feature of different inorganic mass spectrometric techniques [such as TIMS – thermal ionization mass spectrometry, GDMS – glow discharge mass spectrometry, SSMS – spark source mass spectrometry, RIMS – resonance ionization mass spectrometry, SIMS – secondary ion mass spectrometry, ICP-MS – inductively coupled plasma mass spectrometry and LA-ICP-MS (LA – laser ablation) and others] is their capability to determine the isotope ratio [15–19]. In the last few decades TIMS has occupied a favored position for routine measurements and can be used for many elements with a relatively low ionization potential in the positive ion mode and some selected elements with high ionization potential in the negative ion mode [19]. In particular, TIMS with a multiple collector ion detection system has been established as the method of choice for high-precision isotope abundance ratio measurements. A relative external standard deviation (RESD; determined in long term measurements up to 24 h) for isotope ratio measurements down to 0.002% is reported [19]. At present, TIMS is being increasingly replaced for precise isotope ratio measurements by ICP-MS due to its excellent sensitivity, good accuracy and low standard deviations. In addition, ICP-MS has easier sam-

Applications of isotope analysis

Isotope ratio measurements   Tracer experiments   Isotope dilution (primary method)

stable isotopes   unstable isotopes

isotope variation in nature   radioactive waste

* study of chemical reactions
* process control

precise isotope analysis   geochronology

* nuclear fallout
* environmental monitoring

medical and biological studies
* metabolism studies
* sensitvity studies

trace and ultratrace analysis

ple preparation in terms of analyte separation and purification steps. Furthermore, ICP-MS, which is applicable for nearly all elements (TIMS is difficult for elements with high ionization potential), offers a significantly higher sample throughput, is less time-consuming, requires smaller sample sizes (down to the sub-pg range) and does not suffer from time-dependent mass discrimination effects.

2 The state of the art in isotope ratio measurements by ICP-MS

Among the inorganic mass spectrometric techniques, ICP-MS [20] has been established as an extremely efficient and sensitive analytical mass spectrometric technique for the multielement determination of elements in aqueous solutions and digested solid samples at the trace and ultratrace concentration level and it has successfully been applied for precise and accurate isotopic analysis. This is demonstrated by a rapid growth of ICP mass spectrometer installations world-wide, such as different types of quadrupole-based or double-focusing (DF) sector field instruments (e.g. from Hewlett Packard; Perkin Elmer, Sciex; VG Elemental; Micromass; Varian GmbH; Spectro; Seiko and Finnigan MAT) with single and multiple ion collection. The most common ICP mass spectrometers are quadrupole-based instruments (ICP-QMS) which allow isotope ratio measurements with a precision for short-term isotope ratio measurements from 0.1 to 0.5% relative standard deviation (RSD) [15, 21]. In long-term measurements by ICP-QMS an external precision of about 0.05%, e.g. for ^{107}Ag/^{109}Ag [22], ^{207}Pb/^{206}Pb [23] or for ^{235}U/^{238}U ~ 1 (RSD for n = 8; at U concentration of 10 μg L^{-1}), was obtained [21, 24].

An improvement of precision in short-term measurements is possible using double-focusing sector field ICP-MS (e.g. ELEMENT, from Finnigan MAT or Plasma-Trace from Micromass with reverse Nier-Johnson geometry) due to flat top peak shape at low mass resolution, significantly higher sensitivities and lower background down

to 0.1 cps, which results in an improvement of the signal-to-noise ratio compared to quadrupole-based instruments. The capability of double-focusing sector field ICP-MS (using ELEMENT, from Finnigan MAT) with single ion collector at low mass resolution for ^{25}Mg/^{24}Mg and ^{206}Pb/^{207}Pb isotope ratio measurements (at Mg and Pb concentrations of 5 mg L^{-1} and 100 μg L^{-1}, respectively) with an RSD of 0.04% (n = 10) and at medium resolution mode for ^{63}Cu/^{65}Cu (at a Cu concentration of 1 mg L^{-1}) with an RSD of 0.1% (n = 10) was demonstrated by Vanhaecke et al. [25, 26].

Isotope variations of the ^{11}B/^{10}B isotope ratio in surface and ground water using the DF-ICP-MS ELEMENT with a precision of 0.1–0.2% were measured by Gäbler and Bahr [27].

