

Quantification of major and trace elements in water samples by ICP-MS and collision cell to attenuate Ar and Cl-based polyatomic ions

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Received 27th January 2009, Accepted 21st July 2009

First published as an Advance Article on the web 5th August 2009

DOI: 10.1039/b901644a

Inductively coupled plasma mass spectrometry (ICP-MS) is the best fitted analytical technique for multi-element analysis of waters, because of its low detection limits. One limitation is the polyatomic interferences produced in the plasma and in the interface (e.g., $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$, $^{40}\text{Ar}^{16}\text{O}^+$ on $^{56}\text{Fe}^+$, $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$ and $^{40}\text{Ar}^{38}\text{Ar}^+$ on $^{78}\text{Se}^+$). These polyatomic ions can be significantly reduced by ion molecule interactions in a collision cell (CC). Several experiments done in a ICP-MS equipped with a CC pressurized by premixed H_2 7% in He, under optimized gas flow rates, demonstrate the beneficial effect of KED to suppress Ar and Cl-based interferences. These results are opposed to reports where the role of KED was denied. Under such conditions the background equivalent concentration of ^{51}V , ^{52}Cr , ^{56}Fe , ^{63}Cu , ^{75}As and ^{78}Se were improved by two orders of magnitude, allowing the quantification of these elements at low ng L^{-1} level, without the need for mathematical corrections. Moreover, we present results obtained with a multi-mode method of analysis for twenty eight elements in two water certified reference materials (CRM). In this method isotopes free from polyatomic interferences are measured in standard mode and interfered ones using CC mode. The certified and reference values were used to evaluate the analytical trueness, which was better than 5%, with all z-scores within the recommended limit. Intermediate precision was mostly better than 6% and method detection limits are fit for hydrogeochemical studies and to monitor regulated toxic trace elements in waters.

1. Introduction

The increasing exploration of surface and groundwater water resources demands compliant assessment and monitoring, which comprises several constituents including trace elements.^{1–4} Most regulated trace elements can be properly measured by inductively coupled plasma mass spectrometry (ICP-MS), because this multi-element technique is able to provide the appropriate detection limits, at the sub-microgram per litre concentration range.^{5–10}

During analysis, when the sample is in the ICP for analyte ionization and during the extraction process, many side reactions between the plasma gas and sample matrix produce polyatomic ions that overlap several isotopes. As a consequence, the quantification of some elements becomes difficult, especially for isotopes within the mass range of 40 to 80 a.m.u.^{11–15} Background ions caused by plasma gas ($^{40}\text{Ar}^{16}\text{O}^+$ and $^{78,80}\text{Ar}_2^+$) are produced at high levels and they mainly hamper the determination of elements by increasing their detection limits ($^{56}\text{Fe}^+$ and $^{78,80}\text{Se}^+$, respectively). In addition, matrix-based ions cause sample dependent interferences (e.g. $^{35}\text{Cl}^{15}\text{O}^+$ on $^{51}\text{V}^+$, $^{35}\text{Cl}^{15}\text{O}^+\text{H}^+$ on $^{52}\text{Cr}^+$, $^{40}\text{Ar}^{23}\text{Na}^+$ on $^{63}\text{Cu}^+$, $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$, among others) that produce inaccurate results if not avoided or corrected.

The possibilities to deal with such interferences were expanded and improved since ICP-MS instruments equipped with collision cell (CC) or reaction cell (RC) became available.^{16–19} A distinction between CC and RC based on the thermal characteristics of

the cell was proposed by Tanner *et al.*²⁰ Instead of the non trivial set up and update of mathematical correction equations^{9,21–24} or time consuming matrix removal methods,^{6,25–27} interactions between sampled ions and gases in a cell provide simple and effective elimination of undesired polyatomic ions.

