

# Improvement of abundance sensitivity in a quadrupole-based ICP-MS instrument with a hexapole collision cell†

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Received 27th March 2002, Accepted 24th May 2002

First published as an Advance Article on the web 3rd July 2002

High isotopic abundance sensitivity is desirable for the measurement of low-abundance isotopes in the presence of neighboring high-abundance isotopes. This is of interest when analyzing ultra low concentrations of trace elements or isotopes in the presence of elements or isotopes with much higher concentrations (e.g., radionuclides included in a matrix of stable isotopes). In this study, a quadrupole-based inductively coupled plasma mass spectrometer with a hexapole collision cell (ICP-CC-QMS), Platform ICP (Micromass UK), was used to study the improvement of abundance sensitivity using uranium and lutetium as examples. The median kinetic energy of  $^{238}\text{U}^+$  ions was about 1.2 eV and 0.9 eV when helium was introduced as a collision gas at flow rates of 5 ml min<sup>-1</sup> and 10 ml min<sup>-1</sup>, respectively. In the latter case, the proportion of ions with relatively high energy decreased significantly, which improved both the transmission of ions through the hexapole collision cell and mass selection by the quadrupole mass spectrometer. When introducing helium into the collision cell a reduction in peak tail of high-abundance isotopes by up to three orders of magnitude, depending on the mass analyzed, was observed. The abundance sensitivity for  $^{236}\text{U}/^{238}\text{U}$  isotope ratio was improved from  $2.3 \times 10^{-5}$  to  $6.3 \times 10^{-8}$ . Abundance sensitivities as low as  $3.5 \times 10^{-8}$ ,  $6.6 \times 10^{-8}$  and  $2.0 \times 10^{-8}$  were achieved at masses  $m - 2.5$  u,  $m - 1.5$  u and  $m + 2.5$  u ( $m = 174.94$  u for  $^{175}\text{Lu}$ ), respectively. Reducing the kinetic energy also improved the mass resolution by about 10%. However, increasing the mass resolution of the quadrupole instrument had a significantly lower influence on abundance sensitivity than reducing the ion energy by collision with helium atoms. The present study of the effect of the pressurized ion guide on abundance sensitivity was limited to some extent because of the relatively high background count rate of the Daly-type ion detector in the ICP-CC-QMS system. An ion detector possessing a low background would be desirable for further studies. Improved abundance sensitivity can be useful in analyzing long-lived radionuclides like  $^{236}\text{U}$  and  $^{129}\text{I}$  in the presence of high-abundance stable isotopes like  $^{238}\text{U}$  and  $^{127}\text{I}$ .

## Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most powerful inorganic mass spectrometric techniques and is widely used for fast and sensitive multi-element analysis and precise isotope measurement.<sup>1-3</sup> Nowadays, ICP-MS is applied for trace element determination in biological, medical and environmental samples, high-purity materials, semiconductors *etc.*<sup>3</sup> Furthermore, ICP-MS surpasses conventional radioanalytical techniques in sensitivity when analyzing long-lived radionuclides.<sup>4</sup> Quadrupole mass analyzers are employed as standard tools in ICP-MS because of their good sensitivity, wide dynamic range, robustness and relatively low cost. Nevertheless, quadrupole-based ICP-MS possesses some well known limitations, in particular when determination of trace elements or isotope ratios is required in the presence of elements or isotopes with much higher concentrations, which represent potential sources of interference. For instance, such problems arise when measuring solid materials directly without matrix separation or when determining an ultra low concentration of a radionuclide, which is included in the matrix of stable isotopes of the same element. In particular, peak tailing of a high-abundance isotope with mass  $m$  can be observed at neighboring masses  $m \pm 1$ ,  $m \pm 2$  *etc.* in different mass spectrometers.<sup>5-11</sup> The isotopic abundance sensitivity, or abundance sensitivity, is

usually expressed as the ratio of intensity (counts s<sup>-1</sup>) of the peak tail measured at mass  $m - 1$  (or  $m + 1$ ) to intensity (counts s<sup>-1</sup>) of the peak measured at mass  $m$ .<sup>5,10,11</sup> High isotopic abundance sensitivity is desirable for detecting a weak isotope peak directly adjacent to a strong neighboring peak.