Becker and Dietze [28] determined for ^{235}U/^{238}U ~ 1 (at 1 μg L^{-1} uranium) a short-term precision of down to 0.026% RSD (n = 5) by double-focusing sector field ICP-MS (ELEMENT, Finnigan MAT). The high precision in double-focusing sector field ICP-MS was achieved by the application of the shielded torch, which was introduced in quadrupole-based ICP-MS in combination with the cool plasma technique in order to decrease molecular ion formation. With the shielded torch a grounded platinum electrode is inserted between the quartz ICP torch and rf load coil in order to eliminate the secondary discharge between the inductively coupled plasma and the sampling cone. The application of plasma shielding under hot plasma conditions in double-focusing sector field ICP-MS leads to an improvement of sensitivity and detection limits, e.g., the detection limit for ^{239}Pu was determined to be 0.3 pg L^{-1} (compared to 1.7 pg L^{-1} without a shielded torch) by application of a micronebulizer for solution introduction [28]. This excellent detection limit allows the isotope analysis of long-lived radionuclides down to the low pg L^{-1} concentration range using a micronebulizer and down to the sub pg L^{-1} range using an ultrasonic nebulizer. E.g., for the isotope ratio measurements of a ^{230}Th/^{232}Th isotope ratio of 10^{-3} (at 1 μg L^{-1} Th concentration) the precision was 0.6% RSD in quadrupole-based ICP-MS, but in DF-ICP-MS it was twice as good at 0.3% RSD (at

5 ng L^{-1} Th concentration only) [28]. Highly sensitive and precise isotope ratio measurements of Pu, Th and U at the ultratrace level were performed in DF-ICP-MS at low mass resolution [R (m/Δm) = 300]. The precision of Pu isotope ratio measurements in ICP-QMS (Elan 6000, Perkin Elmer, Sciex) at 12 ng L^{-1} using the direct injection high efficiency nebulizer (DIHEN from Meinhard Associates) [29] for solution introduction was 4% and in DF-ICP-MS at the 5 ng L^{-1} level a precision of 0.3% was measured [28]. DF-ICP-MS allows an isotope analysis of Pu at the 10 pg L^{-1} level with sufficient accuracy and precision [28].

In general, the application of double-focusing sector field ICP-MS for isotope ratio measurements at higher mass resolution – which is required for isotopes at given masses that are disturbed by isobaric interferences with molecular ions – results in a decrease of precision due to a significant loss in ion intensity. The precision of isotope ratio measurements at higher mass resolution even at higher element concentrations (up to mg L^{-1}) is always lower than with measurements at low mass resolution in the ultratrace concentration range because flat top peaks are not obtained. This is demonstrated for the ^{42}Ca/^{44}Ca, ^{25}Mg/^{24}Mg and ^{41}K/^{39}K isotope ratio measurements for tracer experiments in biological samples (RSD = 0.4%–0.7% at 50–100 μg L^{-1}) at mass resolution R (m/Δm) of 3000 (for Mg and Ca) and R of 9000 (for K), respectively [11]. Further application of double-focusing sector field ICP-MS for difficult-to-analyse elements at higher mass resolution results [R(m/Δm) = 4000] have been described for isotope ratio measurements ^{42}Ca/^{44}Ca in urine (RSD 0.4% at Ca concentration of 100 mg L^{-1} using the PlasmaTrace 2, Micromass) [30] and ^{34}S/^{32}S in high-purity standard solution (RSD 0.1% at a sulfur concentration of 1 ng g^{-1} using the ELEMENT with a plasma-shielded torch, Finnigan MAT) [31]. The application of precise isotope ratio measurements for the accurate determination of Fe, Co and Zn in human serum by the isotope dilution technique with high-enriched ^{57}Fe, ^{65}Cu and ^{67}Zn isotopes by double-focusing sector field ICP-MS (ELEMENT, Finnigan MAT) is described by Sanz-Mendel and co-workers [14]. The RSD values obtained for the isotope ratios of ^{57}Fe/^{56}Fe, ^{65}Cu/^{63}Cu and ^{67}Zn/^{64}Zn were 0.7%, 0.2% and 0.8%, respectively, for a natural standard aqueous solution with analyte concentration of 50 μg L^{-1}.