Eiden *et al.*^{18,19} originally recognized the unique capabilities of H_2 as a reactive gas for collision cell ICP-MS. Since then, several papers report the successful application of H_2 either alone or mixed with He at different proportions to attenuate ArX^+ and other polyatomic ions, in several matrices.^{28–42} In such applications He is used as a collision gas to enhance ions transmission through collisional focusing.²⁰ Such collisions also decrease the mean kinetic energy of ions and likely favor reactions between ArX^+ and H_2 within the cell.³⁰

The use of H_2 to solve ArX^+ interferences is well known.³⁰ Iglesias *et al.*³¹ investigated the effects of different gases (H_2 , He, NH_3 and N_2O) to alleviate ArO^+ and Ar_2^+ in a hexapole collision cell. They observed that given the low reactivity of H_2 with most analyte ions, mixtures of H_2/He can be effectively used in multi-element analyses. However the same is not true for highly reactive gases, as NH_3 and N_2O , which produce adducts with analyte ions (e.g. $[\text{As}(\text{NH}_3)\text{NH}_2^+]$) and complete (La, As) or partial (Fe, Se, V) shift to the respective oxide.³¹

Optimum gas flow or ideal H_2/He ratio seems to be strongly dependent on the cell design and operating conditions. For instance, even when identical instruments are used, differences in the operation conditions result in different set up of optimum gas flow rates and H_2/He ratios. This is exemplified in studies on the influence of hexapole bias (V_H) to the attenuate the signal of $^{40}\text{Ar}^{16}\text{O}^+$ and of $^{80}\text{Ar}_2^+$ with H_2 and He either alone and in mixtures.^{30,33,35} Boulyga and Becker³⁵ were able to suppress

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ArX⁺ ions at three to five orders of magnitude, using V_H bias between 0 to +1.6 V and H₂/He = 2/4 (2 and 4 mL/min, respectively). Feldmann *et al.*^{30,33} obtained similar interference attenuation, but using V_H bias between -1.5 to -4 V and H₂/He = 5/3.

In general, efficient removal of ArX⁺ occurs with gas flow rates between 4 to 7 mL/min with low, but variable, H₂/He ratios. Niemelä *et al.*³⁷ reported that isotope ratios (⁵⁷Fe/⁵⁶Fe and ⁷⁷Se/⁷⁸Se), were more accurate with premixed 7% H₂ in He (7.5 mL/min) as cell gas, than those obtained with H₂ alone. This improvement was attributed to the beneficial effect of helium as a collision gas when hydrogen is used as a reactive gas. Niemelä *et al.*³⁷ also, reported that addition of more H₂ to the premixed gases no further reduces ArX⁺ (X = Ar, O and Cl) signal. Many investigations focused in the alleviation of interferences of a limited number of elements, mostly Fe, As and Se, and reports regarding the attenuation of other problematic interferences likely to occur during water analyses, as ³⁵Cl¹⁵O⁺ on ⁵¹V⁺ or ³⁵Cl¹⁵O⁺H⁺ on ⁵²Cr⁺ are rarer.⁴⁴

Chrastný *et al.*⁴² compared the use of H₂/He and NH₃/He in a hexapole CC-ICP-MS to attenuate ³⁵Cl¹⁶O⁺ and ⁴⁰Ar³⁵Cl⁺ polyatomic interferences on ⁵¹V⁺ and ⁷⁵As⁺, respectively. Their results⁴² indicate that both gas mixtures effectively eliminate ArCl⁺, but observed that H₂/He is not the ideal gas to attenuate ClO⁺ in samples with high Cl content, and suggest the use of NH₃/He in such cases.

Additionally to the attenuation that can be obtained when the cell is pressurized with a reactive gas, a kinetic energy discrimination (KED) barrier potential can be established between the cell and mass analyzer to provide extra attenuation of polyatomic interferences.³⁸ Since polyatomic ions have larger collision cross sections (higher polarizability compared to elemental ions and eventually a dipole moment) they experience more collisions inside the cell volume and greater loss of kinetic energy.⁴³ Therefore a potential barrier after the cell can be used to prevent them to reach the detector.

