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State-of-the-art and progress in precise and accurate isotope ratio measurements by ICP-MS and LA-ICP-MS†

Plenary Lecture

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The capability to determine isotope abundances is a main feature of mass spectrometry. The precise and accurate determination of isotope ratios is required for different application fields, such as: isotope ratio measurements of stable isotopes in nature, especially for the investigation of isotope variation in nature or age dating; 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; and tracer experiments using highly enriched stable isotopes or long-lived radionuclides in biological or medical studies. Inductively coupled plasma mass spectrometry and laser ablation ICP-MS (LA-ICP-MS) provides excellent sensitivity, precision and good accuracy for isotope ratio measurements with practically no restriction with respect to the ionization potential of the element investigated. Therefore both ICP-MS and LA-ICP-MS are increasingly replacing thermal ionization mass spectrometry (TIMS), which has been used as the dominant analytical technique for precise isotope ratio measurements for many decades. In the last few years instrumental progress for improving figures of merit in isotope ratio measurements in ICP-MS and LA-ICP-MS with a single ion detector has been achieved by the introduction of the collision cell interface, in order to dissociate disturbing argon-based molecular ions, to reduce the kinetic energy of ions and neutralize the disturbing argon ions of the plasma gas (Ar^+). The application of the collision cell in ICP-MS results in higher ion transmission, improved sensitivity and better precision of isotope ratio measurements compared to ICP-MS without the collision cell. The most important instrumental improvement for isotope analysis by sector field ICP-MS was the application of a multiple ion collector device (MC-ICP-MS) (developed about 10 years ago) in order to obtain better precision of isotope ratio measurements of up to 0.002%, RSD.

1 Introduction

Inorganic mass spectrometry is about 100 years old and has yielded important basic results for the development of atomic physics. In 1910 Thomson demonstrated the existence of isotopes of chemical elements with the example of two abundant stable neon isotopes (^{20}Ne and ^{22}Ne) using a parabolic mass spectrograph. Some years later, Aston showed that most chemical elements consist of several isotopes of different mass. Aston adduced the experimental evidence of mass defect and indirectly proved Einstein's equivalence law between mass and energy. With the improvement of mass spectroscopic systems in the following period with respect to sensitivity and mass resolution, the exact mass determination of isotopes and precise determination of isotopic abundances was possible. In 1921 Dempster used a 180° magnetic sector field mass spectrometer with an electrometer for precise electrometric measurements of ion currents and determined isotope abundances of, for example, the three stable Mg isotopes. By 1933, 183 isotopes of 66 elements had been discovered by mass spectrometry and, by 1948, 283 isotopes of 83 elements had been found. Aston alone detected 202 isotopes so that he become known as the father of isotope mass spectrometry.[1,2]

Isotope ratio measurements are important in a number of different application fields (see Fig. 1): for the determination of stable isotopes and long-lived radionuclides by investigations of isotope variation in nature; in environmental monitoring; in geochronology; for quality assurance of fuel material; and for radioactive waste control. Especially for environmental monitoring, in order to gain information about different long-lived radionuclides of Pu or ^{236}U as nuclear fallout from nuclear power plants (NPP) or nuclear weapon tests, ICP-MS is being increasingly used due to its high sensitivity. Furthermore, isotope ratio measurements are of interest for tracer experiments by using the addition of highly enriched stable or unstable isotope spikes in studies of chemical reactions in biological and medical research, in metabolism studies and in the isotope dilution technique as a primary method for the determination of element concentrations at trace and ultratrace levels.[3–11]

In principle, all mass spectrometers can be used for isotope ratio measurements. In Table 1 the precision of direct mass spectrometric methods—where the sample material is evaporized and ionized simultaneously—and post-ionization methods—where the vaporization and ionization of sample materials are separated in space and time—are compared. The precisions of spark source mass spectrometry (SSMS), laser ionization mass spectrometry (LIMS) and resonance ionization mass spectrometry (RIMS) are in the low % range. In contrast, secondary ion mass spectrometry (SIMS), sputtered neutral mass spectrometry (SNMS), thermal ionization mass spectrometry (TIMS), glow discharge mass spectrometry (GDMS) and ICP-MS with a single ion detector allow isotope ratio measurements with precisions between ≈0.02% and 1%. The precision can be improved down to 0.001–0.002%, for example, in TIMS (using Finnigan MAT 261), SIMS (using NanoSIMS, ion microprobe from CAMECA) and ICP-MS (using Plasma 54 from VG Elemental, Nu Plasma from Nu instrument or Neptune from Finnigan MAT) if multi-ion collectors (MC) are

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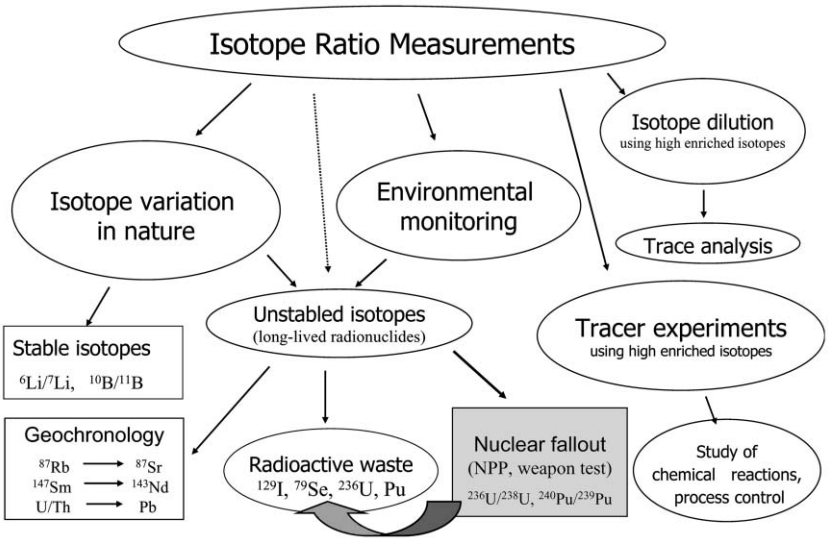

Fig. 1 Application fields of isotope analysis.

Table 1 Precision of mass spectrometric methods

Direct methods			Post ionization methods		
	Single collector	Multi collector		Single collector	Multi collector
SSMS	3–5%	≈1%	TIMS	0.01–1%	0.002–0.01%
LIMS	3–5%	—	GDMS	0.03–1%	—
SIMS	0.01–1	0.002–0.1	SNMS	0.02–1%	—
ICP-MS	0.02–2	0.002–0.01	LA-ICP-MS	0.08–1%	0.006–0.02%
			RIMS	5%	—

used for the simultaneous detection of mass-separated ion currents.

A search in the *Mass Spectrometric Bulletin* revealed that, in the last years of all published papers on isotope ratio measurements using different mass spectrometric techniques (such as ICP-MS, TIMS, SIMS, RIMS and isotope ratio mass spectrometry of gases), the greatest number (about 40%) applied ICP-MS with single- and multi-ion collection. Only in a few percent of papers were isotope ratios studied by LA-ICP-MS. The second largest number of the papers applied isotope ratio mass spectrometry with electron beam ionization for the analysis of gases, for example, for precise isotope ratio measurements of light elements such as oxygen, hydrogen or nitrogen followed by TIMS and SIMS.

Fig. 2 shows the distribution of isotope ratio measurements for different chemical elements. About one third of all publications have been concerned with the isotope analysis of light elements, H, C, N or O, using isotope ratio mass spectrometry (IR-MS) on gases and by accelerator mass spectrometry (AMS) for the determination of ^{14}C, for example. Considering the citations in the *Mass Spectrometric Bulletin*, the most frequently investigated heavy metal was uranium. Together with other long-lived radionuclides about one third of the publications studied the isotope abundances of unstable elements (mostly by ICP-MS).

Applications using isotope ratio measurements are summarized in Fig. 3, the main fields being geology, geochemistry and age dating. About the same number of all published papers used isotope ratio measurements for radioanalytical applications, methodological developments and in the fields of biology, medicine and the environment.

The Periodic Table in Fig. 4 shows which elements have been investigated with respect to isotope composition by ICP-MS and LA-ICP-MS. ICP-MS is not suitable for analyzing gases such as H, O, N or noble gases. No isotope analysis is necessary for elements with only one stable isotope (mono-isotopic elements) except where a long-lived radionuclide exists, such as iodine. In contrast, for the isotope analysis of unstable elements, which possess long-lived radionuclides such as U, Th and transuranium elements, ICP-MS is of the greatest importance.

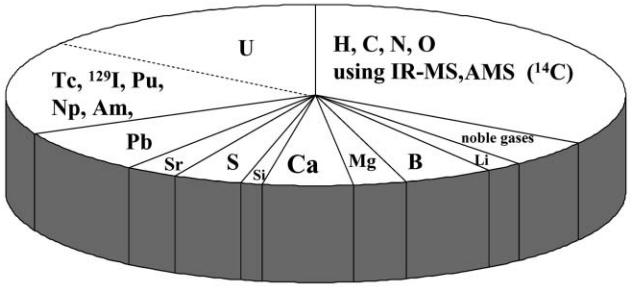

Fig. 2 Isotope ratio measurements by mass spectrometry: proportion of isotope ratio measurements for different elements.

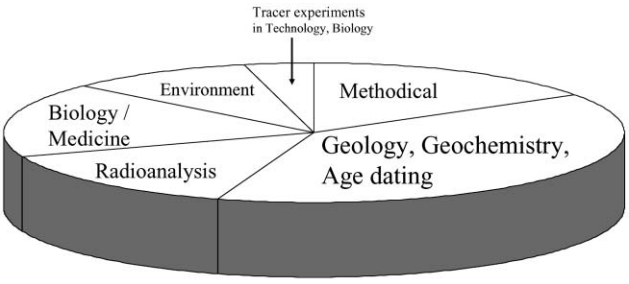

Fig. 3 Application of isotope ratio measurements.