In quadrupole-based ICP-MS, abundance sensitivity is restricted by the number of ions with higher kinetic energy, which may overcome the spatially limited filtering rf field of the quadrupole mass analyzer.<sup>5,12</sup> This limitation can be partially overcome by operation of the quadrupole in higher stability regions<sup>6</sup> or by using a tandem quadrupole mass analyzer.<sup>7</sup> Another way of obtaining a high level of mass separation is by increasing the interaction time of ions with the filtering field, so that, in principle, all ions with incorrect  $m/z$  values must experience a sufficiently strong transverse acceleration and must be rejected.<sup>12,13</sup> Reducing the ion kinetic energy leads to an increase in the residence time of ions in the quadrupole mass analyzer and results in improved mass separation. For that purpose, the ion beam can be moderated by collisions with gas atoms in a collision cell before entering the mass analyzer.

The application of gas targets in inorganic mass spectrometry for reducing the background spectrum and improving the sensitivity in isotopic analysis has been described by Becker and Dietze.<sup>14</sup> The introduction of a collision gas into an rf multipole was found to be useful for improving ion focusing due to a decrease in ion kinetic energy, and for reducing the mean free paths of ions to the dimensions of the rf-multipole when studying the performance of the three-dimensional

†Presented in part at the 2002 Winter Conference on Plasma Spectrochemistry, Scottsdale, AZ, January 6–12, 2002.

quadrupole ion trap.<sup>15</sup> The same effect, the so called “collisional focusing”, has been found for the linear quadrupole ion guide.<sup>16,17</sup> Studies of ion kinetics, dynamics and thermochemistry in pressurized rf quadrupoles have been reviewed in recent works by Douglas<sup>17</sup> and Armentrout.<sup>18</sup> In quadrupole-based ICP-MS with a hexapole collision cell (ICP-CC-QMS), the effect of ion beam moderation by collision with gas atoms decreases the ion energy down to about 2 eV<sup>19</sup> and, therefore, an improvement of abundance sensitivity can be expected in ICP-CC-QMS.

The aim of this work was to study the effect of the hexapole collision cell filled with helium on ion energy distribution and to improve the abundance sensitivity in ICP-CC-QMS, for <sup>236</sup>U analysis in particular, using ion moderation in the collision cell.

## Experimental

### ICP-MS instrumentation

A quadrupole-based ICP-MS instrument with a hexapole collision cell (Platform, Micromass Ltd., Manchester, UK) was used in this study. The ions formed at atmospheric pressure in the argon ICP were accelerated by the application of a negative potential of –600 V to the extraction lens (cone lens) and transported through the hexapole (which was under a potential of –3 V) from the region behind the skimmer cone into the quadrupole mass analyzer. Helium was introduced into the hexapole cell as a collision gas. The nebulizer and collision gas flow rates were controlled by built-in mass flow controllers. A photomultiplier Daly-type detector was used in the configuration with an ion/electron conversion dynode and a photon-producing phosphor plate. The Daly-type ion detector was operated in analogue mode. A Meinhard nebulizer (J.E. Meinhard Associates, Inc., USA) with a Scott double-pass quartz spray chamber cooled to 4 °C was used for solution introduction. For the determination of the minimum detectable <sup>236</sup>U/<sup>238</sup>U ratio, a low-flow microconcentric nebulizer (MCN) with membrane desolvation (Aridus, CETAC Technologies Inc., Omaha, Nebraska, USA) was used for solution introduction in the ICP-MS in order to reduce uranium hydride (UH<sup>+</sup>) ion formation. Aqueous solutions were introduced in the continuous flow mode *via* a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany).

### Reagents

Uranium solution with a natural isotopic composition was prepared as described previously.<sup>20</sup> A single-element standard stock solution of Lu was obtained from Merck (Darmstadt, Germany). Reagents were diluted with deionized Milli-Q water (18 MΩ cm) obtained from a Millipore Milli-Q-Plus water purifier to concentrations in the range of 10 µg l<sup>–1</sup> to 10 mg l<sup>–1</sup>. The solutions were acidified to 1% HNO<sub>3</sub> with sub-boiled nitric acid.

### Measurement procedure

The experimental parameters were first optimized at maximum <sup>238</sup>U<sup>+</sup> ion intensity with respect to torch position, and the optimal rf-power and cooling, auxiliary and nebulizer gas flow rates were selected. The optimized experimental parameters of the ICP-CC-QMS used for isotopic measurements are summarized in Table 1.

