

Sergei F. Boulyga · J. Sabine Becker

ICP–MS with hexapole collision cell for isotope ratio measurements of Ca, Fe, and Se

Received: 15 December 2000 / Revised: 26 March 2001 / Accepted: 27 March 2001

Abstract To avoid mass interferences on analyte ions caused by argon ions and argon molecular ions via reactions with collision gases, an rf hexapole filled with helium and hydrogen has been used in inductively coupled plasma mass spectrometry (ICP–MS), and its performance has been studied. Up to tenfold improvement in sensitivity was observed for heavy elements ($m > 100$ u), because of better ion transmission through the hexapole ion guide. A reduction of argon ions Ar^+ and the molecular ions of argon ArX^+ ($X = \text{O}, \text{Ar}$) by up to three orders of magnitude was achieved in a hexapole collision cell of an ICP–MS (“Platform ICP”, Micromass, Manchester, UK) as a result of gas-phase reactions with hydrogen when the hexapole bias (HB) was set to 0 V; at an HB of 1.6 V argon, and argon-based ions of masses 40 u, 56 u, and 80 u, were reduced by approximately four, two, and five orders of magnitude, respectively. The signal-to-noise ratio $^{80}\text{Se}/^{40}\text{Ar}_2^+$ was improved by more than five orders of magnitude under optimized experimental conditions. Dependence of mass discrimination on collision-cell properties was studied in the mass range 10 u (boron) to 238 u (uranium). Isotopic analysis of the elements affected by mass-spectrometric interference, Ca, Fe, and Se, was performed using a Meinhard nebulizer and an ultrasonic nebulizer (USN). The measured isotope ratios were comparable with tabulated values from IUPAC. Precision of 0.26%, 0.19%, and

0.12%, respectively, and accuracy of 0.13% 0.25%, and 0.92%, respectively, was achieved for isotope ratios $^{44}\text{Ca}/^{40}\text{Ca}$ and $^{56}\text{Fe}/^{57}\text{Fe}$ in $10 \mu\text{g L}^{-1}$ solution nebulized by means of a USN and for $^{78}\text{Se}/^{80}\text{Se}$ in $100 \mu\text{g L}^{-1}$ solution nebulized by means of a Meinhard nebulizer.

Introduction

Determination of the isotopic composition of Ca, Fe, and Se is important in several applications including semiconductor technology, biomedical studies, etc. Inductively coupled plasma mass spectrometry (ICP–MS) has been established as a very sensitive and precise trace analytical technique well suited for multielement analysis of samples from almost every field of scientific and technical interest [1–4] and for precise isotopic analysis [1, 2, 5, 6]. The determination of Ca, Fe, and Se is, however, disturbed by isobaric interferences, because of the formation of molecular ions and atomic ions of argon in ICP–MS. Suppression of interferences has been the aim of many investigations, which have been reviewed elsewhere [7, 8]. Although it is possible to separate most ArX^+ ions ($X = \text{N}, \text{O}, \text{Ar}$) from atomic ions of the analyte by use of double-focusing sector field mass spectrometry (DF-ICP–MS) [9], the use of the high-resolution mode involves a significant loss of ion intensity, as a consequence of very low transmission, which increases detection limits. Another approach used to eliminate argon-based interferences is application of the cold plasma technique in ICP–MS in combination with a shielded ICP torch [10, 11], but this technique limits determination of elements with high ionization potentials, e.g. Se.

Application of gas targets in inorganic mass spectrometry has been proposed [12] for reducing the background spectrum and improving sensitivity in isotopic and trace analysis; this exploits dissociation of interfering molecule ions. Gas-phase ion-molecule chemistry has found wide application in organic mass spectrometry for controlled dissociation of organic compounds and chemical ionization of analyte species in different types of ion source, in-

Dedicated to Dr. habil. Hans-Joachim Dietze on the occasion of his 65th birthday

S. F. Boulyga
Radiation Physics and Chemistry Problems Institute,
220109 Sosny, Minsk, Belarus

J. S. Becker (✉)
Central Department for Analytical Chemistry,
Research Centre Jülich, 52425 Jülich, Germany
e-mail: s.becker@fz-juelich.de

Present address:

S. F. Boulyga,
Central Department for Analytical Chemistry,
Research Centre Jülich, 52425 Jülich, Germany

cluding pressurized rf-multipoles [13]. The physical processes and chemical reactions of ions with neutral species in gas-filled rf-multipoles (i.e. combination of rf-multipole with a collision cell) have been investigated using an ion trap [14], different types of mass spectrometer, and other techniques [15]. Along with neutralization or fragmentation of interfering atomic and molecular ions the pressurized rf-multipole was found to be useful for improving ion focusing, because of ion cooling when studying the performance of the three-dimensional quadrupole ion trap [16]; the same effect, named “collisional focusing”, was subsequently found for the linear quadrupole ion guide [17]. Studies of ion kinetics, dynamics, and thermochemistry in pressurized rf quadrupoles have been reviewed in recent works by Douglas [18] and Armentrout [19].