Recently, a TOF-ICP-MS (Renaissance, LECO) with an ion reflection system has become available on the analytical market for a faster analysis than quadrupole ICP-MS allowing measurements of about 20 000 spectra per second. This property is advantageous for the application of coupling techniques such as HPLC-, CE- or LA-ICP-MS and for speciation analysis. In isotope ratio measurements precision for short-term measurements of down to 0.05% has been reported by different groups [33, 34].

3 Limits for precise and accurate isotope ratio measurements

An important limit for precise and accurate isotope ratio measurements in ICP-MS is the mass discrimination of ions due to the space-charge effect. This effect can be explained as follows. If the positively charged ions which were formed in the inductively coupled plasma leave the skimmer cone, the Coulomb repulsion of charged ions results in a loss of transmission through the ion optical lens system, because the light ions are deflected more than the heavy ones. Space-charge effects in the interface and ion optics region are described in detail by Douglas and Tanner [35]. In general, the mass discrimination (mass bias) is considered using the mass discrimination factor – this is the ratio of the true and measured isotope ratio – for the correction of measured isotope ratios. The mass discrimination factor can be determined using an isotope reference material with certified isotope ratio or where no isotope reference material exists, high-enriched isotope spikes are useful for the determination of the specific mass discrimination factor. Furthermore, for elements where no variation in isotope abundances are expected any standard for calibration can be used for the determination of mass discrimination factor. The mass discrimination per mass unit determined in quadrupole ICP-MS for Elan 5000 measured by Heumann et al. [15] and the Platform ICP-MS with a hexapole collision cell measured in our laboratory[1] are comparable as demonstrated in Fig. 2. For isotope ratios at low masses a mass discrimination higher than 10% was observed. The mass discrimination decreases with increasing mass of isotopes. No significant difference in mass discrimination effects was observed for quadrupole ICP-MS with and without a collision cell.

More details of the influence of different effects (mass discrimination, space charge, interferences, stability of
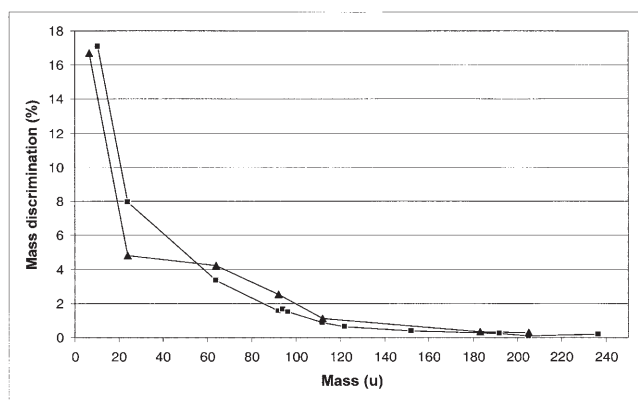

Fig. 2 Mass discrimination per mass unit in ICP-QMS. —■— Platform ICP-MS; —▲— Elan 5000 [1] (rf power 1350 W, nebulizer gas 0.86 L min^{-1}; collision gas: He – 4 ml min^{-1}; H$_2$ – 1.5 min min^{-1}, hexapole bias 0 V)[1]

ion current) on the accuracy and precision of isotope ratio measurements in plasma source mass spectrometry were discussed by Heumann et al. [15].

Further limitations on the determination of isotope ratios are also a low abundance sensitivity in ICP-MS and the dead time of the detector. The abundance sensitivity, which is the contribution of the neighboring peak to the intensity of a measured isotope, can influence the accuracy of isotope abundance measurements. For example, the determination of ^{239}Pu in the presence of a high uranium concentration is very difficult or even impossible with the low abundance sensitivity of ICP-MS. Therefore, the chemical separation of analytes (e.g. U and Pu) is helpful before mass spectrometric measurements. Because in ICP-MS mostly channel electron multiplier and pulse counting systems are used, the dead time of the detector (for counting rates higher than 10^6 cps) is the reason why a lower number of counts are registered than actually occur. Especially, if extreme isotope ratios are to be measured the dead time correction of the detector is necessary to obtain accurate isotope ratio results.

