

Interference-free determination of ultra-trace concentrations of arsenic and selenium using methyl fluoride as a reaction gas in ICP–MS/MS

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Abstract Interference-free conditions, allowing straightforward As and Se determination, can be obtained by using CH₃F (a mixture of 10 % CH₃F and 90 % He) as a reaction gas in tandem ICP–mass spectrometry (ICP–MS/MS). Both target elements react via CH₃F addition and subsequent HF elimination, rendering AsCH₂⁺ and SeCH₂⁺ the respective favored reaction product ions. Instrumental limits of detection were 0.2 ng L⁻¹ for As and below 10 ng L⁻¹ for Se, using either ⁷⁷Se, ⁷⁸Se, or ⁸⁰Se. Neither addition of carbon to the solutions, nor admixing of additional He into the octopole reaction cell resulted in a further improvement of the LoDs, despite the increase in analyte signal intensity. By using synthetic matrices, containing elements giving rise to ions interfering at either the original mass-to-charge ratios or those of the reaction products, absence of spectral overlap could be demonstrated. This conclusion was corroborated by successful As and Se determination in a collection of reference materials from plant, animal, or environmental origin, displaying a considerable range of As and Se contents. These accurate results were obtained via external calibration using Te as an internal standard. The high efficiency reaction between As and CH₃F and the possibility to use the major isotope of Se provides enhanced detection power versus other

techniques, such as sector-field ICP–mass spectrometry, while the possibility to monitor at least three Se isotopes interference-free also enables isotopic analysis.

Keywords Tandem ICP–mass spectrometry ICP–MS/MS · Arsenic and selenium · Chemical resolution · Spectral interference

Introduction

The determination of ultra-trace concentrations of As and Se in a large variety of samples has been the objective of numerous studies for many years. Arsenic is a toxic element that has been classified in category 1 by the International Agency for Research on Cancer (IARC), which means that it is carcinogenic for humans. [1] Selenium is one of the minor elements that, due to its presence in several proteins and enzymes, is essential for biological processes. However, already at concentrations slightly higher than optimum, it becomes toxic to humans. [2] In addition, the antagonistic metabolic effect between As and Se [3] has been typically used to reduce As poisoning effects, and different As-related diseases are linked with Se deficiency [4–6]. For this reason, and although the toxicity and/or beneficial effects of these elements strongly depend(s) on the chemical form [7–10], the determination of the total concentration of As and Se gives invaluable and fast information concerning the associated risks. [11] As a result, analysis of biological and environmental samples for their As and/or Se content(s) is of interest from a biomedical point of view. However, the determination of these metalloids at ultra-trace levels is not simple by means of any atomic spectroscopy technique [12–16]. Inductively coupled plasma–mass spectrometry (ICP–MS) can be considered as the technique of choice for the monitoring of these elements. However, despite its detection power, the determination of As and Se by ICP–

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MS is seriously hampered by the occurrence of both spectral and nonspectral interferences [17].

Matrix effects (nonspectral interferences [18]) are more pronounced for As and Se than for many other elements, due to their high ionization energy (9.81 and 9.75 eV, respectively), and the so-called “carbon effect,” which means that a high amount of carbon, dissolved in the sample or admixed into the ICP, leads to a signal enhancement for both As and Se. Although this effect has been widely described in the literature [19–21], there is no clear consensus concerning the mechanism responsible for it. The carbon effect is hypothesized to result from the charge transfer between C^+ and CH^+ (ionization energy of 11.26 and 10.64 eV, respectively) [22, 23] to atoms of elements with a high ionization energy. However, other characteristics need to be involved, because not for all elements with a high ionization energy such an enhancement is observed. In addition, extremely high amounts of carbon could also result in a signal intensity decrease due to a reduction of the plasma temperature.

Nonspectral interferences [24, 25] can be tackled in different ways (e.g., use of a suitable internal standard [26], or quantification by means of standard addition [27], or by means of isotope dilution [28–31]), but the issue of spectral interferences remains a serious one due to the formation of Ar-based polyatomic ions [32, 33] that affect the determination of $^{75}As^+$ ($^{40}Ar^{35}Cl^+$ and $^{38}Ar^{37}Cl^+$) and $^{77,78,80}Se^+$ ($^{40}Ar^{36}Ar^1H^+$, $^{40}Ar^{37}Cl^+$, $^{40}Ar^{38}Ar^+$, and $^{40}Ar^{40}Ar^+$). While in the case of Se, ^{82}Se can often be monitored interference-free, no such possibility exists for the monoisotopic As.

Different options have been explored to overcome the influence of these interferences, such as the use of analyte/matrix separation (which obviously represents additional work and degrades sample throughput) [34], of mathematical equations (which may not work efficiently if the ratio between the signal of the interferent and that of the analyte is too high) [35], of cool plasma conditions (which results in a significant drop in sensitivity for these elements, owing to their poor ionization efficiency under such working conditions) [36] and of vapor generation systems (the use of which also involves some additional sample pretreatment) [37].

Additionally, more advanced ICP–MS devices permit these spectral interferences to be overcome in a more straightforward way. The use of a sector-field ICP–MS (SF–ICP–MS) instrument, operated at higher mass resolution, is an elegant choice to resolve spectral interferences [38]. However, the maximum resolution setting ($m/\Delta m \sim 10,000$) should be used in the case of As and Se, which involves a reduction in sensitivity of about 2 orders of magnitude, which is sometimes too much for the targeted concentrations. Also, and even using the maximum resolution setting, some polyatomic interferences still cannot be completely resolved (e.g., interference-free measurement of $^{80}Se^+$ is hard to accomplish due to the very high intensity of the $^{40}Ar_2^+$ dimer).

The most widespread approach to deal with the spectral overlap affecting the determination of As and Se nowadays is probably the use of a quadrupole-based ICP–MS (Q–ICP–MS) instrument equipped with a collision–reaction cell [39]. Different gasses can be used to pressurize the cell and ameliorate the conditions for As and/or Se determination. For instance, the combination of a collision gas [40] (typically He) and kinetic energy discrimination can be used to reduce the interferences as, due to their larger size, polyatomic ions lose a larger fraction of their kinetic energy than do mono-atomic ions. However, this strategy is incapable of removing doubly charged interferences and is accompanied by a substantial reduction in sensitivity. Also, reactive gasses (e.g., NH_3 , H_2 , CH_4 , O_2) can be used to selectively react with the interfering ions [41–43], aiming at the monitoring of the analyte ions at their original mass-to-charge ratio. Alternately, also a selective reaction between the analyte ions and the gas molecules [44, 45], resulting in the formation of a reaction product ion that can be measured interference-free at another m/z ratio, is sometimes viable. The efficacy of the latter approach strongly depends on the efficiency and rate of the reaction involved.

Recently, a new configuration of Q–ICP–MS instrumentation was introduced, the so-called triple quadrupole ICP–MS/MS [46–49] setup, which consists of a tandem mass spectrometer with an octopole reaction cell located in-between two quadrupole mass analyzers. This new configuration allows removing all the ions with an m/z ratio different from that of the target nuclide with the first quadrupole, which results in a full control over the reactions that are subsequently taking place in the octopole cell. The second quadrupole then selects one of the possibly many reaction products formed for monitoring and quantification of the target element. This improved control enables the application of nontypical, but highly reactive gasses, offering new possibilities via the conversion of the target elements in reaction product ions, without sacrificing sensitivity by using low efficiency reactions.