McCurdy and Woods⁴⁴ demonstrated that polyatomic ions produced by Ar, C, S and Cl, can be attenuated over 5 orders of magnitude using KED in an octapole CC filled only with an inert gas (He). Although the well documented^{28,36,38,42-44} beneficial role of KED to reduce polyatomic interferences, frequently it is not used.^{37,39,41,45,46}

In this paper we present results from experiments that support the beneficial effect of KED to attenuate both reactive (ArX⁺)^{47,48} and non-reactive polyatomic interferences (ClO⁺)⁴⁷ in a H₂/He cell. The combined effect of H₂ ion-molecule chemistry and KED to solve spectral interferences originated both from the plasma gas and from sample matrix were investigated and used to establish a simple and fast method to the determination of 28 elements, in water samples. The accuracy of the method was assessed by analysis of two water certified reference materials (NIST SRM 1640 and 1643e) during a period of few months.

2. Experimental

A quadrupole ICP-MS *Xseries^{II}* (Thermo, Germany) equipped with a hexapole collision cell (CC) was used. The instrument software allows the rapid switch between standard mode

(no gas, cell vented to mass analyzer chamber) to CC mode, whilst continuously aspirating the sample. The pre-mixed gases H₂ (7%) in He (H₂O and other impurities <5 ppm) were admitted into CC under flow control through stainless steel lines. The measurements were made with nickel sampler and skimmer cones (1.0 mm and 0.7 mm diameter orifices) and conical nebulizer. A glass impact bead spray chamber cooled to 4 °C by a Peltier cooler and a shielded Fassel torch was used to minimize the plasma potential and thereby obtain a low and narrow initial ion energy distribution. Plasma parameters are listed in Table 1.

The daily optimization procedure involved the xyz alignment of the torch, determination of the optimum nebulizer gas flow rate and the ion lens voltage to maximize ¹¹⁵In⁺ signal and obtain low oxide (¹⁴⁰Ce¹⁶O⁺/¹⁴⁰Ce⁺) and double charged ions (¹³⁷Ba⁺⁺/¹³⁷Ba⁺). The detector was operated in dual mode and cross-calibration was performed weakly. Sample was introduced *via* peristaltic pump (orange-yellow tubing) with uptake rate of 0.8 mL min⁻¹. All measurements were made with preconditioned cones, *i.e.*, by aspirating tap water spiked with 300 mg L⁻¹ of CaCl₂. Occasionally, when optimum extraction voltage exceeded -150 V, sampler and skimmer cones were cleaned by sonication in deionized water for 10–15 minutes. Before measurements, cleaned cones were again conditioned for 5 minutes. This procedure reduces instrumental drift efficiently. Unconditioned cones usually show drift in the first set of analysis, due to material deposition on the cones tips.

In the established multi-mode method of analysis, the isotopes susceptible to polyatomic interferences during water analyses were measured in CC mode using specific gas flow rates, as indicated in Table 1. Here sulfur-based polyatomics were not investigated since its major interferences,^{13,45} mainly ³²S¹⁶O⁺, ³⁴S¹⁶O⁺ and ³²S¹⁶O₂⁺, do not overlap the isotopes used in this

Table 1 Typical settings of the ICP-MS

Incident power	1400 W
Extraction	-210 to -160 V
Plasma gas flow	13 L min ⁻¹
Nebulizer flow	0.81 to 0.85 L min ⁻¹
Dwell time	10–30 ms
Measurements	3 × 30 scans
Conditions	¹⁴⁰ Ce ¹⁶ O ⁺ / ¹⁴⁰ Ce ⁺ <2% and ¹³⁷ Ba ⁺⁺ / ¹³⁷ Ba ⁺ <3%
CC mode	
Isotopes and gas flow	6 mL/min for ⁵¹ V 4 mL/min for ³⁹ K, ⁵² Cr, ^{54,56} Fe, ⁵⁵ Mn, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁷⁵ As, ⁷⁸ Se
Hexapole bias	-17 V
Quadrupole bias	-14 V
Differential Aperture (DA)	-26 V
Signal	¹¹⁵ In (1 µg L ⁻¹) >20 kcps and ⁷⁸ Ar ₂ <10 cps
Standard mode	
Isotopes	⁷ Li, ⁹ Be, ¹¹ B, ²³ Na, ²⁵ Mg, ²⁷ Al, ²⁹ Si, ⁴³ Ca, ⁸⁵ Rb, ⁸⁸ Sr, ⁹⁵ Mo, ¹⁰⁷ Ag, ¹¹¹ Cd, ¹²¹ Sb, ¹³⁷ Ba, ²⁰⁵ Tl, ^{206,207,208} Pb
Hexapole bias	-4 V
Quadrupole bias	0.5 V
DA	-36 V
Signal	¹¹⁵ In (1 µg L ⁻¹) > 40 kcps