One of the serious problems in ICP mass spectrometry is that a multitude of different isobaric interferences with analyte ions can occur. For the separation of isobaric interferences of atomic ions [e.g., ^{40}Ca$^+$ and ^{40}Ar$^+$: R(m/Δm) $\approx$ 192 000] high-resolution Fourier transform ion cyclotron resonance mass spectrometers are required, the isobaric interferences of singly-charged atomic ions with double-charged atomic ions [e.g., ^{69}Ga$^+$ and ^{138}Ba^{2+}: R(m/Δm) $\approx$ 2550] and a large number of molecular ions [e.g., ^{80}Se$^+$ and ^{40}Ar$_2$$^+$: R(m/$\Delta$m) $\approx$ 9 500] can often be separated using double-focusing sector field ICP-MS with a maximum mass resolution of 12 000. However, the application of mass spectrometers at high mass resolution yields a significant loss of intensity of analyte ions and an increase of detection limits. Therefore, another possibility to solve the interference problem with disturbing molecular ions, for some analytical applications, is the use of collision cells in ICP-MS.

4 Progress in instrumentation and isotope ratio measurements

The application of the collision cell – which is an old, well-known principle in organic mass spectrometry for controlled collision-induced fragmentation of organic molecules in structure analysis – in inorganic mass spectrometers represents important progress in ICP-MS instrumentation which is relevant for improving the precise determination of isotope ratios. Initial experiments to reduce the molecular ion interferences in ICP-MS were described by Douglas [37]. The collision cell was introduced in ICP-MS by the company Micromass Ltd (Manchester, UK) using a hexapole collision cell (Platform-ICP-MS) to thermalize the ions and to dissociate disturbing molecular ions [38]. The hexapole collision cell – which works as an ion optical lens system – is inserted between the interface and the quadrupole mass analyzer. There is no photon stop

in the Platform instrument. In order to reduce the background in mass spectra by photons from the ICP, the hexapole is mounted off-axis in the collision cell chamber. In the collision cell, collision-induced reactions such as charge transfer and proton transfer reactions take place, causing the dissociation of some argon molecular ions (in particular the argon based molecular ions such as ArO$^+$, ArC$^+$, ArN$^+$, ArH$^+$ and Ar$_2$$^+$ and others) by reaction with H$_2$, and the neutralization of Ar$^+$. Furthermore, a reduction in ion energy spread results in improved ion transmission efficiency, sensitivity of elements and precision in the determination of isotope ratios.

The first application in isotope ratio measurements yielded a precision of 0.086% RSD for ^{206}Pb/^{208}Pb (at 10 μg L^{-1} Pb) [39] and 0.3% RSD for ^{34}S/^{32}S (at 10 –50 mg L^{-1} S) [40]. With Platform ICP-MS using a mixture of hydrogen and helium as the reaction gas a significant increase in ion intensity was observed, for example, a maximum sensitivity of ≈12 500 MHz /ppm for ^{238}U was measured in our laboratory using the Platform ICP-MS with an ultrasonic nebulizer (USN) for solution introduction [36]. This sensitivity achieved with the platform ICP-MS and USN is comparable to the sensitivity of DF-ICP-MS with shielded torch. In contrast, the sensitivity of Platform ICP-MS with a commercial Meinhard nebulizer for ^{238}U was 400 MHz /ppm. Isotope ratio measurements of 10 μg L^{-1} uranium by collision cell ICP-MS using the Platform ICP-MS (see Table 1) and a commercial Meinhard nebulizer for solution introduction yielded a short-term precision of 0.07% RSD (n = 5) and a mass discrimination of 0.42% for the ^{235}U/^{238}U isotope ratio.

Perkin Elmer developed the ICP-MS Elan 6100 DRC with a quadrupole collision cell (on the basis of the Elan 6000) which is inserted between the ion optic lens system and the quadrupole-based analyzer. NH$_3$, CH$_4$, H$_2$ and He were successfully used as the collision gas for different applications, e.g. in microelectronics [41–47]. The application of the dynamic reaction cell results in an improvement of the precision of isotope ratio measurements as demonstrated by Bandura and Tanner [44]. The lead isotope ratios for NIST 981 standard reference material using quadrupole ICP-MS with the collision cell Elan 6100 DCR were determined with short-term precision for the ^{208}Pb/^{207}Pb ratio of 0.05% and the external precision was 0.03% (at 40 μg L^{-1} Pb). VG Elemental has introduced a quadrupole ICP-MS on the basis of PlasmaQuad

Table 1 Uranium isotope ratios by collision cell ICP-QMS ("Platform" quadrupole ICP-MS with hexapole collision cell, Micromass)