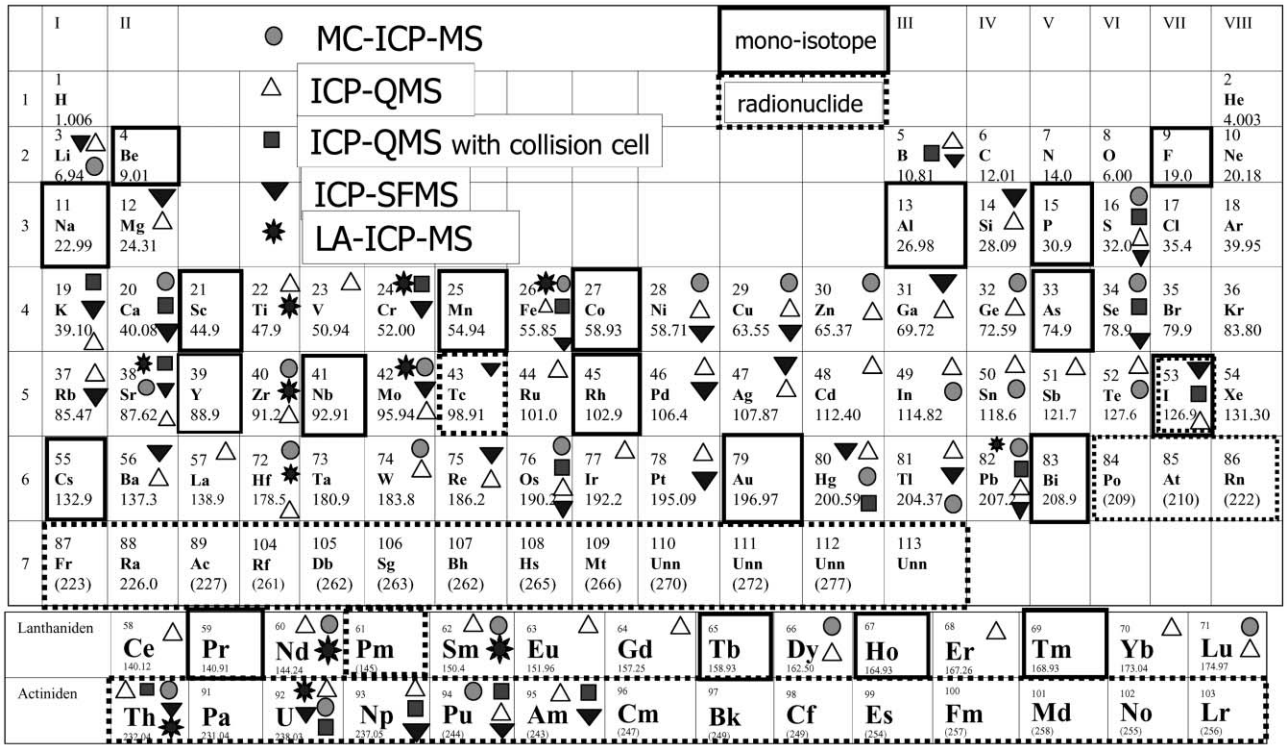

Fig. 4 Application of ICP-MS and LA-ICP-MS in isotope ratio measurements.

The highest precision of isotope ratio measurements has been observed using MC-ICP-MS. A lot of elements marked by the full circles (Fig. 4) have been measured by MC-ICP-MS. Multicollector ICP-MS is particularly appropriate for the geochemically interesting elements where isotope variation in nature is expected, such as Sr, Nd, Pb, Hf or Os.

All elements (except the mono-isotopic elements) have been measured by quadrupole ICP-MS (open triangles) and sector field ICP-MS (full triangles), except Ta due to the very low isotope abundance of ^{180}Ta of 0.001%. For the application of the isotope dilution technique, the isotopic highly enriched ^{180}Ta spike is extremely expensive.

Elements that have been characterized with respect to isotope ratios by ICP-MS with a collision cell are marked by squares. Elements where the isotope analysis is disturbed by molecular ion formation (ArO^+. ArC^+, Ar_2^+, ArH^+) or plasma gas ions (Ar^+), such as Fe, Cr, Se, K and Ca, are usually measured by ICP-MS with a collision cell.

In contrast, comparatively few, selected elements isotope ratios have been analyzed by LA-ICP-MS. Isotope ratio measurements of geologically interesting elements, such as Sr, Pb, Th and U, have been made using all five of the different instrumentation techniques discussed.

2 Limits for precision and accuracy of isotope ratio measurements in ICP-MS and LA-ICP-MS

The precision and accuracy of isotope ratio measurements using ICP-MS and LA-ICP-MS is limited by a number of different sources. One important limit for precise and accurate isotope ratio measurements in ICP-MS is the mass discrimination effect. Table 2 compares the mass discrimination effects and different correction methods in ICP-MS and TIMS.

In ICP-MS the mass discrimination is a result of space charge effects. After the ions formed in the inductively coupled plasma leave the skimmer cone, the Coulomb repulsion of positively charged ions results in a loss of transmission through the ion optical lens system, and the light ions are deflected more than the heavy ones. Therefore in ICP-MS the measured isotope ratio of lighter (L) to heavier isotope (H) is smaller than the true value (*e.g.*, $^{24}Mg/^{26}Mg_{measured} < {}^{24}Mg/^{24}Mg_{true}$). In contrast, in TIMS the mass discrimination effect is a result of preferential evaporation of the lighter isotopes (L) from the sample filament. Therefore in TIMS the measured isotope ratio of lighter (L) to heavier isotope (H) is larger than the true value. Furthermore the mass discrimination effect in TIMS is mass dependent.[4,7] A main advantage of ICP-MS is the

Table 2 Mass discrimination in ICP-MS *vs.* TIMS

	TIMS	ICP-MS
Origin	Preferential evaporation of the lighter isotope from the sample filament	Preferential radial deflection of lighter ions from the center of the ion beam (Space charge effects → Coulomb repulsion of charged ions → loss in ion transmission)
Observation	$(R_{L/H})_{measured} > (R_{L/H})_{true}$	$(R_{L/H})_{measured} < (R_{L/H})_{true}$
Correction method	(1) Calibration with isotope reference standard (for stable, radioactive, radiogenic elements with 2 isotopes *e.g.*, U, Pb, Cu)	(1) and (2) as for TIMS
	(2) Internal normalization, applicable for elements with 3 and more isotopes, where at least one isotope ratio is well established and invariant in nature *e.g.*, Sr, Hf, Nd	(3) External spiking by a mass non-interfering spike element with a well established (invariant in nature) isotope ratio *e.g.*, ^{203}Tl, ^{205}Tl for $^{204,206-208}$Pb, ^{69}Ga, ^{71}Ga for ^{70,72,73,74,76}Ge
Mass discrimination	TIME DEPENDENT	TIME INDEPENDENT

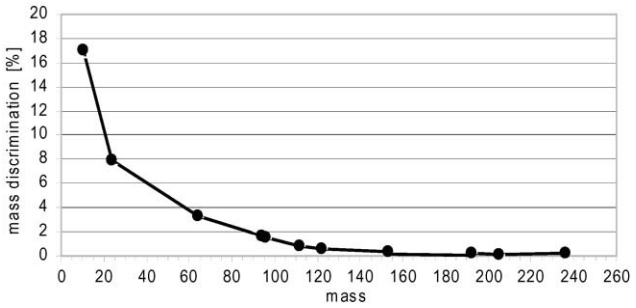

Fig. 5 Mass discrimination in ICP-MS.

Table 3 Mass discrimination (mass bias) correction equation

Power law: $R_{true}/R_{measured} = (1 + C_{pow})^{\Delta m}$ $(1 + C)$—mass disrimination factor, R_{true}—true isotope ratio, $R_{measured}$—measured isotope ratio; Δm—difference of masses
Exponential law: $R_{true}/R_{measured} = \exp(C_{exp}\Delta m)$
Linear law: $R_{true}/R_{measured} = (1 + C_{lin}\Delta m)$

time-independent mass discrimination effect. In general, the mass discrimination is considered in mass spectrometry by looking at the mass bias correction so that the mass discrimination factor - this is the ratio of the true and measured isotope ratio ($R_{true}/R_{measured}$) - can be determined, for example, by using an isotope reference material with a certified isotope ratio. The mass discrimination correction equations, which are used in ICP-MS, are summarized in Table 2.

Fig. 5 shows the mean mass discrimination in ICP-MS. The dependence of mass discrimination as a function of mass determined in quadrupole ICP-MS without and with a collision cell in comparison to sector field ICP-MS with a multi-ion collection is very similar.[4] For isotope ratios at low masses a mass discrimination higher than 10% is observed. The mass discrimination decreases with increasing mass of isotopes.

Mass discrimination correction in ICP-MS (see Table 3) can be performed: 1, using isotope reference materials for elements with two stable isotopes or long-lived radionuclides; 2, by internal normalization when no isotope reference materials exist, which is applicable for elements with three and more isotopes and where at least one isotope ratio is well established and invariant in nature (*e.g.*, for Sr or Hf); and 3, *via* external spiking by a mass of non-interfering spike element with a well established isotope ratio - invariant in nature (*e.g.*, ^{203}Tl and ^{205}Tl for the determination of mass discrimination effects for Pb). Furthermore, certified enriched isotope spikes can be used for mass discrimination correction.

A second source of uncertainty in isotope ratio measurements is the dead time of the ion detector. Because, in mass spectrometers, channel electron multipliers and pulsed counting systems are mostly 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, dead time correction of the detector is necessary. Recently, Ramebäck *et al.* investigated this effect in their report "On the determination of true dead time of a pulse counting system in isotope ratio mass spectrometry".[12]

A further limitation in the determination of isotope ratios is low abundance sensitivity in ICP-MS. The abundance sensitivity, which is the contribution of neighboring peaks to the intensity of a measured isotope, can influence the accuracy of isotope abundance measurements.[4] For example, the determination of ^{239}Pu or ^{236}U ultratraces in the presence of a high uranium concentration is impossible at the low abundance sensitivity of the mass spectrometer.[13]

Further sources of uncertainty are the instrumental background; contamination due to the solution introduction system, the sampler and skimmer cones and lens system; mass scale drift effects; plasma instabilities; drifts on ion intensities; and matrix effects. For example, Galy *et al.*[14] studied matrix effects on Mg isotope ratio measurements by ICP-MS. The addition of Al, Na and Ca to a pure Mg solution induced increasing isotopic shifts of 0.02–0.1% of δ^{26}Mg.[14]

One of the serious problems in ICP mass spectrometry is that a multitude of different isobaric interfences on analyte ions appear. Precise and accurate isotope ratio measurements could be limited by possible isobaric interferences of measured isotopes with isobaric singly charged atomic ions. For the mass spectrometric separation of these isobaric atomic ions, a mass spectrometer with a very high mass resolution is required. For example, the separation of $^{40}Ca^+$ and $^{40}Ar^+$ requires a mass resolution of $m/\Delta m \approx 192\,000$. Ultra-high mass resolving power in the ICP mass spectrum ($m/\Delta m_{10\%} \approx 260\,000$), demonstrated for the mass spectrometric separation of $^{40}Ca^+$ from $^{40}Ar^+$, was obtained with a Fourier transform ion cyclotron resonance mass spectrometer (ICP-FT-ICR-MS) equipped, for example, with a 3-tesla superconducting magnet as described by Barshik *et al.*[15] Using this expensive equipment unwanted ions could be selectively removed prior to transfer to the FT-ICR collision cell by an ion/molecule reaction in an octapole ion guide. A gas-filled collision cell in ICP-MS can help to solve such interference problems.