Natural uranium solution was used for the measurement of ion energy distribution and the minimum detectable <sup>236</sup>U/<sup>238</sup>U ratio. The maximum count rate provided by the Daly detector of the Platform does not exceed 1.3 × 10<sup>8</sup> counts s<sup>–1</sup>. Therefore, a 10 mg l<sup>–1</sup> Lu solution was chosen to obtain a statistically true peak tail for studying abundance sensitivity because Lu contains the isotopes <sup>175</sup>Lu and <sup>176</sup>Lu with abundances

**Table 1** Experimental parameters of the ICP-CC-QMS (Platform, Micromass) used for isotopic analysis

Nebulizer	Meinhard
Spray chamber	Scott double-pass, water-cooled
Rf power/W	1350
Coolant gas flow rate/l min <sup>–1</sup>	13.5
Auxiliary gas flow rate/l min <sup>–1</sup>	1.4
Nebulizer gas flow rate/l min <sup>–1</sup>	0.72
Solution uptake rate/ml min <sup>–1</sup>	0.9
USN heating temperature/°C	—
USN cooling temperature/°C	—
Extraction lens (cone <sup>a</sup> ) potential/V	–600
Transfer lens (hexapole exit <sup>a</sup> ) potential/V	–400
Hexapole bias potential/V	–3.0
Quadrupole bias (ion energy <sup>a</sup> ) potential/V	0.0
Multiplier voltage/V	–450
He gas flow/ml min <sup>–1</sup>	0–10
Dwell time/s	0.2

<sup>a</sup>Given in the documentation of ICP-MS Platform.

differing by approximately 40-fold. Under the experimental conditions, the intensity of the main isotope, <sup>175</sup>Lu (abundance 97.41%), was considerably above the maximum count rate and was therefore calculated from the measured intensity of the low-abundance isotope, <sup>174</sup>Lu (abundance 2.59%), taking into account the isotope ratio<sup>21</sup> and mass discrimination.

When studying abundance sensitivity lower than 10<sup>–6</sup>, the main limiting factors are possible contamination of the stock solution and molecular ion formation, in particular of hydride ions. In order to minimize the effect of these factors on the measurement results, we studied the abundance sensitivity for the isotope with mass *m* (*m* = 174.94 u for <sup>175</sup>Lu) at masses *m* ± 0.5 u, *m* ± 1.5 u, *m* ± 2.5 u *etc.* This approach has the advantage that abundance sensitivity can be measured even when isobaric interferences are present, as the peak tail has a continuous distribution, in contrast to possible disturbing atom and molecule ions at masses *m* ± 1 u, *m* ± 2 u, *m* ± 3 u *etc.*

## Results and discussion

### Energy distribution of ions entering quadrupole mass analyzer

In order to study the energy distribution of ions entering the quadrupole mass analyzer, a positive quadrupole bias potential (0 V to 10 V) was applied (Fig. 1). The relative dependence of the <sup>238</sup>U<sup>+</sup> ion intensity *I* on the applied quadrupole bias potential *P* was measured at different helium flow rates (10 ml min<sup>–1</sup>, 5 ml min<sup>–1</sup> and 0 ml min<sup>–1</sup>; Fig. 2). When introducing the helium, the proportion of ions with relatively high energies was significantly reduced in comparison to when no helium was introduced into the collision cell. Lutetium was chosen as “test” element for the study of abundance sensitivity. A plot of <sup>175</sup>Lu<sup>+</sup> ion intensity *versus* the applied potential had practically the same shape as that given in Fig. 2 for <sup>238</sup>U<sup>+</sup> ions. Using the differentiating curves in Fig. 2 the ion energy distribution at different helium flow rates can be recovered. The dependence of Δ*I*/Δ*P* on *P* was calculated for every interval of quadrupole bias potential for the curves presented in Fig. 2; where Δ*I* is the difference of normalized ion intensity at the start and at the end of the interval of quadrupole bias potential and Δ*P* is the width of the corresponding interval. The abscissa value *P* was calculated as (*P*<sub>1</sub> + *P*<sub>2</sub>)/2; where *P*<sub>1</sub> and *P*<sub>2</sub> are start and end abscissa of the corresponding intervals of quadrupole bias potential, respectively. Charged ions change their kinetic energy in the electrostatic field proportionally to the applied potential and, therefore, the potential scale in Fig. 2 can be transformed to an ion energy scale by multiplying the ion charge value by the applied potential. Fig. 3 presents the calculated results of energy distribution of <sup>238</sup>U<sup>+</sup> ions at different helium flow rates.