The ion-optical properties of higher-order multipoles (hexapoles and octapoles) utilizing rf and dc operation were first investigated by Hagg and Szabo [20]. In this study the hexapole was found to be well suited for transporting, guiding, and confining low-energy ion beams, because of the large region of total ion stability compared with that of quadrupole geometry, although the stability diagram of the hexapole is more diffuse and depends on the initial conditions.

Attenuation of argon molecular ions via gas-phase collisions has been studied in ICP–MS [21] and ion-trap mass spectrometry with an ICP ion source [22]. Hydrogen was applied [23] as a collision gas to remove argon molecular ions. By collision with hydrogen (H_2), Ar^+ ions and molecular ions ArX^+ react via charge transfer ($Ar^+ + H_2 \rightarrow H_2^+ + Ar$), hydrogen atom transfer ($Ar^+ + H_2 \rightarrow ArH^+ + H$), and proton transfer ($ArH^+ + H_2 \rightarrow H_3^+ + Ar$), etc. into ions and neutrals which do not disturb the mass of interest (e.g. $^{40}Ar^{16}O^+$ vs $^{56}Fe^+$, $^{40}Ar^+$ vs $^{40}Ca^+$ etc.).

Recently, a collision cell based on an rf-multipole was introduced in ICP–QMS by various mass spectrometric

companies [24–27]. Inductively coupled quadrupole mass spectrometry with a hexapole collision cell (HEX-ICP–QMS) was found useful for the attenuation of atomic and molecular ions of argon [28, 29], for reducing O_2^+ ions, in the determination of the sulfur isotope ratio [30], and attenuation of metal oxide ions [31]. ICP–MS with a dynamic reaction cell has been used for precise measurement of the isotopic composition of lead and iron [32].

The aim of this work was to determine isotope ratios for elements which are difficult to analyze, e.g. calcium, iron, and selenium, and to study influence of HEX-ICP–MS conditions on mass-discrimination effects. Special attention was paid to improvement of the measurement accuracy for isotopes subjected to spectrometric interference with atomic and molecular ions of argon.

Experimental

Instrumentation used for ICP–MS. A quadrupole-based HEX-ICP–QMS mass spectrometer (“Platform ICP”, Micromass, Manchester, UK) was used for isotope ratio measurements. The ions formed in the ICP were accelerated by application of a negative voltage of -600 V to the extraction lens (cone voltage) and transported through the hexapole from the region behind the skimmer cone into the quadrupole mass analyzer. Helium and hydrogen were introduced into the hexapole cell as collision gases. Because direct control of the operating gas pressure in the hexapole is not possible with the HEX-ICP–QMS, flow rates of collision gases were controlled in this study. The nebulizer and collision gas flow rates are controlled by use of built-in mass flow controllers. A Daly-type photomultiplier detector is used in the configuration with an ion-electron conversion dynode and a photon-producing phosphor plate. The multiplier gain of the ‘Daly’-type ion detector operated in analogue mode was set such that the recorded signal intensity would be equal to the ion-counting rate of a pulse-counting detector [33].

A Meinhard nebulizer (J.E. Meinhard Associates, USA) with a Scott double-pass quartz spray chamber cooled to $4^\circ C$ and an ultrasonic nebulizer (USN U-6000AT+, CETAC Technologies, USA) were used for introduction of solutions.

Table 1 Experimental conditions used for isotope analysis by HEX-ICP–QMS (Platform, Micromass)

Condition	Meinhard nebulizer with Scott double-pass spray chamber	Ultrasonic nebulizer
Rf power, W	1350	1350
Coolant gas flow rate, L min ⁻¹	13.5	13.5
Auxiliary gas flow rate, L min ⁻¹	1.0	0.9
Nebulizer gas flow rate, L min ⁻¹	0.95	0.9
Solution uptake rate, mL min ⁻¹	0.9	2.0
USN heating temperature, °C	–	140
USN cooling temperature, °C	–	3
Cone lens, V	–600	–600
Hexapole exit lens, V	–400	–400
Hexapole bias, V	0.0–2.0	0.0–2.0
Ion energy lens, V	–2.0	–2.0
Multiplier voltage, V	–450	–450
H ₂ gas flow, mL min ⁻¹	2.0	2.0
He gas flow, mL min ⁻¹	4.0	4.0
Dwell time, s	0.2	0.2
Total analysis time, min	1–2	1–2
Number of repeat measurements	6	6
Mass resolution (m/Δm)	300	300
Mass range	9 u–238 u	9 u–238 u