Furthermore, interferences of singly-charged with doubly-charged atomic ions (*e.g.*, $^{91}Zr^+$ and $^{182}W^{2+}$, $m/\Delta m \approx 1\,330$) and with molecular ions have been observed in mass spectra (*e.g.*, $^{80}Se^+$ and $^{40}Ar_2{}^+$, $m/\Delta m \approx 9\,500$) and can often be separated using double-focusing sector field ICP-MS with a maximum mass resolution of 12 000 or by the application of a collision cell in ICP-MS. Using different methods, intensities of disturbing molecular ions can be reduced by special sample introduction systems, *e.g.*, in ICP-MS using a hydride generator (Se, As, Ge), an ultrasonic nebulizer with desolvator (Fe, Ca, K) and a microconcentric nebulizer with desolvator. Furthermore by a careful trace–matrix separation (*e.g.*, extraction, ion chromatography, HPLC, CE), an application of a plasma-shielded torch (in combination with a cool plasma technique) or an application of a collision cell for dissociation of disturbing molecular ions can help to solve interference problems.

More details on sources of uncertainty have been provided by Appelblad *et al.*[16]

3 Instrumentation and capability of ICP-MS for isotope ratio measurements

Fig. 6 gives an overview of ICP-MS instrumentation. The most common ICP mass spectrometers are quadrupole-based instruments (ICP-QMS) without collision cells, for example from Perkin Elmer, Agilent, ThermoElemental and Varian, which allow isotope ratio measurements with a precision for short-term isotope ratio measurements from 0.1 to 0.5% relative standard deviation (RSD).[4,6] For long-term measurements by ICP-QMS, an external precision of about 0.05%, *e.g.*, for ^{107}Ag/^{109}Ag, ^{207}Pb/^{206}Pb or for ^{235}U/^{238}U ~ 1, has been obtained.[17–19]

Quadrupole ICP mass spectrometers with collision cells are produced by Perkin Elmer, Agilent, and ThermoElemental. The first quadrupole ICP-MS with a hexapole collision cell, the "Platform" from Micromass, is also available on the analytical

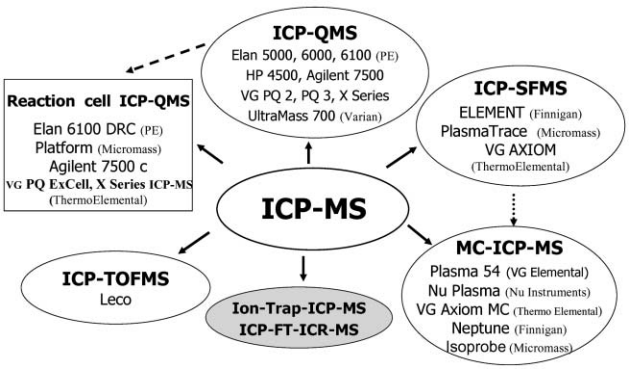

Fig. 6 Overview of ICP-MS instrumentation.

market.[20,21] The Platform instrument—where a hexapole collision cell is additionally used as the ion optical lens system—works without a photon stop and the ion detector is not on the ion optical axis. In contrast, a quadrupole ICP-MS equipped with a linear pressurized rf-driven quadrupole cell, the dynamic reaction cell (DRC), was introduced by Perkin Elmer. The primary function of the DRC is to remove isobaric interferences from the ion beam by controlled ion/molecule reactions.[22]

There are double-focusing sector field ICP mass spectrometers with a single ion collector; the most common being the ELEMENT from Finnigan MAT and the first one being the PlasmaTrace from Micromass. In comparison to quadrupole ICP-MS, an improvement of precision in short-term measurements down to 0.026% RSD was observed by using double-focusing sector field ICP-MS with the shielded torch and a single ion collector, as we demonstrated for the ELEMENT from Finnigan MAT.[4,23] 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 from molecular ions, even at higher element concentrations (up to mg L^{-1}), results in a decrease in precision due to a significant loss in ion intensity and because flat top peaks are not obtained. Sector field mass spectrometers with multiple ion collectors are also available on the analytical market, such as the double-focusing sector field instruments Nu Plasma from Nu Instruments, VG Axiom and Neptune from Finnigan MAT, and the single-focusing sector field ICP-MS with a collision cell, the Isoprobe from Micromass. Using double-focusing sector field ICP-MS with a multiple ion collector, for example the Plasma 54 and Nu Plasma, a precision of one order of magnitude better than with single ion detection, down to 0.002% (20 ppm), has been achieved in isotope ratio analysis.[24,25] ICP-MS with high resolution Fourier transform ion cyclotron resonance and ion trap ICP-MS can also be used for isotope ratio measurements. Collision-induced reactions in a collision cell have been applied in an ion trap ICP-MS in order to dissociate disturbing molecular ions, as demonstrated by Koppenaal and co-workers.[26,27] Using the ICP-MS with a TOF analyzer a precision of 0.05% has been described in the literature.[28]

3.1 Capability of ICP-MS with a collision cell

The introduction of the collision cell in ICP-MS represents important progress in ICP-MS instrumentation, which is relevant for improving the precise determination of isotope ratios. The first investigations of the basic principles and application of the collision cell to improve sensitivity in inorganic ultrasensitive mass spectrometry was published 20 years ago.[29]

By the collision of ions with the collision gas (*e.g.*, He and/or H_2, NH_3) in the gas target the molecular ions are dissociated and the atomic argon ions formed from the plasma gas in the ICP are neutralized. Originally the collision cell was introduced in ICP-MS in order to dissociate disturbing argon-based molecular ions (ArX^+, X = O, N, C, H or Ar) and to neutralize the plasma gas ions (Ar^+).[30–34] Reaction chemistry and collision processes in the gas cell for resolving isobaric interferences in ICP-MS have been described by Bandura *et al.*[30] The effect of reducing molecular ion formation by up to eight orders of magnitude was observed using the Elan 6100 DRC (Perkin Elmer)[30–32] and by up to 4 orders of magnitude using the Platform (Micromass).[33]

Due to the removal of isobaric interferences by collision and gas phase reactions, it is possible to perform isotope analysis of Ca, Fe and Se (which is disturbed in inductively coupled Ar plasma mass spectrometry by Ar^+, ArO^+ and Ar_2^+, respectively). It should be noted that new interferences with molecular ions have also been observed using the collision cell in the Platform instrument. The effect of adventitious water in a hexapole collision cell using a VG PQ ExCell ICP-MS to investigate the origins of molecular ions was described by Dexter *et al.*[34] An additional effect of the collision of atoms (*e.g.*, He) or molecules (H_2, NH_3, CH_4) in the collision cell with the analyte ions is the loss of ion kinetic energy, which results in a reduction of the energy spread (“cooling”) of the ions from several eV to <0.1 eV, improved ion transmission, sensitivity of elements, and improved precision in the determination of isotope ratios.

Results of isotope ratio measurements on selected elements measured by ICP-MS with a hexapole collision cell are summarized in Table 4. Due to possible interferences with Ar^+, ArO^+ and dimer Ar_2^+ molecular ions, the measurement of the isotope ratios $^{40}Ca/^{44}Ca$, $^{56}Fe/^{57}Fe$ and $^{78}Se/^{80}Se$ by ICP-MS is extremely difficult or not possible at all. Whereas for these isotope ratios precisions between 0.2 and 0.3% have been observed using ICP-MS with a hexapole collision cell, a precision of 0.07% was measured for a 10 μg L^{-1} uranium isotope reference solution ($^{235}U/^{238}U \approx 1$) in our laboratory.[4,35]

ICP-MS with a collision cell is extremely well suited for the sensitive determination of the long-lived ^{129}I and ^{79}Se radionuclides. The determination of ^{129}I ($t_{1/2} \approx 1.6 \times 10^7$ a) is of great interest for the environmental monitoring of nuclear fallout, for monitoring of radioactive emissions from nuclear facilities, for thyroid dose reconstruction in contaminated regions after the accident at Chernobyl NPP, and for radwaste control. The determination of the $^{129}I/^{127}I$ ratio in environmental samples requires an abundance sensitivity down to 10^{-10}–10^{-11}. Analytical methods that are mostly applied for the ultrasensitive determination of ^{129}I, such as accelerator mass spectrometry (AMS) and neutron activation analysis

Table 4 Isotope ratio measurement by ICP-CC-QMS with hexapole collision cell; Ca, Fe: 10 μg L^{-1}, Se: 100 μg L^{-1} with Meinhard nebulizer

Isotope ratio	Measured ratio	RSD (%) $n = 6$	Table value IUPAC	Accuracy (%)
$^{40}Ca/^{44}Ca$	46.41	0.26	46.47	0.13
$^{56}Fe/^{57}Fe$	43.41	0.16	43.30	0.25
$^{78}Se/^{80}Se$	0.4747	0.26	0.4791	0.92
$^{235}U/^{238}U$	0.9957	0.07	0.99991[a]	0.42

[a]Uranium isotope laboratory standard (CCLU 500).

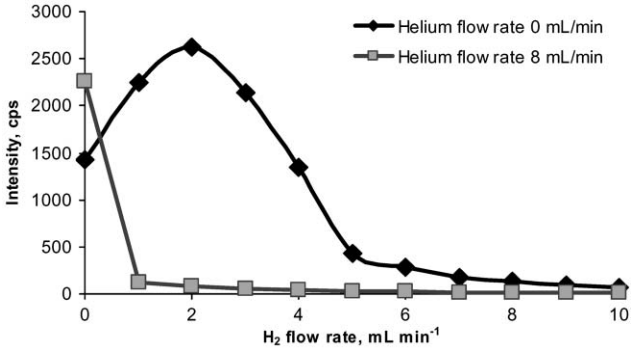

Fig. 7 Background intensity in ICP-CC-QMS with hexapole collision cell at mass 129 u as a function of collision gas flow rates.