Methyl fluoride is a reaction gas that has only been used scarcely in ICP–MS before [50, 51]. However, in a previous work [49], we have demonstrated the possibilities of this reaction gas to resolve spectral overlap in the determination of light metals (Al, Co, Cr, Mn, Ni, Ti, and V) in clinical samples using ICP–MS/MS. The main goal of the current project was to investigate the potential of methyl fluoride as a reaction gas in ICP–MS/MS for dealing with the interferences affecting ultra-trace determination of both As and Se in diverse sample types.

Experimental

Instrumentation

All measurements were carried out using an Agilent 8800 triple quadrupole ICP–MS/MS instrument (Agilent

Technologies, Japan). The sample introduction system comprises a MicroMist nebulizer (400 µL/min) and a Peltier-cooled Scott-type spray chamber (2 °C). The instrument is equipped with two quadrupole mass analyzers (Q1 and Q2) and an octopole collision–reaction cell (ORS³) mounted in-between the two quadrupole units (Q1–ORS³–Q2). The instrument can be used in different operation modes, (i) with the first quadrupole fully open (single quadrupole mode, SQ) or (ii) using both quadrupoles as mass filters (MS/MS mode). This MS/MS mode allows for a better control over the reactions proceeding in the cell and provides the user with the possibility of product ion and precursor ion scanning as a powerful tool for evaluating the reaction product ions formed and selecting the optimum one for quantification processes, and for identifying the parent ion at the origin of polyatomic ions formed through cell reaction, respectively. The cell can be pressurized with different inert or reactive gasses, typically He, H₂, O₂, and NH₃, but in this work, the merits of CH₃F (a mixture of 10 % CH₃F and 90 % He) were evaluated. The CH₃F/He mixture was introduced via the fourth line (typically used for O₂) and with the flow controller calibrated for this gas. As a result, the flow rates given below are expressed in O₂-equivalent milliliters per minute.

A Thermo Element XR sector-field ICP–MS instrument (ThermoScientific, Germany) was used with the aim of comparing the capabilities of both techniques for ultra-trace determination of As and Se.

Reagents and standards

Only high-purity reagents were used during all of the experiments. Water was purified using a Milli-Q Element water purification system (Millipore, France). Pro-analysis 14 M HNO₃ (ChemLab, Belgium) was further purified via sub-boiling distillation. Ultrapure 28 M HF (Fisher Chemicals, Great Britain) and 9.8 M H₂O₂ (Fluka, Belgium) were chosen for sample digestion. Trace select 25 M MeOH for studying the carbon effect was acquired from Sigma-Aldrich, Germany. Throughout the work, appropriate dilutions of 1 g L⁻¹ single-element standard solutions (Instrument Solutions, The Netherlands) were carried out for optimization (As and Se), for internal standardization (Te), for external calibration (standard solutions with concentrations ranging between 0 and 5 µg L⁻¹ of As and Se), and for matrix-matching (Ca, Cl, Gd, Mo, Nb, Nd, Ru, Sm, Y, Zr).

Samples

Reference materials were analyzed for method validation purposes. The list comprises NIST SRM 1515 (Apple leaves), NBS SRM 1575 (Pine needles), NBS SRM 1573 (Tomato leaves), NIST SRM 1568a (Rice flour), BCR CRM 526 (Tuna fish tissue), NCR-CNRC DORM-4 (Fish protein), BCR CRM

414 (Plankton), NBS SRM 1646 (Estuarine sediment), NIST SRM 1566a (Oyster tissue), and NRC-CNRC TORT-3 (Lobster hepatopancreas).

Sample preparation

To avoid contamination, only metal-free tubes were used for standard and sample preparation (15 or 50 mL polypropylene centrifuge tubes, VWR, Belgium). The samples were digested via acid digestion in Teflon Savillex beakers, which had been pre-cleaned with HNO₃ and HCl and subsequently rinsed with Milli-Q water. To complete the mineralization, between 0.1 and 0.2 g of the respective reference materials (except for the apple leaves reference material, for which 0.5 g was digested due to the low concentration of both As and Se) were digested with 4 mL of 14 M HNO₃ and 1 mL of 9.8 M H₂O₂ and, only in the case of NBS SRM 1646 (Estuarine Sediment), an additional 1 mL of 28 M HF. The procedure was completed after heating at 110 °C on a hot plate overnight.

Prior to ICP–MS/MS analysis, the digested materials were diluted 40- and 20-fold for As and Se, respectively, with Milli-Q water.

The final results were calculated on a dry mass basis, taking into account the water content of the reference materials, previously calculated after drying until constant weight.

Results and discussion

As discussed in the introduction, the determination of ultra-trace levels of As and Se using ICP–MS is still a challenge. Different problems are encountered when addressing determination of ultra-trace concentrations of these elements, and there is no straightforward method to deal with all the problems encountered without sacrificing some analytical properties. The objective of this work was to investigate the capabilities of ICP–MS/MS with CH₃F/He as a reaction gas in this context.

Selection of the main product ions formed upon reaction between As and Se and CH₃F/He

In order to study the reactions between CH₃F/He and As and Se, product ion scanning was used to identify the main reaction products. Standard solutions of 5 µg L⁻¹ of As and of Se were measured using different CH₃F/He flow rates to find the most suitable reaction product ions, in terms of sensitivity and limits of detection (LoDs). Due to the monoisotopic character of As, the mass-to-charge ratio of the first quadrupole was fixed at 75, while for Se, an *m/z* setting of 80 was selected because this is the most abundant nuclide. The results are summarized in Fig. 1. In both cases, it is clear that a single

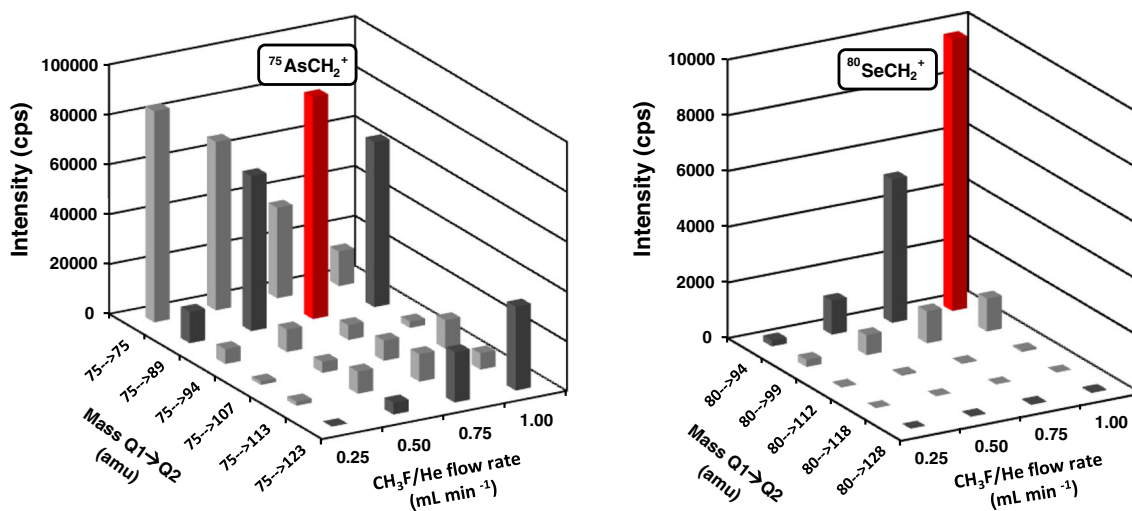


Fig. 1 Identification of the different species formed at different $\text{CH}_3\text{F}/\text{He}$ flow rate settings via product ion scanning. The main reaction product ions are highlighted in red