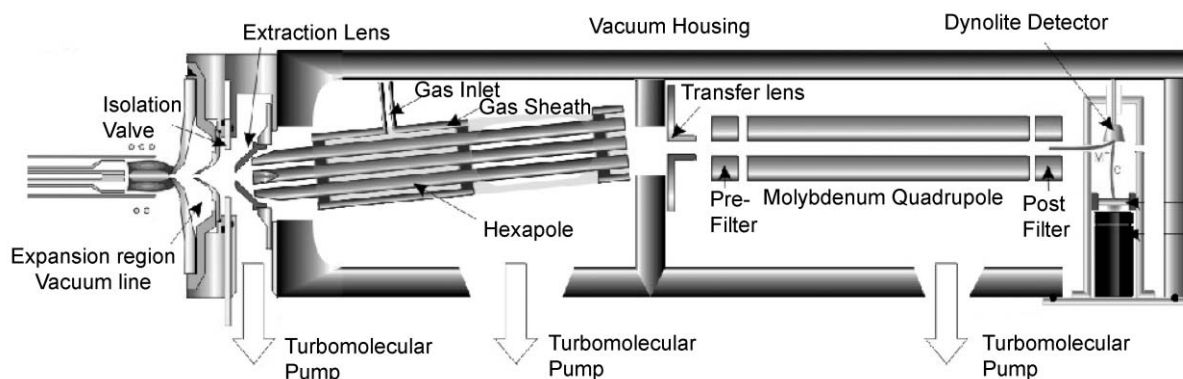


Fig. 1 Schematic diagram of the inductively coupled plasma mass spectrometer with hexapole collision cell (Platform, Micromass).

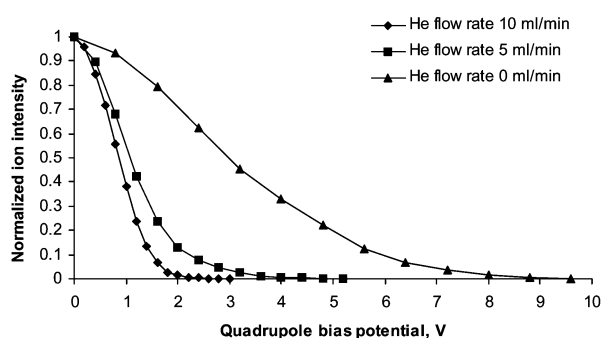


Fig. 2 Dependence of relative  $^{238}\text{U}^+$  ion intensity on quadrupole bias potential and helium flow rate.

The ion energy distribution when no helium is introduced into the hexapole collision cell does not correspond to the energy distribution of ions leaving the expansion region for at least two reasons: the ions possessing relatively high kinetic energy have a greater probability of leaving the focusing region of the rf multipole ion guide in comparison to ions with lower kinetic energy,<sup>15,16</sup> therefore the energy distribution of ions at the hexapole exit “shifts” to the lower energy range; and even if no collision gases are introduced into the collision cell, the gas from the plasma is entrained into the collision cell and increases the pressure within the ion guide to some extent,<sup>22</sup> which also leads to a reduction in the ion kinetic energy. As a result, the observed median energy of the ions entering the quadrupole mass analyzer was about 3.3 eV, which was lower than the energy of the ions formed in the inductively coupled plasma. In addition, a significant tail of high-energy ions was observed when no helium was introduced into the collision cell.