method. Attenuation of chlorine-based interferences was investigated because $^{35}\text{Cl}^{16}\text{O}^+$ and $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ overlap $^{51}\text{V}^+$ and $^{52}\text{Cr}^+$, used to quantify the respective analytes.

The sample analysis starts in CC mode with 6 mL/min H_2/He for $^{51}\text{V}^+$ measurement, followed by reduction of gas flow to 4 mL/min to measure ^{39}K , ^{52}Cr , $^{54,56}\text{Fe}$, ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{78}Se . After this is finished the instrument configuration switches to standard mode to measure the remaining elements. Each change is automatically performed by the instrument software and followed by a short stabilization delay of 10 seconds (user defined). The gas flow rates were set up to overcome polyatomic overlaps considering typical samples matrixes, after the optimization experiments, which are presented below. It is worth noting that the above gas flow rates may be modified according to interference attenuation requirements. Some limitations of the method are also discussed.

Two intermediate calibration solutions were used. The first was made up by the matrix elements Na, Mg, Al, K, Ca, Si, Fe, Mn, Sr and Ba in concentrations ranging from 50 to 1.5 mg L⁻¹ (prepared from 1000 mg L⁻¹ Merck standard solutions). The other contains the trace elements Li, Be, B, V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Mo, Ag, Sb, Tl and Pb at concentrations in the range of 600 to 25 µg L⁻¹ (prepared from High-Purity Standards of 10 mg L⁻¹). All standard solutions were prepared gravimetrically in polypropylene bottles and made up with 1% HNO_3 (v/v).

The working calibration solutions were prepared separately, by diluting each intermediate calibration solution 200, 30 and 5 fold. As matrix and trace elements are calibrated separately, there is no matrix matching between samples and calibration standards. Hence, complete removal of polyatomic interference is crucial to achieve accurate results. This calibration strategy, using two sets of calibration solutions, is more flexible than to combine all elements in a single solution. It was adopted to accommodate the wide range of elemental concentrations and different sample matrixes analyzed together with NIST SRM 1640 (Trace Elements in Natural Water) and SRM 1643e (Trace Elements in Water) certified reference materials (CRM). The results for both CRM have been collected during more than 5 months at different measurement runs.

Usually samples were analyzed in groups of 5–10, bracketed by one CRM to monitor possible signal drift. Recalibration was performed when drift becomes significant (> 20%).

To overcome problems with matrix effects^{49–51} five internal standards (IS) were used. Sc, Y, In, Re and Bi were combined in one solution at concentrations of 350, 100, 100, 80 and 50 µg L⁻¹, respectively. They were added using a Dispensette® (Brand). In general, 100 µL of this solution was combined with the sample aliquot and diluted to a final mass of 10.0 g with HNO_3 1%. $^{45}\text{Sc}^+$ was measured in CC mode and used as IS for the elements measured in this mode. The signals of $^{89}\text{Y}^+$, $^{115}\text{In}^+$, $^{185}\text{Re}^+$ and $^{209}\text{Bi}^+$ were interpolated to correct drift of the remaining analytes. For SRM 1643e only Sc, Y and In were used since this material contains measurable trace amounts of Re and Bi.

Prior determination, SRM 1640 and 1643e were 10 fold diluted. With this dilution factor, the concentrations of all elements in these samples are below the Maximum Contaminant Level (MCLs) for the contaminants specified in the National Primary Drinking Water Regulation (NPDWRs) of U.S.

Environmental Protection Agency (US EPA)⁵² allowing to assess the method accuracy at this level.