product ion shows the highest sensitivity; for both As and Se, there is a selective and efficient reaction with $\text{CH}_3\text{F}/\text{He}$, consisting of CH_3F addition and subsequent HF elimination, resulting in the formation of AsCH_2^+ and SeCH_2^+ . This reaction was studied in a previous work using ICP-SIFT-MS[52], where the same behavior was found for As, but not for Se. With ICP-SIFT-MS, no reaction was seen to take place between Se and CH_3F , which indicates that some differences in reactivity can occur when other types of devices are used. Figure 1 also provides valuable information concerning the optimum $\text{CH}_3\text{F}/\text{He}$ flow rate settings. For As, the AsCH_2^+ signal intensity reaches a maximum at approximately 0.75 mL min^{-1} and then decreases, while the maximum sensitivity for Se is obtained at the highest flow rate setting attainable. It can be assumed that the use of higher flow rates could increase the SeCH_2^+ signal sensitivity even further. In any case, these reaction product ions seem promising to develop interference-free methods for As and Se determination in complex matrices using the MS/MS mode, and they

were selected for further work. A schematic representation of the ICP-MS/MS operation using $\text{CH}_3\text{F}/\text{He}$ for As and Se is shown in Fig. 2.

Method development and optimum instrumental parameters for AsCH_2^+ and SeCH_2^+ monitoring

Once the most suited reaction product ions were identified, the corresponding analytical methods were developed. To further optimize the $\text{CH}_3\text{F}/\text{He}$ flow rate settings, the signal intensity of a standard solution containing $5 \mu\text{g L}^{-1}$ of As and of Se and a blank solution (0.14 M HNO_3) were measured at different flow rates, adjusting the first quadrupole for transition of the mass of the target nuclide (75 and 80 for ^{75}As and ^{80}Se , respectively) and the second for transmission of the mass of the selected reaction product ion (89 and 94 for $^{75}\text{AsCH}_2^+$ and $^{80}\text{SeCH}_2^+$, respectively). The results obtained are shown in Fig. 3, indicating an optimum $\text{CH}_3\text{F}/\text{He}$ flow rate setting of 0.72 (range between 0.60 and 0.80 mL min^{-1}) and

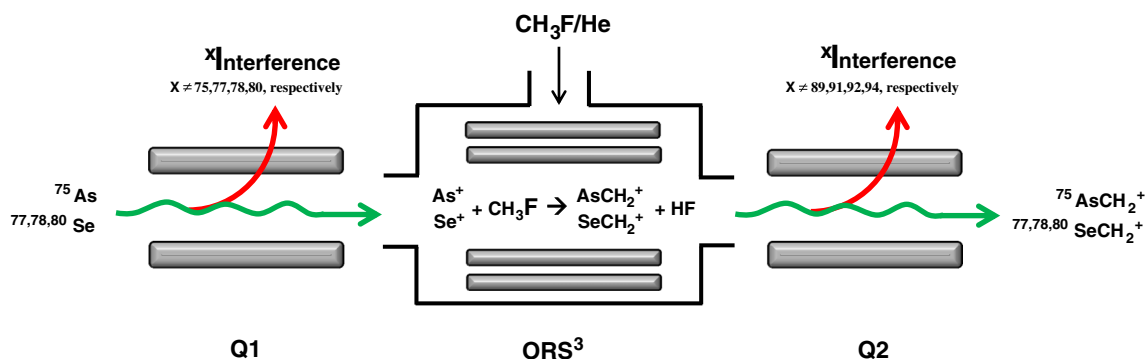


Fig. 2 Schematic representation of ICP-MS/MS operation in the determination of As or Se using $\text{CH}_3\text{F}/\text{He}$ as reaction gas

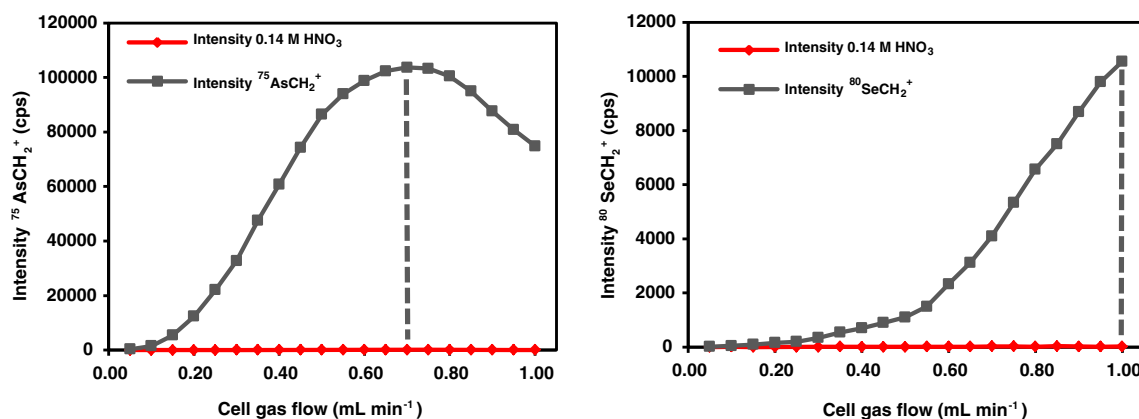


Fig. 3 Selection of CH₃F/He flow rate settings for the selected species (⁷⁵AsCH₂⁺ and ⁸⁰SeCH₂⁺)

1.00 mL min⁻¹ for ⁷⁵AsCH₂⁺ and ⁸⁰SeCH₂⁺, respectively. As previously said, it can be hypothesized that at an even higher CH₃F/He flow rate, the results for Se could even be better. Despite this limitation, the two methods were fully optimized, resulting in the instrument parameters summarized in Table 1. Under the optimum conditions for each of the target elements, a set of standard solutions (concentration between 0 and 5 μg L⁻¹) were measured 10 consecutive times in order to obtain the calibration data and the instrumental limits of detection and of quantification (LoDs and LoQs were calculated as 3 and 10 times $s_{\text{blank}}/\text{slope}$, respectively). The results are given for ⁷⁵As and for three different nuclides of Se (⁷⁷Se, ⁷⁸Se, and ⁸⁰Se) in Table 2. These nuclides were selected in view of the strong Ar-based polyatomic interferences they suffer from and thus, to further prove the robustness of the methods developed.

From the data in Table 2, it is possible to appreciate the difference in sensitivity between As and Se, which cannot be due to the monoisotopic character of As only, but probably also to the higher efficiency of the reaction between CH₃F/He and As. However, excellent instrumental LoDs that are suitable for analysis of real samples were obtained in all cases: 0.2 ng L⁻¹ for As as ⁷⁵AsCH₂⁺ and below 10 ng L⁻¹ for Se as ^{77,78,80}SeCH₂⁺. It needs to be stressed that these are instrumental LoDs, so procedural blanks and sample dilution need to be taken into account for the final LoDs.