Reagents. Single-element standard stock solutions of B, Mg, Fe, Cu, Se, Mo, Rh, Cd, Sb, Eu, Ir, Tl, and U for the measurement of characteristics and quantification purposes were obtained from Merck (Darmstadt, Germany) and from the National Institute of Standards and Technology (NIST). NIST SRM 915 calcium carbonate was used for calcium isotope measurements. An isotopic standard solution of uranium with $^{235}\text{U}/^{238}\text{U} = 0.99991$ (CCLU-500 laboratory standard, Nuclear Research Center, Prague, Czech Republic) [34] was used for measurement of uranium mass bias. Reagents were diluted, with deionized Milli-Q water (18 M Ω) obtained from a Millipore Milli-Q-Plus water purifier, to concentrations in the range 10 to 100 $\mu\text{g L}^{-1}$, the solutions were acidified to 1% HNO_3 with subboiled nitric acid.

Measurement procedure. The experimental conditions were first optimized for maximum ion intensity of the corresponding element in respect of torch position, and selection of the optimum rf-power and cooling, auxiliary and nebulizer gas flow rates. Flow rates of helium and hydrogen introduced into the hexapole cell as collision gases, for study of instrumental characteristics, varied between 0 mL min^{-1} and 10 mL min^{-1} . To obtain better stability of ion intensity dwell and settle times of the quadrupole analyzer were chosen by taking into account instrumental noise frequencies. Optimized experimental conditions of the HEX-ICP-QMS used for isotopic measurements are summarized in Table 1. In this work the data were acquired in six runs, monitoring all isotopes for up to 120 s in each run, i.e. a total of 12 min. The measured isotope ratios in soil samples were corrected by using the measured background, the mass discrimination factors determined experimentally according to a procedure described elsewhere [5], and hydride rate SeH^+ for $^{77}\text{Se}/^{80}\text{Se}$ and $^{78}\text{Se}/^{80}\text{Se}$ ratios. The combined uncertainty of isotope ratio was calculated taking into account standard deviations of the measured ratio, background, and uncertainty of mass discrimination factor as described elsewhere [35]. For $^{77}\text{Se}/^{80}\text{Se}$ and $^{78}\text{Se}/^{80}\text{Se}$ ratio measurements, the uncertainty of the correction factor owing to selenium hydrides SeH^+ was also considered.

Results and discussion

Sensitivity improvement for analyte ions and reduction of argon-based molecular ions

Use of a collision gas in an rf-hexapole resulted in improved sensitivity as a result of ion cooling and reduction of the mean free paths of the ions to the dimensions of the hexapole. Figure 1 shows measured ion intensities of $^7\text{Li}^+$, $^{24}\text{Mg}^+$, $^{103}\text{Rh}^+$, and $^{238}\text{U}^+$ as a function of helium flow rate. These results show that sensitivity was increased by up to one order of magnitude for heavy elements ($m > 100$ u) at higher gas flow rates (corresponding to higher gas pressure), because of improved transmission of the ion beam through the hexapole. When using hydrogen as a collision gas the sensitivity was improved up to threefold for heavy elements. Ion transmission depends strongly on the mass of the analyte ion, the mass of collision gas atoms, and the pressure and chemical properties of the gas [36]. Thus for light elements maximum intensity is reached at a helium flow rate of several mL min^{-1} (see $^{24}\text{Mg}^+$), or a decrease of sensitivity might even be observed (see $^7\text{Li}^+$).

To investigate the efficiency of attenuation of argon-based molecular ions their intensities were measured as a function of hydrogen gas flow rates in a 1% nitric acid blank solution. The experiments (Fig. 2) showed that application of gas-filled collision cells in ICP-QMS enabled reduction of the intensity of argon ions Ar^+ and molecular

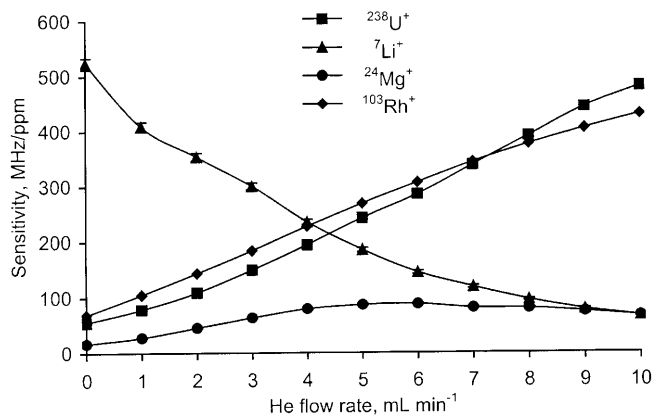


Fig. 1 Dependence of $^7\text{Li}^+$, $^{24}\text{Mg}^+$, $^{103}\text{Rh}^+$, and $^{238}\text{U}^+$ ion sensitivity on helium flow rate. Solution introduced by means of a Meinhard nebulizer, hexapole bias 0.0 V (for other experimental conditions see Table 1)