When helium was introduced into the collision cell the ions

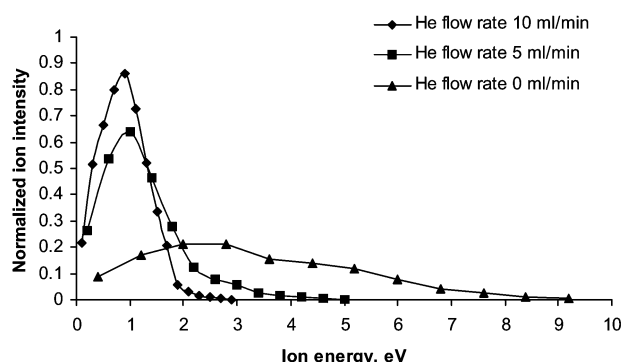
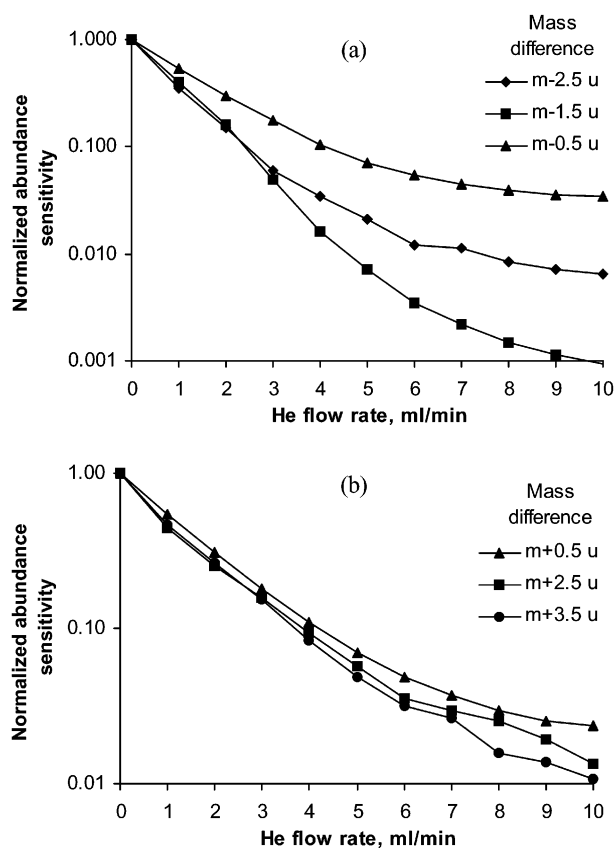


Fig. 3 Energy distribution of  $^{238}\text{U}^+$  ion calculated from the curves in Fig. 2.

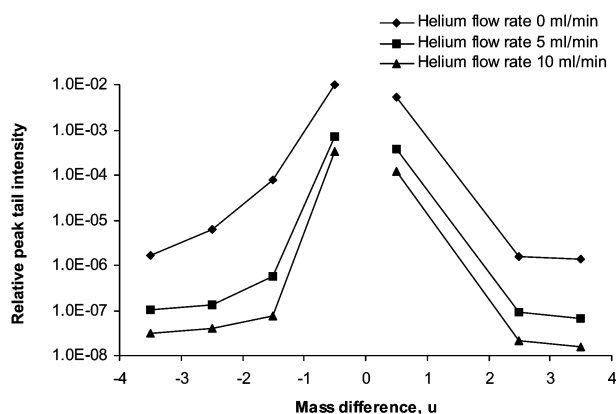
lost their kinetic energy by elastic collision with helium atoms. The design of the collision cell in the Platform creates a pressure gradient on the beam length making it difficult to control the collision gas pressure in the collision cell and to accurately calculate the final ion energy. According to calculation,<sup>23</sup> the ions experienced at least 5 collisions with He atoms at a helium flow rate of  $5 \text{ ml min}^{-1}$ . Thus, introducing He at a flow rate of  $10 \text{ ml min}^{-1}$  would not be sufficient to thermalize the ion beam, but the ion energy spread could be reduced from 20 eV (ion energy distribution without using helium) down to about 2 eV.<sup>19</sup> According to the present study (Fig. 3), the median ion energy was about 1.2 eV and 0.9 eV when introducing helium at flow rates of  $5 \text{ ml min}^{-1}$  and  $10 \text{ ml min}^{-1}$ , respectively. Despite this relatively small difference in median energies, in the latter case the proportion of high-energy ions was significantly lower, which is important for improving mass selection by the quadrupole mass spectrometer (QMS) and, therefore, suppressing peak tailing in the mass spectrum.