Signal intensity enhancement: addition of C and surplus addition of He

Different approaches known to enhance the signal intensity for a variety of analytes were tested in this work. Due to their high ionization energy, As and Se are poorly ionized in the plasma. As described in the introduction, high amounts of carbon can give rise to a substantial increase in the As and Se signal intensities because of the carbon effect. While on the one hand, the situation can complicate quantification and necessitates matrix-matching of the external standards or the

method of standard additions, it is also frequently used to improve the sensitivity. With the aim to evaluate this possibility, different amounts of MeOH (between 0 and 10 %) were added to both the As and Se standards (5 μg L⁻¹). The results are shown in Fig. 4. A signal enhancement is observed in both cases with increasing MeOH-concentration, reaching a maximum when between 4 and 8 % of MeOH is added. This leads to, approximately, a 2- and 2.5-fold improvement for As and Se, respectively. A further increase of the MeOH-concentration in the samples leads to a decrease in the signal intensity for both elements. However, from Fig. 4, it can also

Table 1 Instrument settings for the Agilent 8800 ICP-MS/MS instrument

Agilent 8800		
	As	Se
Reaction gas	CH ₃ F/He	CH ₃ F/He
Scan type	MS/MS	MS/MS
Plasma mode	Low matrix	Low matrix
RF power (W)	1550	1550
Extract 1 (V)	-3.0	-3.9
Q1 bias (V)	-2.0	-1.0
Reaction gas flow rate setting (mL min ⁻¹)	0.72	1.00
Q1→Q2	75→89 125→125	77→91 78→92 80→94 125→125
Octopole bias (V)	-4.1	-4.1
Energy discrimination (V)	-8.4	-8.4
Extract 2 (V)	-185.0	-195.0
Q2 QP bias (V)	-12.5	-12.5
Wait time offset (ms)	2	2
Sweeps / replicate	100	100
Integration time / mass (s)	1	1
Replicates	10	10
Total analysis time/sample (s)	38	65

Table 2 Calibration data and instrumental limits of detection and of quantification obtained for arsenic and selenium using methyl fluoride as reaction gas in ICP–MS/MS

Isotope	CH ₃ F/He flow (mL min ⁻¹)	Q1 (amu)	Q2 (amu)	Sensitivity ^a (L μg ⁻¹)	Intercept ^a (counts s ⁻¹)	R ²	LoD ^b (μg L ⁻¹)	LoQ ^b (μg L ⁻¹)
⁷⁵ As	0.72	75	89	18,160±250	-90±100	0.999994	0.0002	0.0007
⁷⁷ Se		77	91	286±9	2±11	0.99998	0.01	0.04
⁷⁸ Se	1.00	78	92	917±20	7±13	0.99998	0.007	0.02
⁸⁰ Se		80	94	1,944±25	-2±21	0.99997	0.004	0.01

LoD limit of detection, LoQ limit of quantification

^aUncertainties expressed as standard deviation ($n=10$)

^bLoDs and LoQs calculated as 3 and 10 times the standard deviation on 10 consecutive measurements of a blank solution (0.14 M HNO₃), divided by the slope of the calibration curve, respectively

be seen that the signal-to-background ratios and thus, also the LoDs, were actually deteriorated by the use of MeOH, probably because of the impurities present in the solvent. For this reason, admixing MeOH was not further considered.

Another experiment was conducted to investigate whether the addition of a supplemental He flow in the octopole collision/reaction cell (introduced via another line) could affect the reaction between CH₃F/He and the target analytes. This turned out to be the case for As. The results of this experiment are presented in Fig. 5, which shows the signal intensity for 5 μg L⁻¹ of As at different CH₃F/He flow rate settings (range of 0.10–1.00 mL min⁻¹), while the cell was also pressurized with surplus He (range of 0–5 mL min⁻¹).

It can be clearly seen that a higher supplemental He flow shifts the maximum signal intensity for ⁷⁵AsCH₂⁺ toward lower CH₃F/He flow rates. Moreover, the net sensitivity is increased up to 3-fold, if the CH₃F/He flow rate is reduced from 0.72 to 0.20 mL min⁻¹ and the He flow rate is increased from 0 to 5 mL min⁻¹. These results demonstrate that He plays an important role in the reaction between As and CH₃F. It can be hypothesized that the presence of more He slows down the As⁺ ions, resulting in collisional stabilization, which improves the efficiency of the reaction between As and CH₃F. This behavior has already been mentioned in the literature for reactions between other elements and CH₃F [52]. The same

behavior was not observed in the case of Se, for which the addition of a supplemental He flow resulted in a decrease of the signal intensity that could not be compensated with a reduction in the CH₃F/He flow rate, as was the case for As. It seems that for Se, the CH₃F/He flow rate was not high enough to observe the same phenomenon, perhaps due to the instrumental restriction in the CH₃F/He flow rate to 1.00 mL min⁻¹ and the differences in reaction efficiency, as discussed before.

However, it was observed that the signal-to-background ratio also deteriorated when He was added, which in turn led to degraded LoDs. Therefore, use of an additional He flow was disregarded for further work.

Comparison with other cell gasses

In order to better assess the potential of CH₃F/He as a reaction gas for As and Se determination, alternative cell conditions were evaluated (“vented mode,” addition of He only, and addition of O₂), using both the single quadrupole mode (SQ) and the MS/MS mode. Moreover, an SF–ICP–MS device operated in high-resolution mode was used to compare the capabilities of both techniques. The instrument settings for all the methods are provided in the Electronic Supplementary

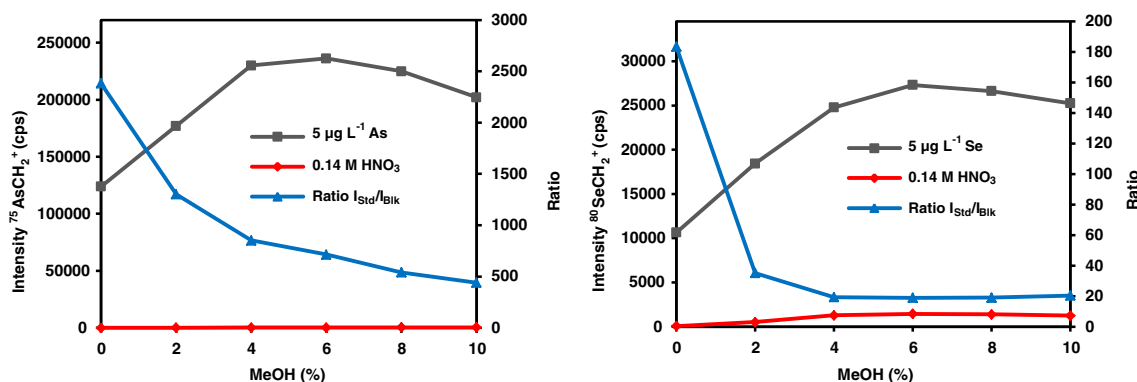


Fig. 4 Signal enhancement produced by the addition of different amounts of MeOH (“carbon effect”)

Material (ESM, Table S1 and Table S2 for ICP-MS/MS and SF-ICP-MS, respectively).