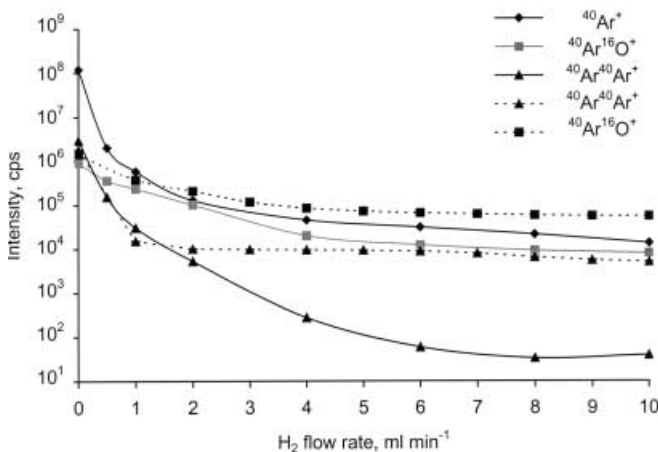


Fig. 2 Dependence on hydrogen flow rates of the intensities of argon ion Ar^+ and of molecular argon-based ions ArX^+ ($X = \text{O}, \text{Ar}$), measured at masses 40 u, 56 u, and 80 u, respectively, in 1% HNO_3 blank solution introduced by means of a Meinhard nebulizer (for other experimental conditions see Table 1). Solid lines correspond to hexapole bias set to 1.6 V, dashed lines correspond to hexapole bias set to 0 V

ions of argon ArX^+ ($X = \text{O}, \text{Ar}$) by up to three orders of magnitude when the hexapole bias (HB) potential was set to 0 V; at an HB of 1.6 V argon and argon-based ions of masses 40 u, 56 u, and 80 u were reduced by approximately four, two, and five orders of magnitude, respectively due to collision-induced reaction of Ar^+ and ArX^+ with hydrogen, and application of the hexapole bias [28, 29, 36]. In addition, Ar^+ , ArO^+ , and ArAr^+ ions are suppressed by the HB after moderation of the ions in a gas-filled collision cell. Although suppression of analyte ion intensities is also observed on applying the hexapole bias, argon molecular ions are cooled more effectively than analyte ions, and they are more affected by the HB (Fig. 3). For instance, the signal-to-noise ratio $^{80}\text{Se}^+ / ^{40}\text{Ar}_2^+$ in 100 $\mu\text{g L}^{-1}$ selenium solution, introduced by means of the Meinhard nebulizer with a Scott double-pass quartz spray chamber, was 0.055 without the use of collision

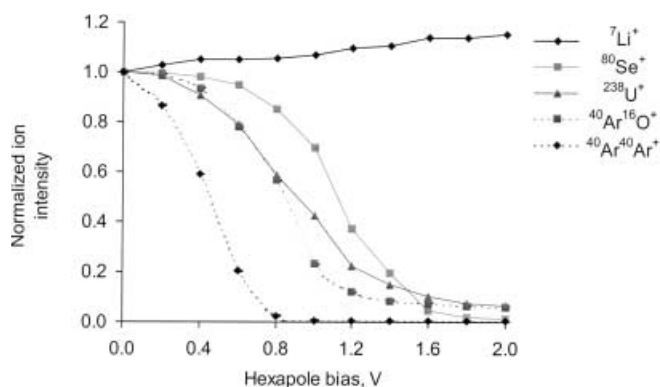


Fig. 3 Dependence of the intensity of analyte ions and argon molecule ions on the hexapole bias normalized to HB = 0 V. The solution was introduced by means of a Meinhard nebulizer (for other experimental conditions see Table 1)