(RNAA), are very expensive, require special equipment and laboratory facilities and are time-consuming. ICP-MS is very advantageous due to the relatively low costs and high sample thoughput, which is especially required for radwaste or environmental control. The problems in ^{129}I determination by ICP-MS are the high background caused by ^{129}Xe impurities in the Ar plasma and the insufficient abundance ratio sensitivity of ^{129}I/^{127}I. Using He and H_2 as the collision gases in ICP-MS with a hexapole collision cell, an efficient reduction of the disturbing background intensity of $^{129}Xe^+$ ions was observed (see Fig. 7). It is therefore possible to decrease the detection limit in comparison to ICP-SFMS by nearly 2 orders of magnitude from100 ng L^{-1} to 3 ng L^{-1}. In this experiment, a special solution introduction system for introducing elemental iodine *via* the gas phase in ICP was applied.[36] The accuracy of ^{129}I determination was investigated by Kerl *et al.*[36] using analysis of ^{129}I-spiked biological SRMs. A ^{129}I concentration of 205 $\pm$ 12 pg mL^{-1} was measured, which is in good agreement with the spiked concentrations of 200 pg mL^{-1} in Citrus Leaves (NIST SRM 1572).

The determination of the long-lived radionuclide ^{79}Se ($t_{1/2} \approx$ 65 000 a) is restricted by several interferences from $^{79}Br^+$, $^{39}K^{40}Ar^+$, $^{63}Cu^{16}O^+$, $^{158}Gd^{2+}$ and $^{158}Dy^{2+}$, which can be reduced using a hydride generator for solution introduction. Whereas the detection limit of ^{79}Se in sector field ICP-MS was 100 pg mL^{-1} by applying hydride generation,[37] in quadrupole ICP-MS with a hexapole collision cell the detection limit could be reduced to 5 pg mL^{-1}, because the disturbing argon hydride molecular ions, $^{38}Ar^{40}Ar^1H^+$, were additionally suppressed. But it should be noted that new interferences may appear in ICP-MS with a collision cell when using hydrogen as the collision gas, so this effect must be considered carefully. At a very low concentration of the long-lived radionuclides of interest in environmental samples, such new interferences of, for instance, hydride ions ($^{78}Se^1H^+$, $^{127}IH_2^+$, $^{235}UH^+$ or $^{238}UH^+$) at masses 79 u, 129 u, 236 u and 239 u for the determination of ^{79}Se, ^{129}I , ^{236}U and ^{239}Pu at ultratrace levels play an important role. Therefore the application of a solution introduction system with a desolvator (*e.g.*, the microconcentric nebulizer, Aridus, from CETAC) is advantageous for ultrasensitive determination of ^{236}U and ^{239}Pu, or an alternative collision gas (for example oxygen) is helpful for ^{129}I determination. In a recent paper, the hydride formation of uranium using different solution introduction systems was studied as a function of experimental parameters.[38] The detection limits of selected long-lived radionuclides, ^{93}Mo, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{151}Sm, ^{236}U and ^{239}Pu, measured by ICP-QMS with a hexapole collision cell were better by one order of magnitude and varied between 0.003 and 0.3 pg mL^{-1} (Table 5). Possible interferences could be eliminated using a hydride generator, aerosol desolvation or a chemical reaction with the collision gas.

Recently, Moens *et al.*[39] demonstrated that ion/molecule reactions in a dynamic reaction cell (DRC) allow the elimination of the $^{87}Rb^+/^{87}Sr^+$ isobaric interference. A special ion/molecular reaction in a collision cell was studied in order to avoid this isobaric interference of atomic ions in the Elan 6100 DRC (Perkin Elmer). The authors analyzed a mixed Sr and Rb solution. After introducing methyl fluoride in the collision cell, Sr formed selective fluoride molecular ions but Rb did not. An interference-free Sr isotope analysis *via* its fluoride ions in the presence of Rb without chemical separation was possible. This technique was applied for Rb-Sr age dating of geological samples, without chemical separation of the analytes. The precision of the age was of the same order as the precision of the TIMS results.

Table 5 Detection limits of long-lived radionuclides in ICP-CC-QMS. Bold type: eliminated using hydride generator; italic type: reduced using solution introduction system with aerosol desolvation; underlined type: eliminated using neutralization reaction with collision gas.

Nuclide	Possible interferences	Detection limit/pg mL^{-1}
^{79}Se	$\mathbf{^{79}Br^+}$, $\mathbf{^{39}K^{40}Ar^+}$, $\mathbf{^{158}Gd^{2+}}$, $\mathbf{^{63}Cu^{16}O^+}$, $^{38}Ar^{40}ArH^+$, $^{78}SeH^+$ [a]	5
^{93}Mo	$^{93}Nb^+$, $^{77}Se^{16}O^+$, $^{92}MoH^+$ [a]	0.1
^{99}Tc	$^{99}Ru^+$, $^{98}MoH^+$ [a]	0.1
^{107}Pd	$^{107}Ag^+$, $^{91}Zr^{16}O^+$, $^{106}PdH^+$ [a]	0.2
^{126}Sn	$^{126}Te^+$, $\underline{^{126}Xe^+}$, $^{110}Pd^{16}O^+$, $^{110}Cd^{16}O^+$	0.3
^{129}I	$\underline{^{129}Xe^+}$, $\underline{^{127}IH_2^+}$ [a]	3
^{151}Sm	$\underline{^{151}Eu^+}$, $^{135}Ba^{16}O^+$	0.2
^{236}U	$^{235}UH^+$ [a]	0.003
^{239}Pu	$^{238}UH^+$ [a]	0.003

[a]New interferences can be appear in ICP-CC-QMS when using hydrogen as collision gas.

3.2 High-precision sector field ICP-MS with multiple ion collection

When do we need high-precision isotope ratio measurements? Highly precise and accurate isotope ratio measurements are required for age dating of geological samples and also for the investigation of fine isotope variations in nature especially of light elements. Whereas H, O, C, N and noble gases are not measurable by ICP-MS, isotope variation in natural samples has been investigated for Li, B, S, Si, Ca, Fe, Cu, Sr, Nd, Hf, Os, Pb, Th and U.[2,5]

Significant progress has been achieved in the instrumental improvement of ICP-MS in order to obtain an improvement of precision of isotope ratio measurements by the introduction of the multi-ion collector device. Plasma 54 from VG Elemental was the first commercial double-focusing sector field ICP-MS with multi-ion collectors with nine Faraday cups.[40–45]

Using the Plasma 54, Anbar *et al.*[46] recently studied the isotope analysis of Mo. Zr or Ru "elemental spikes" were employed to determine the mass discrimination in MC-ICP-MS. The authors determined a "laboratory fractionation" of Mo isotopes of about 0.15% during ion exchange by off-line Mo separation. A possible natural isotope variation of Mo could be determined with a precision of $\pm$0.02%. So far MC-ICP-MS has been used to provide evidence of double β decay of ^{96}Zr *via* ^{96}Mo enrichment in Precambrian zircons, which was demonstrated using multicollector TIMS.[47]

A further application of LA-MC-ICP-MS using the Plasma 54 for Zr isotope ratio measurements in zircon and baddeleyite samples has been recently described by Hirata.[48] The isotope ratios $^{92}Zr/^{90}Zr$ = 0.33394 $\pm$ 0.00002 and $^{96}Zr/^{90}Zr$ = 0.05463 $\pm$ 0.00001 were determined on a Merck reagent with a precision of 0.01–0.02% and 0.03–0.04%, respectively. Neither isotopic variation in the $^{92}Zr/^{94}Zr$ isotope ratio (due to the radiogenic contribution of ^{92}Nb) nor isotopic

Table 6 Results of isotope ratio measurements using MC-ICP-MS (Nu Plasma, Nu Instruments)

	$^{207}Pb/^{204}Pb$ ref. 49 NIST SRM 981	$^{87}Sr/^{86}Sr$ ref. 50 NIST SRM 987	$^{234}U/^{238}U$ ref. 51 Ocean water
GSI result	0.91468(2)	0.71026(2)	$63.0(0.5) \times 10^{-6}$
Certified value	0.91475(5)	0.71026(6)	$62.58(0.12) \times 10^{-6}$[a]

[a]Recommended.

heterogeneity was found for any of the investigated zircon and baddeleyite samples.

The capability of the double-focusing sector field Nu Plasma from Nu Instruments (with Nier–Johnson geometry) with 12 Faraday cups has been demonstrated by Halicz and co-workers[49–51] on a lead and strontium NIST isotope standard reference material (see Table 6) where excellent agreement with certified values was achieved with a precision at 20 ppm (0.002% RSD). Also small isotope ratios, as demonstrated for $^{234}U/^{238}U$ in ocean water, could be measured with good accuracy.

Recently, Kleinhanns *et al.*[52] described precise and accurate isotope determinations of Lu/Hf and Nd/Sm using the MC-ICP-MS Nu Plasma and the application of isotope dilution analysis for element ratios (*e.g.*, Sm/Nd; Hf/Lu) after the chemical separation of analytes from rock digest. Barbaste *et al.*[25] determined $^{87}Sr/^{86}Sr$ isotope ratios in wine using the multiple ion collector ICP-MS, AXIOM, from Thermo-Elemental with a precision of 0.002–0.003%. Strontium was separated from Rb in order to avoid the $^{87}Sr/^{87}Rr$ isobaric interference. A variation of $^{87}Sr/^{86}Sr$ isotope ratios in investigated wine samples of different geographic origin from 0.7047 to 0.7125 (IUPAC table value: 0.7103) was found.

A powerful double-focusing sector field ICP-MS with multiple ion collectors is the NEPTUNE (ThermoFinnigan), which is constructed on the basis of the double-focusing sector field ICP-MS, ELEMENT (but the arrangement of electric and magnetic sector fields is reversed), and the multicollector array of the thermal ionization mass spectrometer, TRITON, from Finnigan MAT. Eight Faraday cups are interchangeable with ion counting detectors in order to measure isotope ratios at very low concentration levels. The precision of the isotope ratio measurements was demonstrated by measuring neodymium at low mass resolution. For example, the standard deviations of the measured Nd isotope ratios, $^{143}Nd/^{144}Nd = 0.5117$ and $^{145}Nd/^{144}Nd = 0.3484$, were 3 and 6 ppm, respectively.[53] In contrast to the ICP-SFMS with a single ion collector (ELEMENT from Finnigan MAT), flat-top peaks were observed using the MC-ICP-MS NEPTUNE at a mass resolution of $R(m/\Delta m) = 4000$, which are important for the precise determination of isotope ratios.