To summarize all the data obtained, the instrumental LoDs observed under different conditions are shown in Table 3. Additionally, all the calibration data are presented in Table 4. Attention should be paid to the fact that this information is partial because the instrumental LoDs reported are not affected by spectral interference due to the absence of the parent elements at the origin of interfering species (basically, Cl) for ⁷⁵As and ⁷⁷Se. For ⁷⁸Se and ⁸⁰Se, the overlap with ³⁸Ar⁴⁰Ar⁺ and ⁴⁰Ar₂⁺, respectively, is always affecting the signals irrespective of the matrix considered. Despite this, Table 3 provides valuable information concerning the instrumental possibilities of the various methods.

Generally speaking, the use of MS/MS involves a reduction in sensitivity, which means that, for samples without spectral interferences, the SQ mode should provide a higher signal intensity. The differences in overall ion transmission efficiency between both modes could be most easily observed when the cell was used in “vented mode” or pressurized with He because in these cases, Q1 and Q2 were set at the same mass (see Table 4). This was not the case with O₂ and CH₃F because in these cases, Q1 is set to the mass of the target nuclide itself and Q2 to that of the corresponding reaction product ion. Under these conditions, both the reaction efficiency and the overall ion transmission efficiency govern the signal intensity. However, the LoD is also determined by the blank level at the mass of the reaction product ion, such that the LoDs when O₂ or CH₃F was used to avoid spectral overlap turned out to be better with double mass selection (MS/MS mode).

When O₂ was selected, the LoD for ⁸⁰Se was higher than that for ⁷⁸Se, despite the higher abundance of the former nuclide. The efficiency of the reaction of As and Se with O₂ is lower than that with CH₃F/He, as can be seen from the sensitivity of both methods, presented in Table 4. Additionally, the signal stability for Se was substantially deteriorated (RSD > 10 %) when using O₂. A final comparison between the three pressurized cell options (He, O₂, and CH₃F/He) used to enable interference-free determinations of As and Se indicates that the use of the novel method, using CH₃F/He and the MS/MS mode, provides improved LoDs for both As and Se in all cases.

When comparing the figures of merit thus obtained with those obtained using SF-ICP-MS, the ICP-MS/MS approach with CH₃F/He as a reaction gas shows an improvement in the LoDs by a factor of 50, 5, and 100 for ⁷⁵As and ^{77,78}Se, respectively, while the accurate monitoring of ⁸⁰Se is not feasible using SF-ICP-MS.

In addition, the LoDs obtained in this work using CH₃F/He in ICP-MS/MS were compared with those obtained using different setups as reported in the literature. This information is shown in Table 5, from which it can be seen that the ICP-

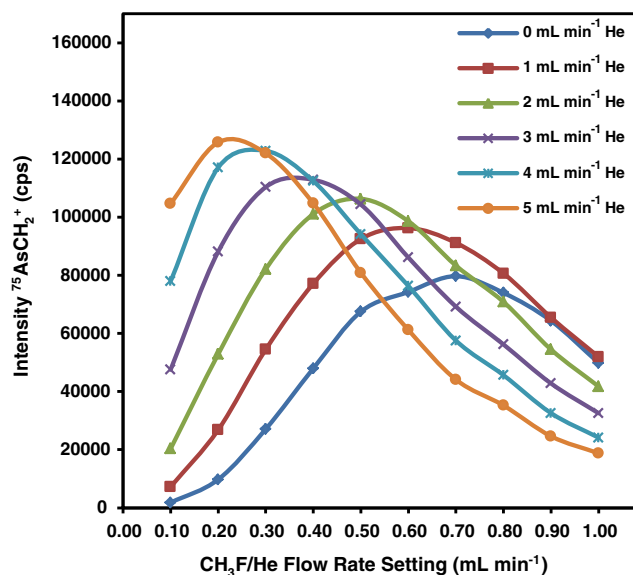


Fig. 5 Signal enhancement produced by the addition of surplus He in the reaction of As with CH₃F/He to form AsCH₂⁺

MS/MS LoDs are superior to those obtained using SF-ICP-MS or other types of Q-ICP-MS instrumentation equipped with a collision-reaction cell.

The true potential and robustness of the methods developed were subsequently assessed through the use of matrix-matched standard solutions containing elements that can give rise to interfering ions. Solutions containing 5 μg L⁻¹ of As or of Se plus 100 μg L⁻¹ of Ca; 500 mg L⁻¹ of Cl, 100 μg L⁻¹ of Gd, of Nd, and of Sm; and 1 μg L⁻¹ of Mo, of Nb, of Ru, of Y, and of

Table 3 Comparison of instrumental limits of detection for As and Se obtained via ICP-MS/MS (using different collision-reaction cell conditions) and via SF-ICP-MS

ICP-MS/MS cell conditions	Scan type	Limits of detection (ng L ⁻¹) ^a			
		⁷⁵ As	⁷⁷ Se	⁷⁸ Se	⁸⁰ Se
“Vented mode”	SQ ^b	0.8	30	– ^c	– ^c
	MS/MS	0.9	50	– ^c	– ^c
He	SQ	1	20	40	– ^c
	MS/MS	2	40	60	– ^c
O ₂	SQ	9	500	200	30
	MS/MS	7	500	9	30
CH ₃ F/He	SQ	1	200	20	10
	MS/MS	0.2	10	7	4
SF-ICP-MS	EScan ^d	10	50	500	– ^c

^a LoDs calculated as three times the standard deviation on 10 consecutive measurements of a blank solution (0.14 M HNO₃), divided by the slope of the calibration curve

^b SQ stands for single quadrupole mode

^c Not measured (Ar-based interference was not resolved)

^d The high resolution setting (*R*~10,000) was used for all As and Se measurements

Table 4 Calibration data obtained for As and Se via ICP–MS/MS (using different collision–reaction cell conditions) and via SF–ICP–MS