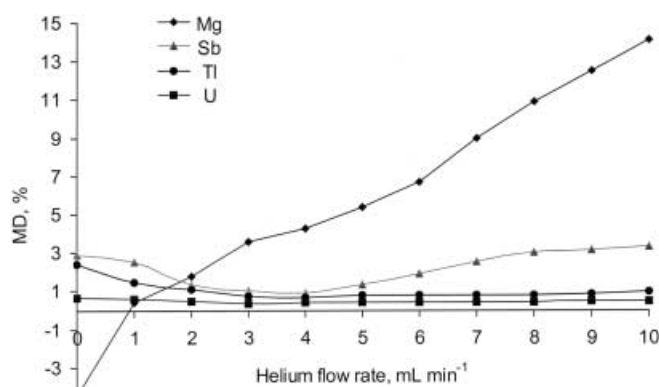


Fig. 4 Mass discrimination, as a function of helium flow rate, for $^{24}\text{Mg}/^{25}\text{Mg}$, $^{121}\text{Sb}/^{123}\text{Sb}$, $^{203}\text{Tl}/^{205}\text{Tl}$, and $^{238}\text{U}/^{238}\text{U}$ isotope ratios. No hydrogen was introduced into the hexapole collision cell, hexapole bias 0 V (for other experimental conditions see Table 1)

gases at a hexapole bias of 0 V. When, however, hydrogen at 2 mL min^{-1} and helium at 8 mL min^{-1} were introduced, this ratio reached 92 and 1.9×10^4 at hexapole biases of 0 V and 1.6 V, respectively. Thus the signal-to-noise ratio for $^{80}\text{Se}^+$ can be improved by more than three orders of magnitude by application of collision gases and by approximately 200-fold by application of the hexapole bias. In this work the overall improvement in signal-to-noise ratio for $^{80}\text{Se}^+$ was 3.4×10^5 .

It should be mentioned that the acid and Milli-Q-water blank must be free from contamination with Ca and Fe if the real extent of $^{40}\text{Ar}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$ reduction is to be apparent, otherwise after reducing $^{40}\text{Ar}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$ ions measured “blank” spectra represent $^{40}\text{Ca}^+$ and $^{56}\text{Fe}^+$ peaks. Obtaining a sufficiently clean experimental environment and tools is, however, very expensive and labor- and time-consuming [37] and was not within the aims of this work.

When hydrogen is introduced as a collision gas the rate of hydride formation must be taken into consideration, because it affects the measurement accuracy of ions of mass $m + 1$. For elements such as Se, Br, etc., especially large amounts of hydride formation (up to 9%) were observed. Interestingly, this result is close to the SeH^+ value reported by Sloth and Larsen [38] when using a dynamic reaction cell filled with methane.

Mass discrimination in HEX-ICP-MS

A gas-filled hexapole collision cell is expected to alter mass discrimination in ICP-MS, because of the mass-dependent transmission efficiency of ions and the changing space charge after removal of Ar^+ ions from the ion beam. Figure 4 shows the dependence of mass discrimination per mass unit (MD) on helium flow rate for Mg, Sb, Tl, and U, measured in $100 \mu\text{g L}^{-1}$ solutions introduced by means of a Meinhard nebulizer with a Scott double-pass spray chamber (the HB was set to 0 V). If no gas was introduced into the hexapole collision cell negative mass

discrimination was observed for light isotopes (see Mg in Fig. 4). The addition of helium altered the mass bias for Mg because light isotopes are scattered by helium atoms, which results in an appreciable change in the ion trajectory and hence ion losses. The mass bias for heavier ions ($m > 100 \text{ u}$) decreased when helium was introduced at a flow rate of up to 4 mL min^{-1} . Further increasing the helium flow rate, however, also resulted in increased mass bias for heavy ions up to uranium. Altered mass discrimination was also observed when introducing hydrogen. The MD values obtained in HEX-ICP-MS by introducing $100 \mu\text{g L}^{-1}$ of multielement solution covering the mass range from 9 u to 238 u are compared in Table 2 with those for Elan 5000 [5]. Changing the hexapole bias from 0 V to 2.0 V reduced mass bias for light isotopes and increased mass bias for heavy isotopes. In addition, mass discrimination per mass unit in HEX-ICP-QMS at an HB of 0 V

Table 2 Mass discrimination per mass unit for different elements in the mass range from 6 u to 238 u (measured by use of HEX-ICP-MS in $100 \mu\text{g L}^{-1}$ multielement solution introduced by means of a Meinhard nebulizer)

Isotope ratio analyzed	Mass discrimination per mass unit, %		
	HEX-ICP-QMS		ICP-QMS Elan 5000 [5]
	HB 0.0	HB 1.6 V	
$^6\text{Li}/^7\text{Li}$	–	–	16.7
$^{10}\text{B}/^{11}\text{B}$	17.1	12.7	–
$^{24}\text{Mg}/^{26}\text{Mg}$	7.9	4.5	4.8
$^{63}\text{Cu}/^{65}\text{Cu}$	3.3	2.1	4.2
$^{92}\text{Mo}/^{98}\text{Mo}$	1.8	1.4	2.5
$^{112}\text{Cd}/^{114}\text{Cd}$	0.86	1.27	1.1
$^{121}\text{Sb}/^{123}\text{Sb}$	0.64	1.22	–
$^{151}\text{Eu}/^{153}\text{Eu}$	0.39	1.16	–
$^{182}\text{W}/^{184}\text{W}$	–	–	0.34
$^{191}\text{Ir}/^{193}\text{Ir}$	0.26	0.67	–
$^{203}\text{Tl}/^{205}\text{Tl}$	0.28	0.55	0.27
$^{235}\text{U}/^{238}\text{U}$	0.21	0.60	–