^{234}U/^{238}U	RSD (%)	^{235}U/^{238}U	RSD (%)	^{236}U/^{238}U	RSD (%)
0.00638	1.5	0.9967	0.16	0.00219	0.8
0.00629	0.8	0.9954	0.20	0.00219	1.2
0.00620	1.0	0.9951	0.17	0.00213	1.2
0.00611	1.0	0.9953	0.09	0.00208	1.1
0.00597	1.9	0.9959	0.23	0.00202	2.3
0.00619	**2.6**	**0.9957**	**0.07**	**0.00212**	**3.5**

Table 2 Isotope ratio measurements by different ICP-MS methods

Isotope ratio	Method	Precision	Sample size	Reference
^{235}U/^{238}U~1	ICP-QMS	0.028%[a]	255 pg	Platzner et al. [24]
^{207}Pb/^{206}Pb~0.9	DRC-ICP-QMS	0.057% 0.027%[a]	440 ng 5.1 μg	Bandura and Tanner [44]
^{235}U/^{238}U~1	DF-ICP-MS	0.026% 0.2%	255 pg 0.5 pg	Becker and Dietze [28]
^{34}S/^{32}S~0.05	Hex-ICP-QMS	0.03%	50–250 μg	Mason et al. [40]
^{137}Ba/^{138}Ba	TOF-ICP-QMS	0.05%	250 ng	Vanhaecke et al. [34]
^{208}Pb/^{206}Pb	MC-ICP-MS	0.006%	100 mg	Rehkämper and Halliday [52]
^{182}W/^{183}W~2	MC-ICP-MS	0.006%	0.5–1 μg	Lee and Halliday [50]
^{63}Cu/^{65}Cu	MC-ICP-MS	0.002%	100 ng	Maréchal et al. [54]

[a] long term precision

3 with a hexapole collision cell PQ EXCELL [48] and a special ion optical lens system in order to reduce the background noise to 0.1 cps. Np determination with pre-concentration of analyte with a detection limit in the sub-pg L^{-1} range and the determination of Pu isotope ratios at the ultratrace level in soil samples after Pu separation was reported by Liezers et al. [48].

Furthermore, collision induced reactions in a collision cell were applied in an ion trap ICP-MS in order to dissociate disturbing molecular ions as demonstrated by Koppenaal and co-workers [49]. The developed plasma source ion trap mass spectrometer with a collision cell allows a significant reduction of many of the molecular ions in ICP-MS. Precise isotope ratio measurements in ICP-MS with the ion trap were reported with a precision of up to 0.06% RSD.

Important progress in the instrumental improvement of ICP-MS in order to obtain a better precision of isotope ratio measurements was achieved by the introduction of the multi-ion collector device. Using double-focusing sector field ICP-MS with multiple ion collector, for example the Plasma 54 [50–55] with nine Faraday cups and the Axiom from VG Elemental, a precision of down to 0.002% was achieved in isotope ratio analysis but the concentration of analyte in the mg L^{-1} concentration range was significantly higher compared to ICP-MS with ion counting detector.

The first multiple collector sector field ICP-MS with a hexapole collision cell available on the analytical market is the IsoProbe from Micromass [56]. The collision cell is used mainly for the thermalization of ions from eV down to 0.1 eV and make the energy distribution of extracted ions more narrow. Therefore, in this instrument just a single magnetic sector field is sufficient for the mass/ charge separation of ions. Ten Faraday channels are arranged for simultaneous multi-ion collection. High-precision isotope ratio measurements using the Faraday cups were performed, mostly at the 1 mg L^{-1} level. In a special arrangement, but in a more expensive sector field ICP-MS, eight ion counting channels can be used for precise isotope ratio measurement at the ultratrace level. The application of the hexapole collision cell, which works effectively with a hydrogen / helium gas mixture, is used for the thermalization of ions and for the dissociation of argon-based molecular ions [56]. So far, a precision for the determination of the ^{82}Se/^{80}Se isotope ratio of 0.0015% has been achieved.

By collision-induced reactions in the hexapole cell, the Ar$^+$ ion intensity was reduced by some orders of magnitude using the neutralization reaction. This allows the determination of ^{40}Ca by ICP-MS. Using the multi-ion collector IsoProbe ICP-MS with a collision cell, the ^{42}Ca/^{40}Ca isotope ratio of 0.0067 was determined with a precision of 0.009% RSD (at 1 mg L^{-1} Ca) in aqueous solution. ^{6}Li/^{7}Li and ^{11}B/^{10}B isotope ratios were measured at the 0.5 mg L^{-1} and 1 mg L^{-1} concentration level as 0.027% RSD and 0.008% RSD, respectively. This precision of isotope ratios in MC-ICP-MS is comparable to those of TIMS [56, 57].