### Abundance sensitivity in ICP-CC-QMS

The dependence of the relative abundance sensitivity measured at high and low masses of the main isotope  $^{175}\text{Lu}$  on helium flow rate is presented in Fig. 4a and b, respectively. The abundance sensitivity was normalized to the abundance sensitivity value measured at the helium flow rate of  $0 \text{ ml min}^{-1}$ . Introduction of helium into the collision cell at a flow rate of  $10 \text{ ml min}^{-1}$  led to a reduction of the peak tail of  $^{175}\text{Lu}$  ( $m = 174.94 \text{ u}$  for  $^{175}\text{Lu}$ ) at mass  $m - 1.5 \text{ u}$  by three orders of magnitude. The peak tail of  $^{175}\text{Lu}$  could not be measured at mass  $m + 1.5 \text{ u}$  because, at this mass, the interference by  $^{176}\text{Lu}$  (peak tail) was significant. Peak tails of  $^{175}\text{Lu}^+$  (i.e., ratio of intensity at masses  $m \pm 0.5 \text{ u}$  to  $^{175}\text{Lu}$  intensity measured at mass  $m = 174.94 \text{ u}$ ) were reduced 30- to 43-fold. Peak tails at masses  $m - 2.5 \text{ u}$  and  $m + 2.5 \text{ u}$  were reduced by a factor of 150 and 75, respectively. The measured peak tail intensities at masses  $m \pm x_n$  ( $x_n = 0.5 \text{ u}$ ,  $1.5 \text{ u}$  and  $2.5 \text{ u}$ ) to peak intensity at mass  $m$  ( $m = 174.94 \text{ u}$  for  $^{175}\text{Lu}$ ) at different helium flow rates are given in Fig. 5. In order to increase the range of helium flow the second gas flow controller was calibrated and employed for helium introduction in addition to the original helium flow controller used in the Platform. The values of the measured ratios are summarized in Table 2. Increasing the He flow rate to approximately  $19 \text{ ml min}^{-1}$  did not perceptibly reduce the measured ratios of peak tail to  $^{175}\text{Lu}^+$  intensity. However, the measured intensities appeared to be limited by the instrument background (backgrounds measured at masses  $m \pm 0.5 \text{ u}$ ,  $m - 1.50 \text{ u}$  and  $m \pm 2.5 \text{ u}$  were in the range of 30 to 50 counts  $\text{s}^{-1}$  due to the dark current of the Daly-type detector used in the ICP-CC-QMS Platform). This made it difficult to investigate abundance sensitivity lower than  $3 \times 10^{-8}$ . In general, a higher peak tail was observed at the low mass side (left side) of the peak, which illustrates a well-known



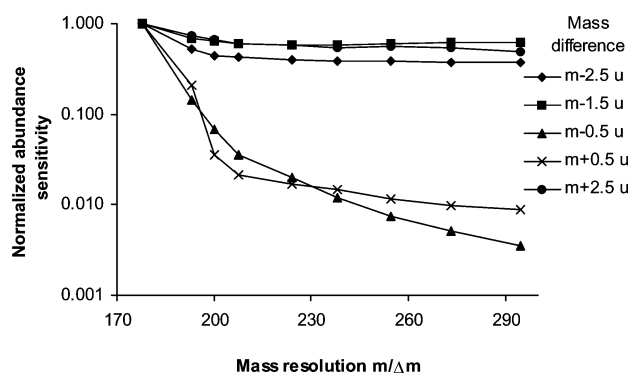
**Fig. 4** Dependence of relative abundance sensitivity measured on the low mass side (a) and high mass side (b) of the main isotope  $^{175}\text{Lu}$  on helium flow rate; mass  $174.94 + 1.5$  u is excluded because of interference by  $^{176}\text{Lu}^+$  ions (peak tail).



**Fig. 5** Dependence of the peak shape measured at masses  $m \pm 0.5$  u,  $m - 1.5$  u and  $m \pm 2.5$  u on helium flow rate ( $m = 174.94$  for  $^{175}\text{Lu}$ ); mass  $m + 1.5$  u is excluded because of interference by  $^{176}\text{Lu}^+$  ions (peak tail).

characteristic of quadrupole mass analyzers with pronounced tailing on the low mass side of the mass peak.<sup>12</sup> In addition, changing the quadrupole bias potential from  $-1$  V to  $+2$  V and, hence, the median energy of the ion beam from approximately  $0$  eV to  $3$  eV did not perceptibly alter the peak tail. This confirms that ions with energies lower than  $3$  eV are effectively separated by the QMS.