Table 3 Mass discrimination per mass unit determined using ratios of different selenium isotopes with correction of hydride formation rate (values without correction are given in brackets) ($100 \mu\text{g L}^{-1}$ Se solution introduced by means of a Meinhard nebulizer)

Isotope ^xSe	$^x\text{Se}/^{78}\text{Se}$	$^x\text{Se}/^{80}\text{Se}$	$^x\text{Se}/^{82}\text{Se}$
^{74}Se	0.040 (0.050)	0.040	0.040
^{76}Se	0.036 (0.053)	0.036	0.036
^{77}Se	0.037 (-0.036)	0.035 (-0.00143)	0.036 (0.0123)
^{78}Se	–	0.033 (0.0164)	0.034 (0.025)
^{80}Se	0.033	–	0.033
^{82}Se	0.034	0.033	–

Table 4 Measured mass discrimination per mass unit and isotope ratios in $20 \mu\text{g L}^{-1}$ calcium solution and iron solution (solution introduced by means of an ultrasonic nebulizer)

Isotope ratio	Mass discrimination
$^{40}\text{Ca}/^{44}\text{Ca}$	0.0526
$^{42}\text{Ca}/^{44}\text{Ca}$	0.0525
$^{43}\text{Ca}/^{44}\text{Ca}$	0.0529
$^{54}\text{Fe}/^{57}\text{Fe}$	0.049
$^{56}\text{Fe}/^{57}\text{Fe}$	0.052

was found to be similar to MD for both the ICP-QMSs, despite different ion optic and ion detection systems.

In general, mass bias in the HEX-ICP-QMS is a complex function of collision cell conditions. In all further isotopic measurements hexapole bias was set 1.6 V to avoid additional mass fractionation, despite the lower rate of reduction of argon ions and argon-based molecule ions.

Determination of the isotope ratio of selenium using an ICP-QMS with a hexapole collision cell and hydrogen as the reaction gas required correction of the experimental results because of formation of selenium hydride ions SeH^+ in the collision cell. The selenium hydride ratio $^{80}\text{Se}^1\text{H}^+ / ^{80}\text{Se}^+$ and mass discrimination per mass unit was investigated in $100 \mu\text{g L}^{-1}$ Se solution introduced by means of the Meinhard nebulizer. The measured $^{80}\text{Se}^1\text{H}^+ / ^{80}\text{Se}^+$ ratio was approximately 9%. Later the measured intensities of $^{77}\text{Se}^+$ and $^{78}\text{Se}^+$ were corrected taking into account the formation of the hydrides $^{76}\text{Se}^1\text{H}^+$ and $^{77}\text{Se}^1\text{H}^+$. Table 3 pre-

sents results from mass-discrimination measurements for different combinations of selenium isotopes calculated with and without correction for hydride formation. Corrected results for different isotope ratios coincided within experimental error.

The MD values for Ca and Fe determined using $20 \mu\text{g L}^{-1}$ Ca and Fe solution introduced by means of an ultrasonic nebulizer are given in Table 4.

Determination of the isotopic composition of calcium, iron, and selenium

The presence of $^{40}\text{Ar}^+$ and the argon-based molecular ions $^{40}\text{Ar}^{14}\text{N}^+$, $^{40}\text{Ar}^{16}\text{O}^+$, $^{36}\text{Ar}^{40}\text{Ar}^+$, and $^{40}\text{Ar}^{40}\text{Ar}^+$ in argon plasma disturbs the measurement of the isotopes ^{40}Ca , ^{54}Fe , ^{56}Fe , ^{76}Se , and ^{80}Se , respectively. As was discussed above, application of a gas-filled hexapole collision cell reduces argon ions and argon molecular ions and hence makes it possible to determine these isotopes. The isotope ratios $^{54}\text{Fe}/^{57}\text{Fe}$, $^{56}\text{Fe}/^{57}\text{Fe}$, $^{40}\text{Ca}/^{44}\text{Ca}$, $^{42}\text{Ca}/^{44}\text{Ca}$, and $^{43}\text{Ca}/^{44}\text{Ca}$ were measured in $10 \mu\text{g L}^{-1}$ Ca and Fe solution introduced by means of an ultrasonic nebulizer using the mass discrimination factors previously determined. It was observed that mass discrimination changed slightly during operation, mainly as a result of clogging effects on the cones. MD values were therefore determined shortly before measuring the isotope ratios of Ca, Fe, and Se. Measured isotope ratios are compared with tabulated values from IUPAC (International Union of Pure and Applied Chemistry) [39] in Table 5. The precision of the $^{56}\text{Fe}/^{57}\text{Fe}$ and $^{40}\text{Ca}/^{44}\text{Ca}$ ratios is comparable with that of other quadrupole instruments for interference-free isotope ratios. The accuracy and precision of selenium isotope ratios measured in $100 \mu\text{g L}^{-1}$ Se solution introduced by means of a Meinhard nebulizer (Table 5) seem to be satisfactory, taking into account the relatively low concentration of analyte. One should note that this determination would be not possible by conventional ICP-MS. Ultrasonic nebulization was affected by a memory effect when selenium was measured; it was, therefore, not used in this work.