Isotope	Agilent 8800							Thermo Element XR		
	Cell conditions	Scan type	Q1 (amu)	Q2 (amu)	Sensitivity ^a (L µg ⁻¹)	Intercept ^a (counts s ⁻¹)	R ²	Sensitivity ^a (L µg ⁻¹)	Intercept ^a (counts s ⁻¹)	R ²
⁷⁵ As	“Vented mode”	SQ	–	75	55,080±420	–410±360	0.999997	824±18	13±12	0.99996
		MS/MS	75	75	28,120±73	133±80	0.999992			
	He	SQ	–	75	11,920±95	218±71	0.999997			
		MS/MS	75	75	3,914±40	–11±37	0.999997			
	O ₂	SQ	–	91	13,010±370	650±260	0.99998			
		MS/MS	75	91	7,250±170	290±190	0.99998			
	CH ₃ F/He	SQ	–	89	34,710±580	–20±170	0.99998			
		MS/MS	75	89	18,160±250	–90±100	0.999994			
⁷⁷ Se	“Vented mode”	SQ	–	77	4,495±56	1090±210	0.99998	67±5	2±5	0.9999
		MS/MS	77	77	2,702±29	660±120	0.99998			
	He	SQ	–	77	492±13	11±11	0.99998			
		MS/MS	77	77	300±8	–0.4±13	0.99995			
	O ₂	SQ	–	93	153±5	240±14	0.998			
		MS/MS	77	93	71±5	34±12	0.9990			
	CH ₃ F/He	SQ	–	91	728±26	3146±72	0.9996			
		MS/MS	77	91	286±10	3±11	0.99998			
⁷⁸ Se	“Vented mode”	SQ	–	78	– ^b	– ^b	– ^b	223±8	28±17	0.9993
		MS/MS	78	78	– ^b	– ^b	– ^b			
	He	SQ	–	78	1,631±16	139±24	0.99998			
		MS/MS	78	78	997±22	99±23	0.999991			
	O ₂	SQ	–	94	405±13	357±16	0.9997			
		MS/MS	78	94	226±8	4±27	0.99995			
	CH ₃ F/He	SQ	–	92	1,945±20	317±43	0.9997			
		MS/MS	78	92	917±20	7±13	0.99998			
⁸⁰ Se	“Vented mode”	SQ	–	80	– ^b	– ^b	– ^b	– ^b		
		MS/MS	80	80	– ^b	– ^b	– ^b			
	He	SQ	–	80	– ^b	– ^b	– ^b			
		MS/MS	80	80	– ^b	– ^b	– ^b			
	O ₂	SQ	–	96	856±25	123±38	0.99998			
		MS/MS	80	96	478±13	54±22	0.99996			
	CH ₃ F/He	SQ	–	94	4,075±30	175±33	0.99997			
		MS/MS	80	94	1,944±25	–2±22	0.99997			

^aUncertainties expressed as standard deviation ($n=10$)

^bNot measured: the ³⁸Ar⁴⁰Ar⁺ and ⁴⁰Ar⁴⁰Ar⁺ signals were not fully resolved from the analyte signal

Zr were analyzed. While the use of He allows the polyatomic interferences (except for ⁴⁰Ar⁴⁰Ar⁺) [40] to be resolved, doubly charged interferences (e.g., ¹⁵⁰Nd²⁺, ^{150,154}Sm²⁺, ^{154,156,160}Gd²⁺) cannot be dealt with. When using O₂ or CH₃F/He, in the SQ mode, isobaric ions having the same m/z ratio as the reaction product ion (e.g., ⁸⁹Y⁺, ^{91,94,96}Zr⁺, ⁹³Nb⁺, ^{94,96}Mo⁺, and ⁹⁶Ru⁺), as well as all polyatomic interfering ions, formed either in the plasma or in the cell, still present a problem. However, in MS/MS mode, both reaction gasses were able to resolve all the spectral overlaps. Moreover, CH₃F/He shows a better performance than O₂ because of

the higher reaction efficiency with both As and Se, thus leading to better LoDs.

Results obtained for the determination of As and Se in reference materials

A number of reference materials were selected to further validate the methods relying to the use of ICP–MS/MS with CH₃F/He. The materials were of plant, animal, or environmental origin, and a wide range of concentrations was covered.

Table 5 Comparison of ICP-MS/MS LoDs with those reported in the literature for other ICP-MS setups

Authors	Instrumentation	Mode	LoDs (ng L ⁻¹)			
			⁷⁵ As	⁷⁷ Se	⁷⁸ Se	⁸⁰ Se
Townsend et al. [38]	SF-ICP-MS	High mass resolution	95	170	–	–
Sloth [53]	Q-ICP-MS	CH ₄ in quadrupole-based collision/reaction cell	–	–	–	6
Chéry et al. [54]	Q-ICP-MS	CO in quadrupole-based collision/reaction cell	–	250	–	10
Frank et al. [55]	SF-ICP-MS	High mass resolution	3	–	–	–
Darrouzès et al. [33]	Q-ICP-MS	H ₂ /He in octopole-based collision/reaction cell	25	–	45	35
Pick et al. [56]	Q-ICP-MS	O ₂ (As) CH ₄ (Se) in quadrupole-based collision/reaction cell	30	–	–	160
Li et al. [57]	Q-ICP-MS	H ₂ /He in hexapole-based collision/reaction cell	25	–	95	–
This work	ICP-MS/MS	CH ₃ F/He	0.2	10	7	4

External calibration was used for quantification with Te as an internal standard (selected on the basis of the closeness of its ionization energy and chemical behavior to those of the target elements) to correct for matrix effects, instrument instability, and signal drift. For each reference material, several aliquots from four separate digestions were diluted and analyzed.

The results are presented in Table 6, which shows the average of 20 measurements, obtained from four different digestions, each one measured five consecutive times. At the 95 % level of significance, all the results obtained are in good agreement with the corresponding certified value ($t < t_{\text{critical}}$),

which demonstrates that the methods developed enable the straightforward determination of As and Se at different concentration levels and in various matrix types, whereby the problem of both spectral and nonspectral interferences is avoided.

Additionally, a good agreement was found among the three selected Se nuclides, thus enabling the monitoring of the most abundant isotope (⁸⁰Se), which is often prohibited when using other approaches (e.g., SF-ICP-MS), and also permitting isotopic analysis when required in the context of elemental assay via isotope dilution or tracer experiments.

Table 6 Results obtained for certified reference materials using CH₃F/He and ICP-MS/MS

Sample description	Arsenic		Selenium			
	Average±SD (μg g ⁻¹) ^a	Certified value (μg g ⁻¹)	Average±SD (μg g ⁻¹) ^a			Certified value (μg g ⁻¹)
	⁷⁵ As		⁷⁷ Se	⁷⁸ Se	⁸⁰ Se	
NIST SRM 1515 Apple leaves	0.038±0.002	0.038±0.007	0.055±0.007	0.050±0.003	0.049±0.004	0.050±0.009
NBS SRM 1575 Pine needles	0.23±0.01	0.21±0.04	–	–	–	–
NBS SRM 1573 Tomato leaves	0.30±0.01	0.27±0.05	–	–	–	–
NIST SRM 1568a Rice flour	0.27±0.01	0.29±0.03	0.35±0.04	0.35±0.02	0.35±0.01	0.38±0.04
BCR CRM 526 Tuna fish tissue	5.02±0.07	4.80±0.30	–	–	–	–
NCR-CNRC DORM-4 Fish protein	6.79±0.06	6.80±0.64	3.65±0.10	3.64±0.07	3.63±0.03	3.56±0.34
BCR-414 Plankton	6.95±0.09	6.82±0.28	1.75±0.09	1.72±0.05	1.77±0.03	1.75±0.10
NBS SRM 1646 Estuarine sediment	11.07±0.15	11.6±1.3	0.64±0.04	0.63±0.03	0.65±0.02	0.6 ^b
NIST SRM 1566a Oyster tissue	14.01±0.20	14.0±1.2	2.23±0.09	2.22±0.06	2.22±0.04	2.21±0.24
NRC-CNRC TORT-3 Lobster hepatopancreas	60.74±1.33	59.5±3.8	11.03±0.22	11.09±0.09	11.07±0.12	10.9±1.0

^aUncertainties expressed as standard deviation ($n=20$)

^bIndicative value

The accuracy of the determination was proven for all the reference materials, including NIST SRM 1515 (Apple Leaves), despite its low As and Se concentrations and the presence of considerable amounts of Nd and Sm (leading to doubly charged interferences that cannot be overcome by using a collision gas (e.g., He), as discussed in the previous section).