Ultrapure water was obtained by Milli-Q system (Millipore) with a resistivity >18.2 M Ω.cm. Nitric acid, 37% (Merck, p.a.) was purified by sub-ebullition in a quartz device (Milestone, Germany) and hydrochloric acid, 30.9% (Merck, Suprapur) was used without further purification. All used bottles were previously overnight cleaned with 10% HNO_3 and double rinsed with ultrapure water prior use. 1% HNO_3 was frequently analyzed to determine instrumental blank and possible memory effects, which were typically <0.01 µg L⁻¹ for most trace analytes. NaCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, p.a.) and ^{50}Cr spike solution (Alfa Aesar) were used in complementary tests. All acidified solutions were made by dilution on a v/v basis.

3. Results and discussion

3.1 Assessment of CC tuning

Prior to each set of measurements the instrument is tuned in the standard and CC modes, following manufacturer recommendations. In CC mode, the hexapole bias (V_H) is set to -17 V, because it corresponds to the optimum ion transmission potential when the cell is pressurized, and the quadrupole bias (V_Q) is set to -14 V, to yield a kinetic energy discrimination of 3 V ($\text{KED} = V_Q - V_H = 3\text{V}$). After that, the flow of the gas mixture (7% H_2 in He) is adjusted to provide less than 10 cps at m/z 78. This is typically obtained with gas flow close to 4 mL/min, and then lenses and focus are tuned for maximum ^{115}In signal (>20 kcps ppb⁻¹).

With this instrument KED can also be applied by biasing the differential aperture (DA), however DA potential was kept more negative than the hexapole, meaning that the applied KED corresponds to the difference between V_Q and V_H . This is not usually informed in papers regarding the use of collision cells, and the lack of this information can cause some misunderstanding in relation to the actual use or not of KED.

The preferential removal of polyatomic interfering ions $^{35}\text{Cl}^{16}\text{O}^+$, $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ and $^{40}\text{Ar}^{35}\text{Cl}^+$ from the analytes $^{51}\text{V}^+$, $^{50,52}\text{Cr}^+$ and $^{75}\text{As}^+$ by changing the KED barrier is shown in Fig. 1 (a) and (b). In Fig 1 (a) analytes, in 1% HNO_3 , and Cl-based interferences produced by 1% HCl were measured separately using the same gas flow rate. The high intensity signal of interferences produced by 1% HCl cannot be completely attenuated using a gas flow rate of 4 mL/min, but the analyte/polyatomic ions ratio is improved by increasing the KED.

In Fig. 1(b) the preferential attenuation of $^{35}\text{Cl}^{16}\text{O}^+$, interfering on $^{51}\text{V}^+$, is highlighted in relation to the chromium isotope at nominal mass 50, using gas flow rate of 6 mL/min and typical Cl level of natural waters. As $^{50}\text{Cr}^+$ is not interfered by Cl-based polyatomics and there is no Cr at mass 51, both masses could be monitored together in the same solution (Cr in 1% HNO_3 spiked with and 200 mg L⁻¹ of Cl, using NaCl). The signal of $^{35}\text{Cl}^{16}\text{O}^+$ was attenuated over 4 orders of magnitude until reaching background levels (<2 count.s⁻¹). But a simultaneous decrease in analyte signal was observed, almost of one tenth. The net effect is an improvement close to 3 orders of magnitude. Data of Fig 1 (a and b) show that after the multiple collisions with the cell gas, polyatomic ions possess lower axial kinetic energy than