Recently, Lahaye (at the University of Frankfurt, Frankfurt, Germany)[54] measured *in-situ* Hf isotope ratios in zircons and strontium isotope ratios in several magmatic plagioclase by microlocal analysis using LA-ICP-MS (MC-ICP-MS: NEPTUNE) at low mass resolution. Lahaye achieved excellent precision in the low ppm range and found good agreement with reference data determined by TIMS.

The only single-focusing sector field ICP-MS with a hexapole collision cell and multi-ion collectors (MC-ICP-CC-MS) is the IsoProbe, produced by Micromass. The collision cell is mainly used for reducing the energy spread of ions from several eV to less than 1 eV. 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. Furthermore, a collision gas or a gas mixture of hydrogen/helium in the collision cell is used for the dissociation of molecular ions (Ar_2^+, ArO^+, ArN^+, ArC^+ and others). So a very precise isotope analysis with relative standard deviations of 0.01% and 0.0015% for $^{54}Fe/^{56}Fe$ and $^{82}Se/^{80}Se$ isotope ratios, respectively, is possible. Furthermore, by collision-induced reactions in the hexapole cell, the Ar^+ ion intensity was reduced by some orders of magnitude due to a neutralization reaction. This allowed the determination of ^{40}Ca by ICP-MS at ng L^{-1} concentration levels. Using the IsoProbe multi-ion collector ICP-MS with a collision cell, a $^{42}Ca/^{40}Ca$ isotope ratio of 0.0067 was determined with a precision of 0.009% RSD (at 1 mg L^{-1} Ca concentration) 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 levels as 0.027% RSD and 0.008% RSD, respectively. This precision of isotope ratios in MC-ICP-MS is comparable to those of TIMS with multiple ion collectors.[55,56]

The capability of MC-ICP-MS and MC-TIMS, in comparison to single ion collector ICP-MS, was demonstrated by iron isotope ratio measurements.[57] The precision achieved by applying different ICP-MS equipment for isotope ratio measurements on iron is shown in Table 7. Whereas the precision for iron isotope ratios using a quadrupole ICP-MS was between 0.2 and 0.5%,[59] the precision was improved by the application of a collision cell in quadrupole ICP-MS by nearly one order of magnitude.[60] An excellent precision of 0.004%, but only for the $^{54}Fe/^{56}Fe$ isotope ratio, was measured using the MC-ICP-CC-MS with a hexapole collision cell.[61] Using the multicollector ICP-MS, Plasma 54, Anbar *et al.*[62] reported precisions between 0.015 and 0.03% (RSD). The application of laser ablation ICP-MS using a multicollector instrument on real geological samples yielded a short-term stability of 0.1% for different iron isotope ratios due to inhomogeneous Fe distribution.[63]

In addition, a precision of 0.002% RSD has been reported for iron isotope ratio measurements by by MC-TIMS.[58,64] All the measurements were performed at low mass resolution. In contrast, iron isotope ratio measurements with the Neptune from ThermoFinnigan were performed at a mass resolution of about 8000 using different solution introduction systems. A separation of disturbing molecular ions from different iron isotopes was therefore possible. Weyer *et al.*[65] determined iron isotope ratios on a ^{57}Fe-spiked standard reference solution with a precision between 0.01 and 0.006% and found little isotope variation, less than 0.1%, in the natural water samples and the geological reference standard BCR 2.

The detection limits and precision of isotope ratio measurements using different ICP mass spectrometers are compared in Table 8. Whereas the double focusing sector field ICP-MS with a single ion collector shows the lowest detection limits down to 0.04 pg L^{-1} for selected long-lived radionuclides,[23,66] the best

Table 7 Precision of iron isotope ratio measurements by ICP-MS at low mass resolution[57]

Method	$^{54}Fe/^{56}Fe$	$^{57}Fe/^{56}Fe$	$^{58}Fe/^{56}Fe$	Reference
ICP-QMS	—	0.22%	0.47%	Witthaker *et al.*[59]
ICP-QMS (DRC)	0.05%	0.06%	—	Bandura *et al.*[60]
MC-ICP-CC-MS	0.004%	0.18%	—	Turner[61]
MC-ICP-MS	—	0.015%	0.03%	Anbar *et al.*[62]
LA-MC-ICP-MS	0.1%	0.1%	—	Hirata and Ohno[63]
MC-TIMS	—	0.006%	0.002%	Walczyk[64]

Table 8 Detection limits and precision for isotope ratio measurements in ICP-MS

	Detection limits/ng L^{-1}	Precision for isotope ratio measurement (RSD)	Reference
ICP-QMS	0.01–0.6	0.1–0.5%	Heumann *et al.*[6]
		0.05% (long term stability)	Platzner *et al.*[19]
ICP-CC-QMS	0.003–0.01	0.07–0.1 %	Becker, Dietze[4]
ICP-TOFMS	0.1–1	0.05–0.1%	Vanhaecke *et al.*[28]
ICP-SFMS ($m/\Delta m$ = 300)	0.00004–0.005	0.02–0.1%	Becker, Dietze[23]
MC-ICP-SFMS	0.0001[51]–0.0002	0.002–0.02%	Maréchal *et al.*[24]
MC-TIMS	(Sample size, 100 ng)	0.002%	Walczyk[64]

precision down to 0.002% was obtained by multi-ion collector ICP-MS.

4 Selected applications of ICP-MS and LA-ICP-MS

4.1 Geological research

The main field of application for ICP-MS and LA-ICP-MS is geological research, including geochronology, isotope variation in nature and geochemistry (see Fig. 3).

The physical method of geochronology is based on measurements of the isotope ratio, *i.e.*, geochronology (age dating using the following radioactive decay: $^{87}Rb \rightarrow {}^{87}Sr$, $^{147}Sm \rightarrow {}^{143}Nd$, $U/Th \rightarrow Pb$, $^{187}Re \rightarrow {}^{187}Os$, $^{176}Lu \rightarrow {}^{176}Hf$) is an essential field in the earth sciences, which would not have been possible without mass spectrometry. So SIMS enables U- and Th-rich minerals to be analyzed *in situ* to obtain accurate U, Th-Pb ages ($^{207}Pb/^{235}U$, $^{206}Pb/^{238}U$, $^{208}Pb/^{232}Th$).[2,67] Important textbooks on isotope ratio measurements, including different applications in age dating, have been published by Platzner[5] and DeLaeter.[2]

An accurate method for $^{206}Pb/^{238}U$ age determination on single zircon grains by LA-ICP-QMS using a quadrupole mass spectrometer (Elan 6000, PE SCIEX) was described by Li *et al.*[68] The authors investigated and considered Pb/U fractionation on zircon during laser ablation. They measured $^{207}Pb/^{206}Pb$, $^{206}Pb/^{238}U$ isotope ratios and determined the age of billion-year-old zircons, which were in good agreement with TIMS. For example, the age *via* the $^{206}Pb/^{238}U$ ratio of old zircon grains was determined in LA-ICP-QMS as 1846 $\pm$ 0.072 Ma *vs.* 1884 $\pm$ 0.005 Ma in TIMS, which requires time-consuming sample preparation steps.

For geochemists the sensitive and precise isotope analysis of Os for Re-Os dating[69–71] is interesting, where ^{187}Os is formed by the β decay of ^{187}Re with a half-life of 4×10^{10}. Therefore ^{187}Os is a powerful geochemical tracer. A highly enriched natural ^{187}Os sample with an isotope abundance of 99.44%[72] (IUPAC table value: 1.96%[73]) was characterized by ICP-QMS in three laboratories in Switzerland, Belgium and Germany and good agreement was found in comparison to SIMS, SNMS and GDMS measurements. The best precision for isotope abundance measurement of ^{187}Os was obtained in 1995 using SIMS with a single ion collector (CAMECA 4f IMS; ^{187}Os = 99.46 $\pm$ 0.01%).[72]

Recently, Boulyga *et al.*[74] and Halicz[51] investigated two ^{187}Os-enriched natural Os samples using double-focusing sector field ICP-MS with single-ion and multiple ion collector systems in our laboratory and in Israel. An ^{187}Os abundance of 98.93% was found and was in good agreement. This enrichment of ^{187}Os in both samples is the result of the β decay of ^{187}Re in old minerals.

Furthermore, by measuring the abundance of selected osmium isotopes on metallic osmium from Johnson Matthey chemicals using different ICP-MS equipment (ICP-SFMS, ICP-CC-QMS and MC-ICP-MS), a 17% enrichment of ^{187}Os in comparison to the table value from IUPAC of 1.96% was found. The precision of the $^{188}Os/^{192}Os$ isotope ratio measurement on the metallic osmium sample was 0.09% for double focusing sector field ICP-MS with a single ion collector, 0.08% for quadrupole ICP-MS with a hexapole collsion cell (ICP-CC-QMS) and 0.003% using MC-ICP-MS from Nu Instruments.

In situ Os isotope ratio analysis of iridosmines with a precision for microlocal isotope ratio measurement of 0.05% was performed by Hirata *et al.* with LA-MC-ICP-MS using the VG Plasma 54.[75]

Similar to Os, the isotope ratio measurement of Hf is of great interest to isotope geochemists due to the β decay of ^{176}Lu with a half-life of 3.6×10^{10} a, which results in an enrichment of ^{176}Hf[2]. In the IUPAC table of isotopic composition of elements, an isotope variation of ^{176}Hf from 5.206 to 5.271% in nature is mentioned.[73] Using the ICP-SFMS instrument, ELEMENT, with a single ion collector and a Hf solution from Merck for calibration purposes we measured a ^{176}Hf abundance of 5.26%; the standard deviation of measured hafnium isotope ratios being between 0.08% and 0.15%. The typical mass spectrum of Hf with a natural isotope pattern is shown in Fig. 8a. The $^{176}Hf/^{177}Hf$ isotope ratios, using hafnium oxide from Johnson Matthey Chemicals, measured with different multicollector instruments were determined with excellent agreement and the precision between 12 and 14 ppm (see Table 9). ICP-MS - where no restriction exists with respect to the ionization potential of element of interest - was advantageous in comparison to TIMS [TIMS is difficult for elements with relatively high ionization potential such as Hf (6.65 eV)].