Table 5 Measured isotope ratios for selenium, with correction of mass discrimination and hydride formation ($10 \mu\text{g L}^{-1}$ Ca and Fe solutions were introduced by means of an ultrasonic nebulizer, $100 \mu\text{g L}^{-1}$ Se solution was introduced by means of a Meinhard nebulizer)

Isotope ratio	Experimental value	RSD of the measured ratio ($n = 6$), %	Combined uncertainty, %	From IUPAC [39]	Accuracy of measured ratio (II-V)/V, %
I	II	III	IV	V	VI
$^{40}\text{Ca}/^{44}\text{Ca}$	46.41	0.26	0.41	46.47	0.13
$^{42}\text{Ca}/^{44}\text{Ca}$	0.311	0.40	0.59	0.310	-0.32
$^{43}\text{Ca}/^{44}\text{Ca}$	0.0653	0.82	1.2	0.0647	-0.93
$^{54}\text{Fe}/^{57}\text{Fe}$	2.755	0.22	0.36	2.758	0.11
$^{56}\text{Fe}/^{57}\text{Fe}$	43.41	0.16	0.28	43.30	-0.25
$^{74}\text{Se}/^{80}\text{Se}$	0.0175	0.75	1.4	0.01794	2.45
$^{76}\text{Se}/^{80}\text{Se}$	0.1876	0.25	0.55	0.1889	0.69
$^{77}\text{Se}/^{80}\text{Se}$	0.1526	0.33	0.70	0.1539	0.84
$^{78}\text{Se}/^{80}\text{Se}$	0.4747	0.26	0.58	0.4791	0.92
$^{82}\text{Se}/^{80}\text{Se}$	0.1714	0.20	0.39	0.1760	2.61

Conclusion

The application of a gas-filled hexapole collision cell is an effective tool for improving sensitivity and reducing argon-based molecular ions and hence improving accuracy and precision in isotopic measurements of “difficult-to-analyze” elements. Background ion intensities caused by argon ions and argon-based molecular ions at masses of 40 u, 56 u, and 80 u were reduced by several orders of magnitude by collision-induced reaction with hydrogen and helium as collision gases and application of a hexapole bias. Measurement of isotopic ratios of calcium ($^{40}\text{Ca}/^{44}\text{Ca}$, $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{43}\text{Ca}/^{44}\text{Ca}$), iron ($^{54}\text{Fe}/^{57}\text{Fe}$ and $^{56}\text{Fe}/^{57}\text{Fe}$) and selenium ($^{74}\text{Se}/^{80}\text{Se}$, $^{76}\text{Se}/^{80}\text{Se}$, $^{77}\text{Se}/^{80}\text{Se}$, $^{78}\text{Se}/^{80}\text{Se}$ and $^{82}\text{Se}/^{80}\text{Se}$) yielded good accuracy and precision of HEX-ICP-QMS using relatively low concentrations of analyte (10 $\mu\text{g L}^{-1}$ Ca and Fe nebulized by means of an USN and 100 $\mu\text{g L}^{-1}$ Se nebulized by means of a Meinhard nebulizer). When hydrogen was used as collision gas, however, the hydride ratio increased substantially, reaching 9% for non-metallic elements. It is, therefore, important to correct selenium isotope ratios measured by ICP-QMS with a collision cell, to take hydride formation into account.

Acknowledgements SFB gratefully acknowledges a research fellowship from the Alexander von Humboldt Foundation, Bonn, Germany.