Application of a pressurized ion guide in ICP-QMS influences different characteristics of the mass spectrometer, such as sensitivity, mass resolution and abundance sensitivity. For instance, decreasing the ion kinetic energy by introducing helium into the collision cell alters the resolution of the quadrupole mass analyzer, because the resolution is inversely proportional to the maximum axial ion energy.<sup>12</sup> In turn, the ICP-QMS characteristics are interdependent; in particular isotopic abundance sensitivity is dependent on the QMS resolution and on the overall shape of the mass peak.<sup>12</sup> In order to distinguish the effect of changing ion kinetic energy on abundance sensitivity from the effect arising from the change in mass resolution, this last effect was also studied. Under the experimental conditions applied in the present study, the mass resolution ( $m/\Delta m$ ) at mass  $175$  u measured using the 90% valley criteria increased from  $180$  to  $200$  when the helium flow rate was changed from  $0$   $\text{ml min}^{-1}$  to  $10$   $\text{ml min}^{-1}$ . In order to study the effect of resolution of abundance sensitivity, the resolution of the analyzer was changed in the present study from  $170$  to  $300$  by changing the slope of the mass scan line, i.e., by changing the ratio of dc and rf amplitudes. Fig. 6 presents the dependence of relative abundance sensitivity on the mass resolution of the QMS measured at mass  $175$  u (note, that the resolution of the QMS analyzer is mass dependent, i.e., the resolution is lower for the lower masses). The abundance sensitivity was normalized to the abundance sensitivity value measured at mass resolution of  $170$ . The mass resolution was measured for the  $^{175}\text{Lu}^+$  peak using the 90% valley criteria. Increasing the mass resolution from  $180$  to  $300$  narrowed the peak and improved the abundance sensitivity measured at masses  $m \pm 0.5$  u by



**Fig. 6** Dependence of relative abundance sensitivity measured at masses  $m \pm 0.5$  u,  $m - 1.5$  u and  $m \pm 2.5$  u on resolution ( $m = 174.94$  for  $^{175}\text{Lu}$ ); mass  $m + 1.5$  u is excluded because of interference by  $^{176}\text{Lu}^+$  ions (peak tail).

**Table 2** Dependence of abundance sensitivity measured at masses  $m \pm 0.5$  u,  $m - 1.5$  u and  $m \pm 2.5$  u on helium flow rate ( $m = 174.94$  for  $^{175}\text{Lu}$ ); mass  $m + 1.5$  u is excluded because of interference by  $^{176}\text{Lu}^+$  ions (peak tail)

He flow rate/ $\text{ml min}^{-1}$	Measured ratio of peak tail intensity at mass $m \pm x_n$ ( $x_n = 0.5$ u, $1.5$ u and $2.5$ u) to peak intensity at mass $m$ ( $m = 174.94$ for $^{175}\text{Lu}$ )					
	$m - 2.5$	$m - 1.5$	$m - 0.5$	$m + 0.5$	$m + 2.5$	$m + 3.5$
10	$4.0 \times 10^{-8}$	$7.4 \times 10^{-8}$	$3.38 \times 10^{-4}$	$1.24 \times 10^{-4}$	$2.1 \times 10^{-8}$	$1.52 \times 10^{-8}$
19 (approximately <sup>a</sup> )	$3.5 \times 10^{-8}$	$6.6 \times 10^{-8}$	$3.32 \times 10^{-4}$	$1.19 \times 10^{-4}$	$2.0 \times 10^{-8}$	$1.36 \times 10^{-8}$

<sup>a</sup>Helium flow rate was increased by using the second gas flow controller calibrated and employed for helium introduction in addition to the original helium flow controller used in the Platform ICP.

more than two orders of magnitude. In particular, a sharp decrease of the peak wings at mass  $m \pm 0.5$  u was only observed when the QMS resolution was changed from 180 to 210 because the mass peak was too wide in this resolution range. Hence even a relatively small resolution increase resulted in significant peak narrowing. When changing the QMS resolution from 210 to 300, abundance sensitivity measured at mass  $m \pm 0.5$  u was reduced 3- to 10-fold. Extensive wings of the peak at masses  $m \pm 1.5$  u,  $m \pm 2.5$  u *etc.* were only reduced by a factor of 1.7 to 3 when the mass resolution was increased from 180 to 300. In general, these results correspond to the calculated reduction of simulated selectivity by a factor of 3 to 5 at masses  $40 \pm 0.5$  u when changing the QMS resolution from 50 to 100.<sup>12</sup> Increasing the mass resolution to more than 300 at mass  $m = 175$  u resulted in significant intensity losses and, therefore, the resolution range above 300 was not studied.