For comparison with the isotope pattern of hafnium in natural samples, which is important for geological research, quite different isotope abundances for hafnium were measured in our laboratory in a highly radioactive solution of an irradiated tantalum target (see Fig. 8b) for nuclear research. The tantalum from a spallation neutron source was irradiated with 800 MeV protons over a period of several years. The spallation nuclides of hafnium formed by the irradiation of tantalum showed increasing abundances with increasing mass. In order to avoid contamination of the instrument, highly radioactive tantalum was dissolved and separated before the ICP-MS measurements.[81] Furthermore, micro-nebulization for the introduction of a small volume of radioactive solution into the ICP-MS was applied. This isotopic pattern of hafnium was similar (but with higher ion intensities) to that observed for the rare earth element (REE) distribution in the irradiated tantalum target. In order to avoid isobaric interferences of spallation nuclides, the ICP-MS measurements of REEs were performed after their on-line separation by HPLC,[81,82] or CE.[83]

4.2 Environmental, biological and medical research

Environmental, biological and medical research is a large field of application for ICP-MS. Besides the study of isotope variation in environmental samples, tracer experiments with highly enriched stable isotopes are performed and the isotope dilution technique is important for quantification purposes.

Krupp *et al.*[84] developed an analytical method for precise isotope ratio measurements of lead species by capillary gas chromatography (GC) ICP-MS using a sector field multi-collector instrument with a hexapole collision cell (MC-ICP-CC-MS, Isoprobe, Micromass). Volatile lead species ($PbEt_4$)

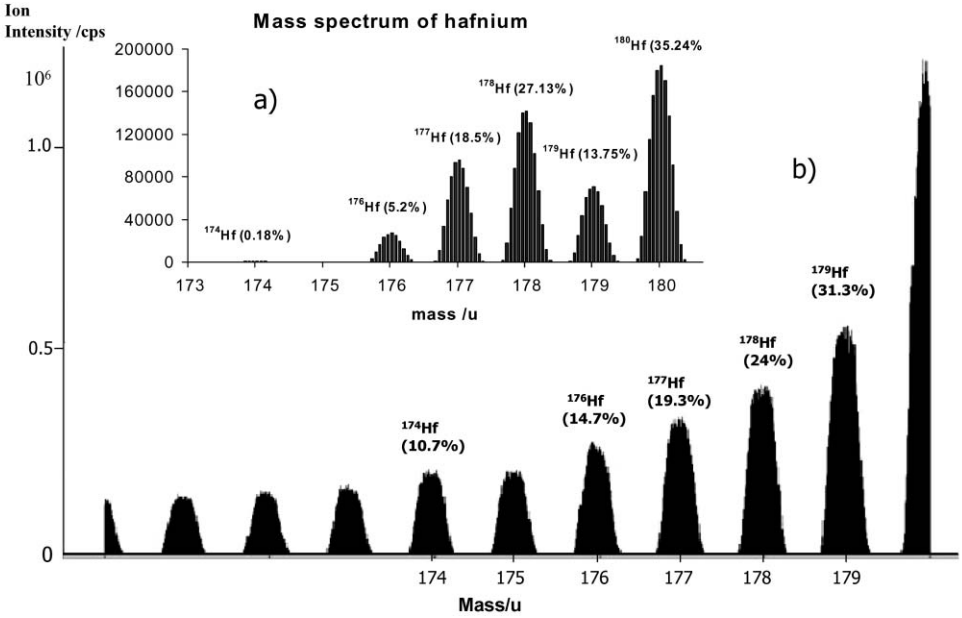

Fig. 8 Mass spectrum of hafnium in natural samples (a), and in an irradiated tantalum target (b).

Table 9 $^{176}Hf/^{177}Hf$ isotope ratio measured by MC-ICP-MS and MC-TIMS

	$^{176}Hf/^{177}Hf$	RSD (ppm)	Reference
Mean JMC-475	0.282161	13 (2σ)	Halliday *et al.*[76]
MC-ICP-MS (Plasma 54)	0.282149	14 (2σ)	Halliday *et al.*[77]
MC-ICP-MS (Plasma 54)	0.282155	14 (2σ)	Blichert-Toft *et al.*[78]
MC-ICP-MS (Nu Instrument)	0.282189	12 (2σ)	Kleinhanns *et al.*[52]
MC-TIMS	0.282155	14 (2σ)	Nowell *et al.*[79]
MC-ICP-MS (NEPTUNE)	0.282158	11 (1σ)	Schwieters *et al.*[80]

were prepared from NIST 981 and dissolved in iso-octane before analysis.

Determination of the lead isotope ratio was carried out by GC-ICP-CC-MS using the multicollector instrument on transient signals of Pb isotopes. The $^{206}Pb/^{208}Pb$ isotope ratio for 50 pg was determined with a precision of 0.02% and for 0.05 pg with 0.8%. The accuracy of measured isotope ratios varied between 0.05% and 0.5% as a function of sample size.

Isotope ratio measurements for a range of organolead compounds (trimethyl lead, dimethyl lead, triethyl lead, diethyl lead and inorganic lead) by GC-ICP-QMS using a quadrupole ICP-MS (HP 4500) were described recently by Encinar *et al.*[85]

An analytical method for the measurement of high-precision isotope ratios of mercury in coals using transient signals was developed recently by Evans *et al.*[86] Hg (1 ng) was loaded onto a gold trap. The Hg in coal was released by pyrolysis at 1200 °C. The sample introduction system from gold traps was combined with the addition of Tl through use of the Aridus microconcentric nebulizer with desolvator (CETAC Technologies, USA). The transient signals of Hg isotopes were measured and a change in the isotope ratio of Hg as a function of time was considered. By the comparing of the $^{200}Hg/^{202}Hg$ isotope ratio measured using five different MC-ICP-MS systems (see Fig. 6), the authors demonstrated a good agreement with the IUPAC value of 0.7734 $\pm$ 32 and did not observe any isotope variation of the measured mercury isotope ratios in natural coal and fly ash samples when compared with the values from NIST 1632b standard reference material.

In contrast, low isotope variations of the light element magnesium were recently observed for different magnesium compounds by Galy *et al.*[14] using the Nu Plasma MC-ICP-MS. The isotopic shift of the measured δ-Mg-25 value as a function of the δ-Mg-26 value with respect to the isotope standard reference material, NIST 980, for metallic Mg, Mg solution, magnesia, magnesite and chlorophyll showed a linear correlation with a maximum isotope variation of the ^{26}Mg isotope of 0.4%. It is interesting to note that, according to the IUPAC table of isotopic composition of elements, no variation of Mg in nature has been reported.[73] To determine the accuracy of Mg isotope ratios, Galy *et al.*[14] analyzed the isotope standard reference material NIST SRM 980 by MC-ICP-MS and measured a slightly higher $^{26}Mg/^{24}Mg$ isotope ratio of 0.13983 (4) than the certified value of 0.13932 (26) (the precision is given in parentheses). The $^{26}Mg/^{24}Mg$ isotope ratio of 0.13980 (2) had already been measured by Wasserburg and co-workers[87,88] using MC-TIMS 30 years previously with as good a precision as is possible today with MC-ICP-MS. In comparison, the $^{26}Mg/^{24}Mg$ isotope ratio of 0.13958 (36)[89] in NIST SRM 980 was determined using ICP-QMS (Elan 6000) and was in better agreement with the certified value but with one order of magnitude poorer precision (given in parenthesis) than observed with multi-collector instruments.

Highly enriched isotopes in tracer experiments were used at the Research Centre Juelich, for example, to explain the mechanism of mineral element uptake and transport in plants. Nutrient solutions were spiked with highly enriched ^{26}Mg, ^{41}K and ^{44}Ca isotopes and parts of the plants were analysed mass spectrometrically with respect to isotope ratios.[90] Whereas the lateral element distribution in parts of the plant were measured by secondary ion mass spectrometry (SIMS), ICP-MS was useful for the precise determination of the isotope ratios of these elements. For such tracer experiments—where large changes in isotope ratios were expected—single-ion collector ICP mass spectrometers were sufficient. We investigated the long-term stability of magnesium isotope ratio measurements using a quadrupole ICP-MS (Elan 6000) with micronebulization and observed a precision of 0.14% and an accuracy of 0.17% over 32 hours.[89] In comparison to the $^{26}Mg/^{24}Mg$ isotope ratio in nature (see above), a maximum enrichment of nearly 300-fold was found in a small amount of spiked nutrient solution. The Mg concentration in spiked nutrient solutions

was determined by ICP-QMS using the reverse isotope dilution technique.[89]

$^{26}Mg/^{24}Mg$ isotope ratio measurements in tracer experiments to quantify the Mg ion transport in tilapia (a fish species) were performed with ICP-SFMS by Wannemacker *et al.*[91] Due to the relatively high amount of C, Na, P, S, K and Ca, the ICP-SFMS ELEMENT was used at medium mass resolution ($m/\Delta m = 3000$) in order to separate disturbing interferences (*e.g.*, $^{48}Ca^{2+}$, $^{12}C_2^+$, $^{12}C^{14}N^+$). The obtained precision of 0.2–0.5% RSD in these tracer experiments was in agreement with previous results by Becker and Dietze[90] using ICP-SFMS at mass resolution 3000 for Mg isotope ratio determination in the presence of a high matrix concentration for tracer experiments on biological samples.

4.3 Application of isotope dilution analysis in ICP-MS

Isotope dilution analysis (IDA) is an excellent and important quantification technique in mass spectrometry for accurate trace element determination. In IDA one or two highly enriched isotope tracers or "spikes" (the latter is the so-called double spike technique) of the element to be determined with well-known concentrations are added to the sample (mixed and well homogenized with solid sample or aqueous solution). The trace element concentration was found by measuring changed isotope ratios in the sample-spike mixture (X) compared to those in sample (S) and highly enriched isotope tracer (T) using the eqn. (1):

$$Q_s = Q_T \times (T-X)/(X-S) \times m_s/m_T \quad (1)$$

where Q_s is the element concentration in the sample; Q_T is the element concentration in the highly enriched tracer; T is the isotope ratio of two selected isotopes in the highly enriched tracer; S is the isotope ratio of these two selected isotopes in the sample; X is the measured isotope ratio of the two selected isotopes in the mixture; and m_S and m_T are the atomic mass of the element in nature and of the isotopic enriched element, respectively. IDA is applicable to all elements with at least two stable isotopes or long-lived radionulides.