The precision attainable was checked via the RSD (%), which includes the measurement precision, as well as the contribution from the sample preparation. Still, RSD values lower than 5 % were found for all reference materials in the case of As. These RSD values improve down to 1–2 % for reference materials with concentrations exceeding $1 \mu\text{g g}^{-1}$. In the case of Se, RSD values better than 3 % were found for ^{80}Se , better than 5 % for ^{78}Se and better than 10 % for ^{77}Se , except for NIST SRM 1515 (Apple leaves), for which, due to the low concentration, the RSD values found were 13, 6, and 8 % for $^{77,78,80}\text{Se}$, respectively. Except in this case, the RSDs found are in good agreement with the trend expected on the basis of the isotopic abundance of the nuclides monitored (RSD via $^{77}\text{Se} > ^{78}\text{Se} > ^{80}\text{Se}$).

Conclusion

In this work, the capabilities of $\text{CH}_3\text{F}/\text{He}$ as a reaction gas in ICP–MS/MS for the ultra-trace determination of As and Se in diverse sample types have been demonstrated. This approach provides interference-free conditions, permitting As and Se determination via AsCH_2^+ and SeCH_2^+ , respectively, with high accuracy and precision. The instrumental LoD for As was calculated to be 0.2 ng L^{-1} , while those for all of the Se nuclides studied were below 10 ng L^{-1} . For Se, the approach developed is suited for interference-free element determination via all of the isotopes investigated. As a result, also the utility in speciation and isotopic analysis (e.g., tracer studies and elemental assay via isotope dilution) can be assumed feasible.

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References

- Roy P, Saha A (2002) Metabolism and toxicity of arsenic: a human carcinogen. *Curr Sci* 82:38–45
- Tinggi U (2003) Essentiality and toxicity of selenium and its status in Australia: a review. *Toxicol Lett* 137:103–110
- Sun H-J, Rathinasabapathi B, Wu B, Luo J, Pu L-P, Ma L-Q (2014) Arsenic and selenium toxicity and their interactive effects in humans. *Environ Int* 69:148–158
- Huang Z, Pei Q, Sun G, Zhang S, Liang J, Gao Y, Zhang X (2008) Low selenium status affects arsenic metabolites in an arsenic exposed population with skin lesions. *Clin Chim Acta* 387:139–144
- Kolachi NF, Kazi TG, Wadhwa SK, Afridi HI, Baig JA, Khan S, Shah F (2011) Evaluation of selenium in biological sample of arsenic exposed female skin lesions and skin cancer patients with related to non-exposed skin cancer patients. *Sci Total Environ* 409:3092–3097
- Sah S, Vandenberg A, Smits J (2013) Treating chronic arsenic toxicity with high selenium lentil diets. *Toxicol Appl Pharmacol* 272:256–262
- Vassileva E, Becker A, Broekaert JAC (2001) Determination of arsenic and selenium species in groundwater and soil extracts by ion chromatography coupled to inductively coupled plasma mass spectrometry. *Anal Chim Acta* 441:135–146
- Iserte MO, Roig-Navarro AF, Hernández F (2004) Simultaneous determination of arsenic and selenium species in phosphoric acid extracts of sediment samples by HPLC-ICP-MS. *Anal Chim Acta* 527:97–104
- Wang R-Y, Hsu Y-L, Chang L-F, Jiang S-J (2007) Speciation analysis of arsenic and selenium compounds in environmental and biological samples by ion chromatography-inductively coupled plasma dynamic reaction cell mass spectrometer. *Anal Chim Acta* 590:239–244
- Tonietto GB, Godoy JM, Oliveira AC, de Souza MV (2010) Simultaneous speciation of arsenic (As(III), MMA, DMA, and As(V)) and selenium (Se(IV), Se(VI), and SeCN⁻) in petroleum refinery aqueous streams. *Anal Bioanal Chem* 397:1755–1761
- Balaba RS, Smart RB (2012) Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater. *Chemosphere* 89:1437–1442
- Chan CCY, Sadana RS (1992) Determination of arsenic and selenium in environmental samples by flow-injection hydride generation atomic absorption spectrometry. *Anal Chim Acta* 270:213–238
- Ding WW, Sturgeon RE (1996) Evaluation of electrochemical hydride generation for the determination of arsenic and selenium in sea water by graphite furnace atomic absorption with in situ concentration. *Spectrochim Acta B* 51:1325–1334
- Cai Y (2000) Speciation and analysis of mercury, arsenic, and selenium by atomic fluorescence spectrometry. *TrAC Trends Anal Chem* 19:62–66
- Beccaloni E, Musmeci L, Stacul E (2002) Determination of As in environmental solid matrix. *Anal Bioanal Chem* 374:1230–1236
- Resano M, Flórez MR, García-Ruiz E (2014) Progress in the determination of metalloids and non-metals by means of high-resolution continuum source atomic or molecular absorption spectrometry. A critical review. *Anal Bioanal Chem* 406:2239–2259
- Goossens J, Vanhaecke F, Moens L, Dams R (1993) Elimination of interferences in the determination of arsenic and selenium in biological samples by inductively coupled plasma mass spectrometry. *Anal Chim Acta* 280:137–143
- Vanhaecke F, Riondato J, Moens L, Dams R (1996) Non-spectral interferences encountered with a commercially available high resolution ICP-mass spectrometer. *Fresenius J Anal Chem* 355:397–400
- Allain P, Jaunault L, Mauras Y, Mermet J-M, Delaporte T (1991) Signal enhancement of elements due to the presence of carbon-containing compounds in inductively coupled plasma mass spectrometry. *Anal Chem* 63:1497–1498
- Larsen EH, Stürup S (1994) Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation. *J Anal At Spectrom* 9:1099–1105
- Kovačević M, Goessler W, Mikac N, Veber M (2005) Matrix effects during phosphorus determination with quadrupole inductively coupled plasma mass spectrometry. *Anal Bioanal Chem* 383:145–151
- Grindlay G, Mora J, Md L-V, Vanhaecke F (2013) A systematic study on the influence of carbon on the behavior of hard-to-ionize elements