References

1. Taylor HE, Huff R, Montaser A, Novel Applications of ICPMS. In *Inductively Coupled Plasma Mass Spectrometry*, Montaser A (ed.), Wiley-VCH, 1998, 681–807
2. Becker JS, Dietze HJ (2000) *Int J Mass Spectrom* 197:1–35
3. Taylor A, Branch S, Halls DJ, Owen LMW, White M (1999) *J Anal At Spectrom* 14:717–781
4. Cave MR, Butler O, Cook JM, Cresser MS, Garden LM, Holden AJ, Miles DL (1999) *J Anal At Spectrom* 14:279–352
5. Heumann KG, Gallus SM, Raedlinger G, Vogl J (1998) *J Anal At Spectrom* 13:1001–1008
6. Becker JS, Dietze HJ, Fresenius J Anal Chem 368:23–30
7. Becker JS, Dietze HJ (1998) *Spectrochim Acta B* 53:1475–1506
8. Jakubowski N, Moens L, Vanhaecke F (1998) *Spectrochim Acta B* 53:1739–1763
9. Becker JS, Dietze HJ (1997) *J Anal At Spectrom* 12:881–889
10. Jiang SJ, Houk RS, Stevens MA (1988) *Anal Chem* 60:1217–1221
11. Sakata K, Kawabata K (1994) *Spectrochim Acta B* 49B:1027–1038
12. Becker JS, Dietze HJ (1983) *Isotopenpraxis* 19:105–112
13. Harrison AG, *Chemical ionization mass spectrometry*, CRC Press, Boca Raton, Florida, 1992
14. March RE, Hughes RJ, *Quadrupole storage mass spectrometry*, Chemical Analysis, 102, John Wiley and Sons, 1989, 496
15. Farrar JM, Saunders WH, *Techniques for the Study of Ion-Molecule Reactions*, John Wiley and Sons, 1988, 652
16. Bonner RF, March RE, Durup J (1976) *Int J Mass Spectrom Ion Phys* 22:17–51
17. Douglas DJ, French JB (1992) *J Am Soc Mass Spectrom* 3:398–408
18. Douglas DJ (1998) *J Am Soc Mass Spectrom* 9:101–113
19. Armentrout PB (2000) *Int J Mass Spectrom* 200:219–241
20. Hagg C, Szabo I (1986) *Int J Mass Spectrom* 73:237–275
21. Rowan JT, Houk RS (1989) *Appl Spectrosc* 43:976–980
22. Koppelaar DW, Barinaga CJ, Smith MR (1994) *J Anal At Spectrom* 9:1053–1058
23. Eiden GC, Barinaga CJ, Koppelaar DW (1996) *J Anal At Spectrom* 11:317–322
24. Turner P, Merren T, Speakman J, Haines C, *Interface studies in the ICP-MS spectrometer*. In: *Plasma source mass spectrometry. Developments and applications*. Holland G, Tanner SD (eds), Special Publication of the Royal Society of Chemistry (No. 202), Cambridge, 1997, pp 28–34
25. Tanner SD, Baranov VI, *Fundamental processes impacting performance of an ICP-MS dynamic reaction cell*. In: *Plasma source mass spectrometry. New developments and applications*. Holland G, Tanner SD (eds), The Royal Society of Chemistry, Cambridge, 1999, pp 46–62
26. Baranov VI, Tanner SD, (1999) *J Anal At Spectrom* 14:1133–1142
27. Tanner SD, Baranov VI (1999) *J Am Soc Mass Spectrom* 10:1083–1094
28. Feldmann I, Jakubowski N, Stuewer D (1999) *Fresenius J Anal Chem* 365:415–421
29. Feldmann I, Jakubowski N, Thomas C, Stuewer D (1999) *Fresenius J Anal Chem* 365:422–428
30. Mason PRD, Kaspers K, van Bergen MJ (1999) *J Anal At Spectrom* 14:1067–1074
31. Du Zh, Houk RS (2000) *J Anal At Spectrom* 15:383–388
32. Bandura DR, Baranov VI, Tanner SD, (2000) *J Anal At Spectrom* 15:921–928
33. Speakman J, Turner PJ, Eaton AN, Abou-Shakra F, Palacz Z, Haines RC, *European Winter Conference on Plasma Spectrochemistry*, Pau, France, 10–15 January 1999
34. Platzner IT, Becker JS, Dietze HJ (1999) *Atom Spectrosc* 20:6–12
35. EURACHEM/CITAC Guide, *Quantifying Uncertainty in Analytical Measurement*, Second Edition Ellison SLR, Rosslein M, Williams A (eds), London, 2000, 120
36. Boulyga SF, Dietze HJ, Becker JS (2001) *Mikrochim Acta* (in press)
37. Tanner SD, Baranov VI, Vollkopf U (2000) *J Anal At Spectrom* 15:1261–1269
38. Sloth JJ, Larsen EH (2000) *J Anal At Spectrom* 15:669–672
39. Rosman KJR, Taylor PDP (eds) (1999) *J Anal At Spectrom* 14, 5N-23N