Recently, Finnigan MAT constructed a multiple ion collector, ICP-MS NEPTUNE, on the basis of a double-focusing sector field with Nier-Johnson geometry [58]. Eight Faraday cups are interchangeable with ion counting detectors in order to measure isotope ratios at very low concentration levels. In contrast to the DF-ICP-MS with single ion collector (ELEMENT from Finnigan MAT), flat-top peaks were observed at a mass resolution of R(m/Δm) = 4000, which are important for the precise determination of isotope ratios.

Table 2 compares the different ICP mass spectrometric techniques with respect to their precision and sample size. The best precision was observed by isotope ratio measurements with MC-ICP-MS. For example, Lee and Halliday [50] determined the ^{182}W/^{183}W isotope ratio in aqueous solutions by MC-ICP-MS with a precision of 0.006% RSD. Whereas MC-ICP-MS with Faraday cups requires relatively high sample amount, the use of channel electron multipliers in ICP-MS allows the measurements of low ion currents and thus a reduction of the amount of analyte down to the sub-pg range is possible as demonstrated by investigations using the sensitive double-focusing sector field ICP-MS.

5 Selected applications

Determination of Mg isotope ratios for tracer experiments in plants and application of isotope dilution

Interesting research topics at the Research Centre Jülich are investigations on the distribution and transport of mineral elements in plants. In order to explain the mechanism of

Table 3 Results of Mg isotope analysis in tracer experiments and determination of Mg concentrations by reverse isotope dilution technique

Sample	Isotope ratios		Concentration (µg/g)	
	$^{25}Mg/^{24}Mg$	$^{26}Mg/^{24}Mg$	ICP-MS	ICP-OES
	Trace experiments			
1	0.290 ± 0.001	19.92 ± 0.04	13.4 ± 0.5	12.3 ± 0.6
2	0.203 ± 0.001	7.84 ± 0.03	19.3 ± 0.6	17.8 ± 0.9
3	0.517 ± 0.002	40.40 ± 0.18	14.9 ± 0.5	13.8 ± 0.7
	NIST 980 (natural Mg)			
certified	0.1266 ± 0.001	0.1393 ± 0.0003		

mineral element uptake and transport in plants tracer experiments were performed using highly enriched stable isotopes of Mg, K and Ca. Whereas the lateral element distribution in parts of the plant was measured by secondary ion mass spectrometry (SIMS), ICP-MS is useful for the precise determination of the isotope ratios of these elements [11].

For Mg isotope ratio measurements on small samples of biological material (e.g. nutrient solution doped with enriched ^{26}Mg) an analytical procedure was developed using the quadrupole ICP-MS (Elan 6000, Perkin Elmer, Sciex) with micronebulization [59]. The mass bias was determined using the magnesium isotope standard NIST 980, and the accuracy of the isotope ratio measurements was checked on a sample with natural Mg isotope abundances. In Table 3 the results of isotope ratio measurements of Mg are summarized. A precision of 0.4–2 % at the 1 µg L^{-1} concentration level was obtained in these routine short-term measurements in nutrient solution in presence of high Ca and K concentrations.

For the determination of magnesium concentration in ^{26}Mg-spiked nutrient solution the reverse isotope ratio dilution was applied, that means Mg with natural isotope composition (we used the magnesium isotope standard reference material NIST 980) and known concentration was added to the sample for quantification purposes. Details of the analytical procedure are discussed by Dombovári et al. [59]. Considering the small sample volume available (< 1 mL) the measured Mg concentrations measured by reverse isotope analysis are in agreement with the ICP-OES values.

Application of flow injection for isotope ratio measurements of small sample volumes

Microanalytical techniques such as µ-FI-ICP-MS (µ-FI microflow injection) is of special interest in radioactive waste and environmental research where very small sample volumes have to be characterized. In order to inject small sample volumes (> 1 µL) of aqueous solution in a continuous flow of 2% nitric acid a HPLC injection valve was coupled to the microconcentric nebulizer for small droplet formation. The application of µ-FI-ICP-MS using

a quadrupole based instrument for the Th determination in aqueous solution by isotope dilution techniques was described in [24]. The ^{232}Th (in 2% nitric acid continuous flow) solution was spiked with 20 µL of a 4 µg L^{-1} ^{230}Th solution and the ^{232}Th concentration can be calculated using the known formula for isotope dilution analysis.