Improved abundance sensitivity is useful for analyzing the long-lived radionuclide  $^{236}\text{U}$  in the presence of the high-abundance isotope  $^{238}\text{U}$ . When changing the helium flow rate from 0 ml min<sup>-1</sup> to 10 ml min<sup>-1</sup> the abundance sensitivity for  $^{236}\text{U}/^{238}\text{U}$  isotope ratio (measured in 10 mg l<sup>-1</sup> uranium solution) improved from  $2.3 \times 10^{-5}$  to  $6.3 \times 10^{-8}$ . Note, that the experimentally measured value was raised to some extent by uranium hydride ions  $^{235}\text{UH}^+$ . Thus, uranium hydride formation ratio  $\text{UH}^+/\text{U}^+$  was  $2.3 \times 10^{-6}$ , which resulted in a  $^{235}\text{UH}^+/\text{U}^+$  ratio of about  $1.7 \times 10^{-8}$ . The abundance sensitivity for one mass unit below  $^{238}\text{U}^+$  was about  $2 \times 10^{-7}$ . For comparison, the abundance sensitivity for one mass unit below the high-intensity peak varied between  $10^{-6}$  and  $1.5 \times 10^{-5}$  when different sector field ICP-MS instruments were used.<sup>11,24</sup>

In general, further improvement of abundance sensitivity is possible by optimizing the quadrupole design and increasing the operation frequency, so that the number of rf cycles would increase. However, the parameters mentioned above were not optimized in the present work, which resulted in relatively poor abundance sensitivity when no helium was introduced into the collision cell. Thus, the initial abundance sensitivity for the  $^{236}\text{U}/^{238}\text{U}$  isotope ratio was about 40-fold worse than the value achieved in quadrupole-based ICP-MS without a collision cell.<sup>25</sup> Nevertheless, ion beam moderation in the collision cell improved the abundance sensitivity by almost 400 times.

High abundance sensitivity can also be important when analyzing  $^{239}\text{Pu}$  in a uranium matrix (*e.g.*, penetrator), because the  $^{238}\text{U}^+$  peak tail (in addition to  $^{238}\text{UH}^+$  ions) may interfere with  $^{239}\text{Pu}^+$  even after separation of plutonium and uranium<sup>26</sup> with a decontamination factor of  $5.7 \times 10^{-6}$ . Another promising field of application for ICP-CC-QMS is the analysis of  $^{129}\text{I}$ . When determining long-lived  $^{129}\text{I}$ , the collision cell can be useful both for improving abundance sensitivity (as the high-abundance isotope  $^{127}\text{I}$  is usually present) and for reducing interference from  $^{129}\text{Xe}^+$  using gas-phase reactions (for instance using oxygen as the collision gas<sup>27</sup>).

## Conclusion

This study confirmed that peak tailing is reduced in ICP-CC-QMS with a helium-filled collision cell down to between  $2 \times 10^{-8}$  and  $6 \times 10^{-8}$  depending on the mass analyzed. Reducing kinetic energy also improved mass resolution by about 10%. However, increasing the QMS resolution had a significantly lower influence on abundance sensitivity than reducing the ion energy by collision with helium atoms. For the measurement of abundance sensitivity, it is very important to reduce the background as much as possible. In this work the background

count rate of the Daly-type detector used in the ICP-CC-QMS was 30 to 50 counts s<sup>-1</sup>, which limited the study of the effect of the pressurized ion guide on abundance sensitivity. An ion detector with a low background would be desirable for further studies. Better abundance sensitivity can be achieved by optimizing the design of the QMS rods and increasing the operation frequency. We intend to use ICP-CC-QMS with improved abundance sensitivity for analyzing  $^{236}\text{U}$  and  $^{129}\text{I}$  in future studies.

## Acknowledgements

The authors thank Dr. H.-J. Dietze for valuable discussions. S.F.B. acknowledges support from Micromass, UK for attendance at the 2002 Winter Conference on Plasma Spectrochemistry.

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