Due to the advantages of a definitive and accurate analytical method for the determination of element concentration *via* isotope ratio measurements, IDA is increasingly used in ICP-MS.

For example, Heumann's group determined Si in biological or clinical samples by ICP-SFMS[92] and methylmercury in aquatic systems by GC-ICP-QMS using the isotope dilution technique.[93] Lambertson *et al.*[94] studied Hg species in sea sediments by GC-ICP-QMS. Evans *et al.* reported on high-accuracy analysis of sulfur in diesel fuel by the isotope dilution technique.[95]

To an increasing extent the isotope dilution technique has been being applied in the certification of reference materials, *e.g.*, of Hg in polyethylene certified reference materials (CRM 680 and 681), or Cd and Tl in high-purity Zn (CRM 325/2R). ID-ICP-MS has yielded the most accurate data, as demonstrated recently by Vogl.[96]

In past years, on-line chromatographic techniques such as HPLC and CE coupled to ICP-MS with the isotope dilution technique have been used for element quantification in speciation analysis. An interesting application of the isotope dilution technique in medical research was proposed recently by Prange and co-workers,[97,98] who added highly enriched ^{34}S, ^{65}Cu, ^{68}Zn and ^{116}Cd spikes to the interface of the CE-ICP-MS system. The authors separated isoforms of metallothionein (*e.g.*, of rabbit liver) by capillary electrophoresis and quantified S, Cd, Cu and Zn concentrations in isoforms by ICP-SFMS using the isotope dilution technique.

4.4 Determination of long-lived radionuclides

The excellent capability of ICP-MS and LA-ICP-MS can be demonstrated especially for the determination of long-lived radionuclides. At the present time both techniques are powerful analytical methods for solving many analytical tasks. For example, radwaste control for routine analysis of radioactive samples in nuclear power plants for the final storage of radioactive waste requires fast analytical methods that allow long-lived radionuclides to be measured in many samples in a short time with a high degree of accuracy and precision. Furthermore, the measurement of contamination and enrichment of selected radioactive nuclides (*e.g.*, ^{129}I as an environmental indicator of nuclear accidents, ^{99}Tc or ^{79}Se as fission products, and ^{237}Np, ^{236}U, ^{239}Pu, ^{240}Pu, ^{241}Am and others) at ultralow concentration levels for environmental monitoring of fallout from nuclear weapons testing, nuclear power plants or nuclear accidents is of increasing interest. Using conventional radiochemical methods, the determination of long-lived radionuclides at a low concentration level requires careful chemical separation and enrichment of analytes (*e.g.*, by ion exchange or chromatography), which is mostly time consuming. Compared to radioanalytical methods, ICP-MS (and LA-ICP-MS) possesses a high isotope selectivity at high sample throughput and sample preparation is often easier or can be avoided altogether, *e.g.*, by LA-ICP-MS. In order to reduce the dose to the operator and possible contamination of instruments and tools, the development of microanalytical methods are of great interest.

The lowest detection limits in ICP-SFMS, down to 0.04 pg L^{-1}, were determined for several actinides (*e.g.*, for ^{239}Pu, ^{241}Am, ^{237}Np without chemical enrichment) in the high mass range.[23]

Using sector field ICP-MS we determined $^{240}Pu/^{239}Pu$ isotope ratios at different analyte concentration levels down to 10 pg L^{-1} using the ELEMENT and micronebulization, with a precision of Pu isotope ratio measurement at 100 pg L^{-1} in aqueous solution of 2%.[23] In order to reduce the sample volume, flow injection with a 10 μL sample loop was applied for the determination of Pu isotope ratios in wipe tests. For example, by using flow injection ICP-SFMS in 10 μL radwaste solution, we determined a $^{240}Pu/^{239}Pu$ isotope ratio of 0.26 ± 0.2.

Recently, plutonium isotope analysis at femtogram to nanogram levels was described by Taylor *et al.*[99] using MC-ICP-CC-MS (with a hexapole collision cell, Isoprobe, Micromass). In order to correct for instrumental mass bias and instrumental drifts, the authors applied the double-spike technique using a $^{236}U/^{233}U$ mixture with an isotope ratio of about 1. Very small isotope ratios of ^{239}Pu and ^{240}Pu in relation to ^{236}U of down to 10^{-7} were determined with a precision of 2 and 4%, respectively. These results of isotope ratio measurements of $^{240}Pu/^{239}Pu$ at the several hundred to 100 pg L^{-1} level obtained by MC-ICP-CC-MS with good accuracy and precision were in good agreement with TIMS results. With decreasing analyte concentration, the standard deviation of the isotope ratios measured by MC-ICP-CC-MS increased.[99]

Quetel *et al.*[100] compared the precision of $^{233}U/^{238}U$ solutions for different isotope ratios (from 1 down to about 10^{-3}) using sector field ICP-MS with single and multi-ion collectors in comparison to quadrupole ICP-MS. As expected, using MC-ICP-MS (Nu Plasma) the best precision of isotope ratio measurements was measured at an analyte concentration of 1 mg L^{-1} in aqueous solution (*vs.* 1 μg L^{-1} in ICP-SFMS and 10 μg L^{-1} in ICP-QMS). It is well known that the precision (RSD) for ion counting systems and small isotope ratios is limited by counting statistics. With decreasing isotope ratio the RSD increases by about an order of magnitude. Somewhat surprising is the local minimum and the relatively poorer precision for a relatively high isotope ratio of $^{233}U/^{238}U$ in the

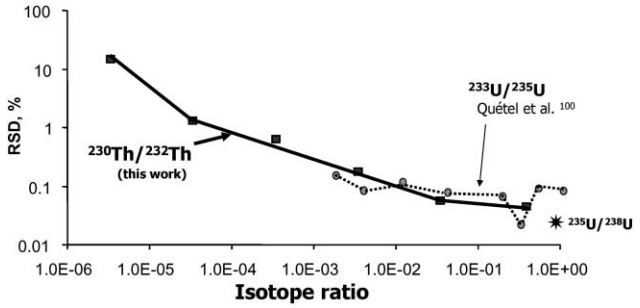

Fig. 9 Precision of isotope ratio measurements in ICP-SFMS.

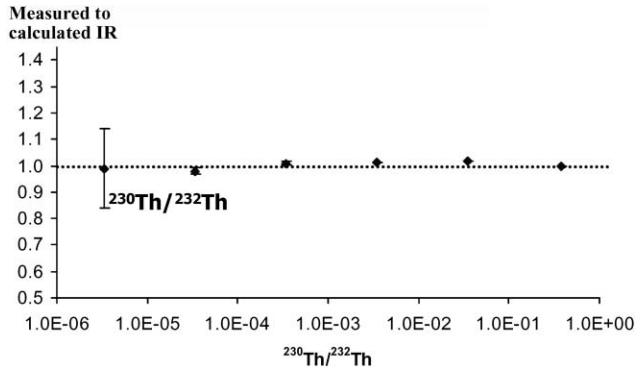

Fig. 10 Accuracy of isotope ratio (IR) measurements for $^{230}Th/^{232}Th$ in ICP-SFMS at a Th concentration of 1 μg L^{-1}.

curve measured using the ELEMENT 2 (see Fig. 9). In order to study small isotope ratios, we measured the $^{230}Th/^{232}Th$ isotope ratios down to 6×10^{-6} by ICP-SFMS. As expected, shown in Fig. 10, the RSD increased with decreasing isotope ratio. For comparison the curve of $^{233}U/^{238}U$ from Quetel *et al.* is shown.[100] The best precision which we measured using the sector field ICP-MS "ELEMENT" for the Th isotope ratio was 0.04% for $^{230}Th/^{232}Th = 0.8$ (due to higher instrumental background) whereas for the $^{235}U/^{238}U$ ratio of 1, it was 0.026%,[23] which is comparable to the minimum in Quetel's curve.

The good accuracy of different measured Th isotope ratios is demonstrated in Fig. 10. Whereas, for the isotope ratio of 6×10^{-6} at a Th concentration of 1 ng L^{-1} using an ICP-SFMS with a single ion collector, a precision of about 15% was observed, Turner *et al.*[101] reported a precision of 1.1% for MC-ICP-MS measurements of 5 ng L^{-1} in solution using the Nu Plasma. For the reduction of sample amount of radioactive solution, the figures of merit of different commercial micronebulizers for solution introduction in ICP-MS were studied in our laboratory.[23,66,101–103] The figures of merits for the Micromist nebulizer (Glass Expansion, Pty. Ltd., Camberwell, Australia), the quartz direct injection high efficiency nebulizer (DIHEN, J.E. Meinhard Associates, Inc., Santa Ana, USA), and the Aridus, in comparison to the ultrasonic nebulizer (USN with desolvator both from CETAC Technologies, Omaha, USA) are summarized in Table 10. The highest sensitivity was observed using the USN and the best overall detection efficiency for the DIHEN at a low solution uptake rate of 10 μL min^{-1}.

Radioactive waste solutions were analyzed, for example, using the DIHEN (which works without a spray chamber and does not produce waste solution) at a solution uptake rate of down to 1 μL min^{-1} by ICP-SFMS. The sensitivity at a solution uptake rate of 10 μL min^{-1} is comparable to the sensitivity of quadrupole ICP-MS. The accuracy and precision of ICP-SFMS using the DIHEN for solution introduction was demonstrated by the analysis of the uranium isotope standard solution NIST U-020 at different concentrations from 100–1000 ng L^{-1} where the measured isotope ratios fitted the certified uranium isotope ratio of 0.02081 +/− 0.00002 very well.[103]

Further applications of different micronebulization systems for solution introduction in ICP-MS to determine uranium isotope ratios, especially of ^{236}U content in hot particles such as nuclear fallout from the Chernobyl accident, have been published.[74,104] The determination of ^{236}U content as a consequence of nuclear fallout from the reactor accident in Chernobyl soil sample is of special interest in order to study the behavior of contamination in the environment of long-lived nuclides. In all investigated soil samples collected close to Chernobyl, non-natural ^{236}U was detected with an abundance between 0.0972–0.00017% from the radioactive fallout due to the accident in 1986.