Furthermore, µ-FI-ICP-MS was applied for Cr determination in DNA by isotope dilution technique [18]. For the separation of isobaric interference of $^{52}Cr^+$ and $^{40}Ar^{12}C^+$ the measurements using a double-focusing sector field ICP-MS were performed at a mass resolution of R(m/Δm) = 3000. Mass spectrometric measurement at this mass resolution is connected with a loss in sensitivity of about one order of magnitude compared to measurement at low mass resolution (R = 300). Ten repetitions of solution injection (20 µl sample loop, Cr concentration 10 µg L^{-1}) yielded a precision of 1.3% RSD. This good precision is a precondition for the application of flow injection in isotope dilution analysis. The use of isotope dilution combined with flow injection is demonstrated by the determination of Cr in DNA. Due to the small DNA volume available the diluted sample (1:10) is injected using the µ-flow injection principle (20 µL of sample solution was injected in a continuous flow of 2% HNO$_3$ which is spiked with high-enriched ^{53}Cr (^{53}Cr isotope abundance – 84.3%; 1 µg L^{-1} Cr)) and the Cr concentration was determined as demonstrated in [18].

Isotope ratio measurements of uranium in Chernobyl samples by ICP-MS

The determination of accurate uranium isotope ratios in environmental samples is important in order to determine the fallout due to the nuclear accident in the Chernobyl nuclear power plant in 1986. The isotope analysis of uranium in soil samples from the Chernobyl area was performed in our laboratory after digestion of the soil samples and uranium separation by liquid-liquid extraction. The measurements were performed by DF-ICP-MS (ELEMENT, Finnigan MAT) using the micronebulizer for solution introduction. Details of the analytical procedure are described in a previous paper [21]. The mass bias for isotope ratios of uranium was determined and the analytical method was checked on the isotope standard reference material CCLU-500 ($^{235}U/^{238}U = 0.99991$). The results of isotope ratio measurements of uranium in soil samples from the Chernobyl area for different depths are summarized in Table 4. In all soil samples from the Chernobyl

Table 4 Distribution of $^{235}U/^{238}U$ and $^{236}U/^{238}U$ ratios over the soil depth in the Chernobyl vicinity

Depth	$^{235}U/^{238}U$	RSD (%)	$^{236}U/^{238}U$	RSD (%)
0– 5 cm	0.01006	2.9	0.000959	7.2
5–10 cm	0.00869	3.6	0.000545	8.6
10–15 cm	0.00776	3.8	0.000229	9.6
15–20 cm	0.00725	11	0.000035	32

Fig. 3 Part of the ICP mass spectrum of lanthanides with natural isotope abundances separated by capillary electrophoresis [64]
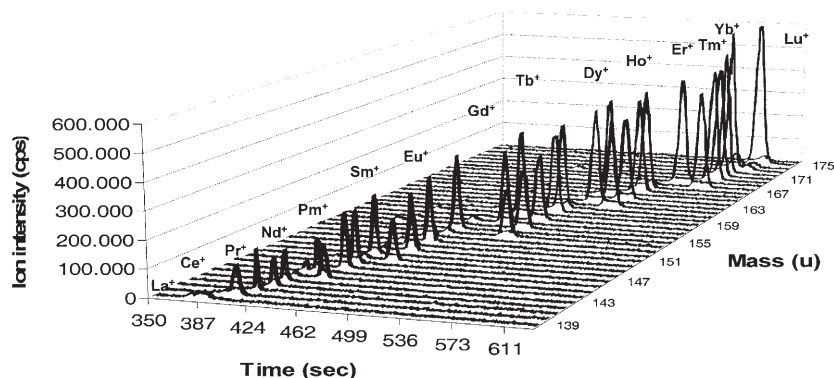
area non-natural ^{236}U from the radioactive fallout was detected. With increasing depth from the surface a decreasing contamination with non-natural ^{236}U (a decreasing $^{236}U/^{238}U$ isotope ratio) in soil samples was found. Furthermore, a decreasing $^{235}U/^{238}U$ isotope ratio as a result of the soil contamination with nuclear power plant uranium was measured with increasing depth. At a depth of 15–20 cm the natural $^{235}U/^{238}U$ isotope ratio of 0.00725 was observed.