- in inductively coupled plasma-mass spectrometry. *Spectrochim Acta B* 86:42–49
23. Nakazawa T, Suzuki D, Sakuma H, Furuta N (2014) Comparison of signal enhancement by co-existing carbon and by co-existing bromine in inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 29:1299–1305
 24. Kim Y-S, Kawaguchi H, Tanaka T, Mizuike A (1990) Non-spectroscopic matrix interferences in inductively coupled plasma-mass spectrometry. *Spectrochim Acta B* 45(3):333–339
 25. Vanhaecke F, Dams R, Vandecasteele C (1993) 'Zone Model' as an explanation for signal behaviour and non-spectral interferences in inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 8:433–438
 26. Al-Ammar AS, Gupta RK, Barnes RM (1999) Correction for non-spectroscopic matrix effects in inductively coupled plasma-mass spectrometry by common analyte internal standardization. *Spectrochim Acta B* 54:1849–1860
 27. Salin ED, Antler M, Bort G (2004) Evaluation of the simultaneous use of standard additions and internal standards calibration techniques for inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 19:1498–1500
 28. Jr RLW, Eberhardt KR, Beary ES, Fassett JD (1997) Protocol for isotope dilution using inductively coupled plasma-mass spectrometry (ICP-MS) for the determination of inorganic elements. *Metrologia* 34:87–96
 29. Reyes LH, Gayón JMM, Alonso JIG, Sanz-Medel A (2003) Determination of selenium in biological materials by isotope dilution analysis with an octapole reaction system ICP-MS. *J Anal At Spectrom* 18:11–16
 30. Park CJ, Song H (2005) Determination of arsenic in biological samples by inductively coupled plasma mass spectrometry with selenium as an internal standard. *J Anal At Spectrom* 20:436–440
 31. Castillo A, Boix C, Fabregat N, Roig-Navarro AF, Rodríguez-Castrillón LA (2012) Rapid screening of arsenic species in urine from exposed human by inductively coupled plasma mass spectrometry with germanium as internal standard. *J Anal At Spectrom* 27:354–358
 32. Boulyga SF, Becker JS (2001) ICP-MS with hexapole collision cell for isotope ratio measurements of Ca, Fe, and Se. *Fresenius J Anal Chem* 370:618–623
 33. Darrouzès J, Bueno M, Lespès G, Holeman M, Potin-Gautier M (2007) Optimisation of ICPMS collision/reaction cell conditions for the simultaneous removal of argon based interferences of arsenic and selenium in water samples. *Talanta* 71:2080–2084
 34. Zhang Z, Chen S, Yu H, Sun M, Liu W (2004) Simultaneous determination of arsenic, selenium, and mercury by ion exchange-vapor generation-inductively coupled plasma-mass spectrometry. *Anal Chim Acta* 513:417–423
 35. Colon M, Hidalgo M, Iglesias M (2009) Correction strategies over spectral interferences for arsenic determination in aqueous samples with complex matrices by quadrupole ICP-MS. *J Anal At Spectrom* 24:518–521
 36. Tanner SD (1995) Characterization of ionization and matrix suppression in inductively coupled 'cold' plasma mass spectrometry. *J Anal At Spectrom* 10:905–921
 37. Musil S, Pétursdóttir AH, Raab A, Gunnlaugsdóttir H, Krupp E, Jr F (2014) Speciation without chromatography using selective hydride generation: inorganic arsenic in rice and samples of marine origin. *Anal Chem* 86:993–999
 38. Townsend AT (1999) The determination of arsenic and selenium in standard reference materials using sector field ICP-MS in high resolution mode. *Fresenius J Anal Chem* 364:521–526
 39. D'Ilio S, Violante N, Majorani C, Petrucci F (2011) Dynamic reaction cell ICP-MS for determination of total As, Cr, Se and V in complex matrices: still a challenge? A review. *Anal Chim Acta* 698:6–13
 40. Niemelä M, Perämäki P, Kola H, Piispanen J (2003) Determination of arsenic, iron and selenium in moss samples using hexapole collision cell, inductively coupled plasma-mass spectrometry. *Anal Chim Acta* 493:3–12
 41. Resano M, Ruiz EG, Mihuez VG, Móriéz ÁM, Záray G, Vanhaecke F (2007) Rapid screening method for arsenic speciation by combining thin layer chromatography and laser ablation-inductively coupled plasma-dynamic reaction cell-mass spectrometry. *J Anal At Spectrom* 22:1158–1162
 42. Colon M, Hidalgo M, Iglesias M (2011) Arsenic determination by ICP-QMS with octapole collision/reaction cell. Overcome of matrix effects under vented and pressurized cell conditions. *Talanta* 85: 1941–1947
 43. Guo W, Hu S, Wang Y, Zhang L, Hu Z, Zhang J (2013) Trace determination of selenium in biological samples by CH₄-Ar mixed gas plasma DRC-ICP-MS. *Microchem J* 108:106–112
 44. Guo W, Hu S, Li X, Zhao J, Jin S, Liu W, Zhang H (2001) Use of ion-molecule reactions and methanol addition to improve arsenic determination in high chlorine food samples by DRC-ICP-MS. *Talanta* 84: 887–894
 45. Grotti M, Frache R (2007) Direct determination of arsenic in seawater by reaction cell inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 22:1481–1487
 46. Fernández SD, Sugishama N, Encinar JR, Sanz-Medel A (2012) Triple Quad ICPMS (ICPQQQ) as a new tool for absolute quantitative proteomics and phosphoproteomics. *Anal Chem* 84:5851–5857
 47. Balcaen L, Woods G, Resano M, Vanhaecke F (2013) Accurate determination of S in organic matrices using isotope dilution ICP-MS/MS. *J Anal At Spectrom* 28:33–39
 48. Balcaen L, Bolea-Fernandez E, Resano M, Vanhaecke F (2014) Accurate determination of ultra-trace levels of Ti in blood serum using ICP-MS/MS. *Anal Chim Acta* 809:1–8
 49. Bolea-Fernandez E, Balcaen L, Resano M, Vanhaecke F. Potential of methyl fluoride as a universal reaction gas to overcome spectral interference in the determination of ultra-trace concentrations of metals in biofluids using ICP-MS/MS. *Anal Chem* 86:7969–7977
 50. Moens LJ, Vanhaecke F, Bandura DR, Baranov VI, Tanner SD (2001) Elimination of isobaric interferences in ICP-MS, using ion-molecule reaction chemistry: Rb/Sr age determination of magmatic rocks, a case study. *J Anal At Spectrom* 16:991–994
 51. Nonose N, Ohata M, Narukawa T, Hioki A, Chiba K (2009) Removal of isobaric interferences in isotope dilution analysis of vanadium in silicon nitride fine ceramics powder by DRC-ICP-MS. *J Anal At Spectrom* 24:310–319
 52. Zhao X, Koyanagi GK, Bohme DK (2006) Reactions of methyl fluoride with atomic transition-metal and main-group cations: gas-phase room-temperature kinetics and periodicities in reactivity. *J Phys Chem A* 110:10607–10618
 53. Sloth JJ, Larsen EH (2000) The application of inductively coupled plasma dynamic reaction cell mass spectrometry for measurement of selenium isotopes, isotope ratios and chromatographic detection of selenoamino acids. *J Anal At Spectrom* 15:669–672
 54. Chéry CC, Günther D, Cornelis R, Vanhaecke F, Moens L (2003) Detection of metals in proteins by means of polyacrylamide gel electrophoresis and laser ablation-inductively coupled plasma-mass spectrometry: application to selenium. *Electrophoresis* 24:3305–3313
 55. Frank J, Krachler M, Shotyk W (2005) Direct determination of arsenic in acid digests of plant and peat samples using HG-AAS and ICP-SF-MS. *Anal Chim Acta* 530:307–316
 56. Pick D, Leiterer M, Einax JW (2010) Reduction of polyatomic interferences in biological material using dynamic reaction cell ICP-MS. *Microchem J* 95:315–319
 57. Li X, Dai S, Zhang W, Li T, Zheng X, Chen W (2014) Determination of As and Se in coal and coal combustion products using closed vessel microwave digestion and collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS). *Int J Coal Geol* 124:1–4