Table 11 shows comparative measurements on soil samples at different depths from the Chernobyl area. The uranium isotope ratio measurements performed in our laboratory by ICP-SFMS and in Halicz's laboratory in Jerusalem using the MC-ICP-MS Nu Instrument are in excellent agreement. The highest contamination of ^{236}U was found at the soil surface. The contamination of soil sample decreased with increasing depth. Furthermore, an enrichment of ^{235}U up to 1% was detected on the soil surface as a result of soil contamination with nuclear power plant uranium and a decreasing $^{235}U/^{238}U$ isotope ratio was measured with increasing depth. At a depth of 15–20 cm the $^{235}U/^{238}U$ isotope ratio in nature of 0.00725 (see IUPAC table of isotopic composition of elements[73]) was observed. The precision of MC-ICP-MS was about one order of magnitude better in comparison to that of single collector ICP-SFMS.[74]

Recently we analyzed depleted uranium in Kosovo soil and penetrator samples and found the same uranium isotope composition with respect to the $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratio [with $^{235}U/^{238}U = (2.02 \pm 0.01) \cdot 10^{-3}$ and $^{236}U/^{238}U = (3.14 \pm 0.40) \cdot 10^{-6}$] in the soil and penetrator sample

Table 11 $^{236}U/^{238}U$ in Chernobyl soil samples

Depth/cm	ICP-SFMS[a] Element	MC-ICP-MS[b] Nu instruments
0–5	$(6.74 \pm 0.12) \times 10^{-4}$	$(6.74 \pm 0.02) \times 10^{-4}$
5–10	$(5.3 \pm 0.3) \times 10^{-5}$	$(5.38 \pm 0.03) \times 10^{-5}$
10–15	$(1.6 \pm 0.1) \times 10^{-5}$	$(1.63 \pm 0.1) \times 10^{-5}$

[a]This work; [b]L. Halicz, Geological Survey of Israel, Jerusalem.[51]

Table 10 Characteristics of ICP-SFMS for uranium determination using different solution introduction systems

	Uptake rate/ mL min^{-1}	Sensitivity/ MHz ppm^{-1}	Overall detection efficiency/ counts fg^{-1}	UH^+/U^+
MicroMist	0.2	1900	570	1.8×10^{-4}
Q-DIHEN	0.010–0.060	600–1200	3600–1200	1×10^{-4}–5×10^{-4}
Aridus	0.1	3900	2340	3.2×10^{-5}
USN[a]	2.0	18000	540	3.8×10^{-5}

[a]USN with desolvator (USN without desolvator: 22 000 MHz ppm^{-1})

Table 12 Uranium isotopic ratios in water samples in presence of high concentration of matrix elements (Na ~ 130 mg L^{-1}, Mg ~ 30 mg L^{-1}, Ca ~ 46–93 mg L^{-1}) from the Sea of Galilee (for different depths) and in Sahina spring[a]

Sample	Uranium concentration/ μg L^{-1}	ICP-SFMS (this work)		MC-ICP-MS[a]
		$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{234}U/^{238}U$
LU 63 (-30 m)	0.65	$(8.4 \pm 0.5) \times 10^{-5}$	$(7.24 \pm 0.03) \times 10^{-3}$	$(8.9 \pm 0.1) \times 10^{-5}$
LU 63 (-20 m)	0.65	$(8.4 \pm 0.5) \times 10^{-5}$	$(7.24 \pm 0.03) \times 10^{-3}$	$(8.9 \pm 0.1) \times 10^{-5}$
LU 63 (-10 m)	0.66	$(8.4 \pm 0.5) \times 10^{-5}$	$(7.24 \pm 0.04) \times 10^{-3}$	$(8.9 \pm 0.1) \times 10^{-5}$
Sahina spring	4.5	$(6.4 \pm 0.3) \times 10^{-5}$	$(7.24 \pm 0.03) \times 10^{-3}$	$(6.9 \pm 0.1) \times 10^{-5}$
Table value		5.54×10^{-5}	7.25×10^{-3}	

[a]L. Halicz, Geological Survey of Israel, Jerusalem.[51]

investigated. The finding of an additional experimental was interesting, according to which the Pu detected in Kosovo soil samples (both contaminated and uncontaminated with depleted uranium) was a result of nuclear fallout from the Chernobyl accident, as demonstrated by the measured isotope ratio [$^{240}Pu/^{239}Pu$ (measured) of 0.35 ± 0.10 *vs.* Chernobyl fallout of $^{240}Pu/^{239}Pu$ ~0.33].[38]

Furthermore, Amselfelder red wine from Kosovo was investigated in our laboratory, with respect to uranium concentration and to contamination with depleted uranium, by ICP-SFMS using the microconcentric nebulizer Aridus with a desolvator for solution introduction. In different red wine samples a uranium concentration of 0.145 ± 0.011 μg L^{-1} was found, which is the normal background concentration. Depleted uranium and plutonium ($<10^{-5}$ μg L^{-1}) was not detectable.

In order to study the small isotope variation of uranium in nature, we investigated, together with the Geological Survey in Jerusalem,[51] water samples from the Sea of Galilee (at depths of 10 to 30 m) and the Sahina spring. Uranium concentrations in the Sea of Galilee and Sahina spring, which were found to be 0.7 μg L^{-1} and 4.5 μg L^{-1}, respectively, and uranium isotope ratios were determined in the presence of relatively high concentrations of matrix elements (Na = ~130 mg L^{-1}, Mg = ~30 mg L^{-1}, Ca = ~50–90 mg L^{-1}). The results of isotope ratio measurements of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ are summarized in Table 12. Whereas the measured $^{235}U/^{238}U$ isotope ratios are in agreement with the IUPAC table of isotopic composition of elements,[73] for the $^{234}U/^{238}U$ isotope ratio a significant enrichment by a factor of 1.5 using ICP-SFMS with a single ion collector (in good agreement with MC-ICP-MS[51]) was found. The more precise multi-collector measurements were performed using the MC-ICP-MS Nu Plasma.[51] The reason for the variation of $^{234}U/^{238}U$ in natural water samples from the Sea of Galilee (enrichment of ^{234}U abundance) can be explained as a result of the α decay of ^{238}U ($t_{1/2}$ - 4450 Ma) *via* short-lived ^{234}Th and ^{234}Pa nuclides (due to β^- decay with $t_{1/2}$ of 2.4 days and 6.7 h, respectively) in ^{234}U ($t_{1/2}$ - 0.245 Ma) *via* chemical activity (recoil effect). The isobaric daughter radionuclides (^{234}Th, ^{234}Pa and ^{234}U) leave the crystal lattice as ions (*e.g.*, in the mineral) and become free. Therefore, decay products are more chemically active than the parent ^{238}U radionuclides. The leaching of ^{234}Th and ^{234}Pa in aqua environments leads to ^{234}U enrichment in water. Also the Sahina spring shows a significant enrichment of 16% for ^{234}U in comparison to the value of the IUPAC table of isotopic composition of elements.[73]

Isotope ratio measurements by LA-ICP-MS allow a direct isotope analysis of solid samples without sample preparation. Nevertheless, in spite of the advantages of LA-ICP-MS, this technique has only been used in a few percent of published papers on the determination of isotope ratios. Most studies were performed in geological research as demonstrated by selected examples in this review. LA-ICP-MS will have increasing acceptance in the future especially for isotope ratio measurements in microlocal analysis. But the inhomogeneous distribution of analytes results in a decreasing precision. Furthermore, isotope fractionation effects at a laser power density of $<10^9$ W cm^{-2} can occur resulting in incorrect data.[105] One other problem is possible interferences with molecular ions, as demonstrated by LA-ICP-MS measurements of $^{230}Th/^{232}Th$ isotope ratios in solid radioactive waste samples, in comparison to ICP-MS measurements after digestion and Th separation.[23] Where no interference problems occur a good agreement between isotope ratios measured by LA-ICP-MS and ICP-MS after analyte separation has been found, as demonstrated for $^{235}U/^{238}U$ determination in radioactive silt, filter and ash samples.[23] The precise isotope analysis of uranium has been demonstrated in radioactive waste graphite using LA-ICP-SFMS. The $^{236}U/^{238}U$ isotope ratio of 10^{-4} was determined with a precision of 0.7%.[105] The detection limit for ^{233}U was 1.3 pg g^{-1} in a graphite matrix.

Different applications of laser ablation multiple ion collector ICP-MS for the determination of the isotope composition of Sr, Hf, W, and Pb in reference materials and geological samples are summarized in ref. 76.

A new calibration procedure in LA-ICP-MS for trace element determination on small amounts of high-purity platinum nano-clusters by on-line isotope dilution was introduced recently.[106] For the determination of Pb using on-line isotope dilution with LA-ICP-MS an isotope-enriched spike, ^{204}Pb solution [$^{204}Pb_{spike}$–51.2% *vs.* $^{204}Pb_{sample}$ (table value)–1.4%] was nebulized with a microconcentric nebulizer with the Aridus desolvator (Cetac Instruments, Ohio, USA). After some minutes the laser ablation of the platinum nano-clusters was started and, after an additional time, 2% nitric acid was nebulized instead of the spike solution. The change in $^{204}Pb/^{206}Pb$ isotope ratios during this procedure was measured. In all solution-based calibration strategies the different element sensitivities must be considered. After correction of the difference in sensitivities in LA-ICP-MS and ICP-MS, the Pb concentration was determined using the isotope dilution technique.

5 Future trends in isotope ratio measurements

What are the future trends in isotope ratio measurements? If we look for an answer we should ask, 'What are the limits to isotope ratio measurements or where is a development required?' With respect to the interference problem, an improvement in mass resolution by further development of ion trap or Fourier transform ion cyclotrom resonance mass spectrometry would be helpful. In order to reduce the instrumental background, new materials or an improvement in the vacuum system are required. For the measurement of very low isotope ratios, new ion detectors with very low noise should be developed. To improve abundance sensitivity, multistage MS-MS instruments could be applied.

Further requirements concern the lowering of isotope abundances to be measured, the lowering of detection limits,

smaller sample sizes and decreasing volumes of chemicals and waste. Especially, the improvement of isotope ratio measurements will be linked with an improvement of coupling techniques, as also will be more precise results with higher accuracy. Furthermore, there is a lack of suitable isotope reference materials so that new ones must be developed. The instrument users require more automation and miniaturization, but, for mass spectrometers there are physical limits.

6 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 sensitivity and very low detection limits, isotope ratio measurements are possible with very small sample amounts of analyte and for solid samples where mostly only simple preparation steps are required (compared to the time-consuming TIMS). The determination of isotope ratios with precisions of down to 0.02% RSD is possible with double-focusing sector field ICP-MS (with single ion collector), 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 using 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. Future trends in ICP-MS are further developments in multi-collector ICP-MS, collision cell devices, ion traps and coupling techniques.

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