Determination of spallation nuclide abundances in an irradiated tantalum target by HPLC-ICP-MS and CE-ICP-MS

In past years, on-line chromatographic coupling techniques such as HPLC and CE coupled to ICP-MS with the isotope dilution technique have been used for speciation analysis [60–62]. We used both coupling techniques in our lab for the separation of isobaric interferences in radioactive material, for example for the isotope analysis of rare earth elements in a tantalum target irradiated in a spallation neutron source with 800 MeV protons. The determination of the abundance of spallation nuclides verified the theoretical results. The separation of the tantalum matrix by liquid extraction was performed in order to reduce the high ^{182}Ta activity.

Recently, HPLC coupled to the sensitive double-focusing sector field ICP-MS ELEMENT [63] was successfully applied for the separation of isobaric interferences of long-lived radionuclides and stable isotopes [e.g. isobaric interference of stable ^{154}Gd isotope and the long-lived ^{154}Dy radionuclide ($\tau_{1/2} = 3 \cdot 10^6$a) or stable ^{146}Nd isotope and the long-lived ^{146}Sm radionuclide ($\tau_{1/2} = 10^8$a)]. All 14 rare earth elements (REE) in the irradiated tantalum target were separated and determined by HPLC-ICP-MS. Of interest is, that the experimental results of mass spectrometric measurements confirmed the theoretical calculation of spallation nuclides in the irradiated tantalum target.

In order to reduce the high radioactive solution volume of the digested irradiated tantalum target the capillary electrophoresis system (Waters Quanta 4000) was coupled to the DF-ICP-MS ELEMENT. The optimization of coupling technique and the analysis of spallation nuclides

Table 5 Nuclide abundances of gadolinium (%) produced via spallation reactions in an irradiated tantalum target

Nuclide	Nature	Theory	CE-ICP-MS	HPLC-ICP-MS
^{148}Gd	–	15.8	19.4	20.7
^{150}Gd	–	18.3	18.8	18.4
^{152}Gd	0.2	27.2	22.1	22.7
^{154}Gd	2.15	2.6	< 3.4	< 1.1
^{155}Gd	14.7	34.4	33.4	33.9
^{156}Gd	20.5	0.57	–	< 1.1
^{157}Gd	15.7	0.40	–	< 1.9
^{158}Gd	24.9	–	–	–
^{160}Gd	21.9	–	–	–

in the irradiated tantalum target is described by Day et al. [64]. In Fig. 3, a mass spectrum of all rare earth elements in the irradiated tantalum target separated and measured by CE-ICP-MS is shown. In agreement with the theoretical prediction for the rare earth elements, an increase of ion intensity was found with increasing mass, the highest ion intensity being for $^{175}Lu^+$. All REE were well separated with respect to the analytes by capillary electrophoresis using a sample volume of 30 nL only at the 800 µg L^{-1} concentration level of each lanthanide element. In Table 5 the nuclide abundances of gadolinium produced via a spallation reaction in an irradiated tantalum target separated and measured by HPLC-ICP-MS of 10 µL of highly radioactive digested and diluted solution and CE-ICP-MS of 30 nL sample volume are compared. It is shown, that the abundance distribution of spallation nuclides of gadolinium is quite different from the gadolinium isotopes which were measured in the natural samples (left column). With respect to the small sample volume used, the agreement of analytical results is excellent and the theory is confirmed. The precision of isotope abundances measured using both techniques is in the low % range.

Conclusions

It was shown that ICP-MS can be applied as a fast analytical technique for precise and accurate isotope ratio measurements in aqueous solution. Due to the excellent sensi-

tivity and very low detection limits, isotope ratio measurements are possible with very small sample amounts of analyte, and for solid samples mostly only simple preparation steps are required (compared to the time-consuming TIMS). The determination of isotope ratios with precision of down to 0.02% RSD are possible with double-focusing sector field ICP-MS, which allows the determination of isotope ratios with extremely low detection limits.

The insertion of the collision cell in ICP-MS results in new interesting applications for precise isotope ratio measurements of elements difficult to determine in ICP-MS (Ca, Se, Fe). The precision of ICP-MS is improved to 0.002% by multiple ion collection.

CE- and HPLC-ICP-MS are important for isotope ratio measurements on small sample solutions and if the separation of analytes is required.

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