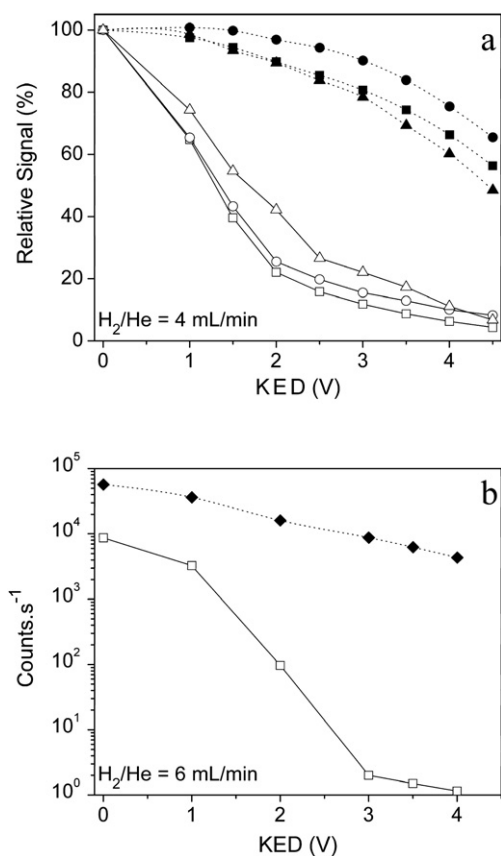


Fig. 1 Preferential attenuation of polyatomic ions signal by increasing the KED barrier at constant gas flow (7% H_2 in He). a) $^{51}V^+$ (■), $^{52}Cr^+$ (●) and $^{75}As^+$ (▲) in 1% HNO_3 . $^{35}Cl^{16}O^+$ (□), $^{35}Cl^{16}O^+H^+$ (○) and $^{40}Ar^{35}Cl^+$ (Δ) in 1% HCl; b) $^{50}Cr^+$ (◆) and $^{35}Cl^{16}O^+$ (□), measured together in 1% HNO_3 spiked with 200 mg L^{-1} of Cl. Notice that ordinate units of the two panels are different.

monatomic ions, and thus are effectively attenuated by KED of 3V, which provides satisfactory decrease of polyatomic ions signal and improved analyte/interference ratios.

A KED value equal to zero was obtained by setting the quadrupole bias equal to the hexapole bias ($V_Q = V_H = -17V$). The V_Q was scanned to produce a KED potential of 4.5 V. This approach was adopted because it provides a fixed ion kinetic energy within the CC, since the V_H was held constant. If the hexapole bias had been scanned, the KED efficiency could be underestimated.⁴³

The progressive removal of Ar and Cl-based interferences, occurring at nominal masses 51, 52, 56, 75, 78 and 80, with the increase of the gas flow rate into CC is presented in Fig. 2. The investigated polyatomic ions can be attenuated up to 4 to 5 orders of magnitude, however sensitivity is severely affected at high gas flow rates.

The increase in signal intensity of analyte and polyatomic ions (Fig. 2), with gas flow up to 2 mL/min is related to collisional focusing.²⁰ Once the pressure is increased the ions migrate to the axis of the hexapole resulting in better ion transmission. The detected signal thus increases until scattering losses dominate and/or the axial kinetic energy of the ion becomes smaller than KED. The small improvement in the ion signal here

observed is attributed to the use of a shielded torch, which reduces the capacity of the cell to perform focusing as a result of ion energy reduction.⁴⁴ And as pointed by Leonhard *et al.*,²⁸ if the ion beam is already well focused, collisional focusing does not necessarily lead to a substantial improvement in ion transmission efficiency.

It is also evident that if gas flow rate is used in excess, compared to the demand for polyatomic interference attenuation, a deteriorated BEC is obtained. This can be visualized in Fig 2 (d and e) where $ArCl^+$ and Ar_2^+ were totally attenuated with gas flow rates of 5-6 mL/min and further gas addition only diminished the analyte sensitivity unnecessarily.

The following discussion is centered in optimizing the conditions of gas flow rates capable to reduce the contribution of polyatomic ions to an insignificant level during real water samples analyzes, while trying to keep sensitivity as high as possible. Therefore, minimal flow rates were selected. To define the necessary gas flow the background equivalent concentration (BEC) was employed. BEC was estimated as:

$$BEC(\mu\text{g L}^{-1}) = \frac{\text{counts.s}^{-1}_{\text{polyatomic ions}} \times \text{conc. analyte}}{\text{counts.s}^{-1}_{\text{analyte}} 10\mu\text{g L}^{-1}}$$

In the above equation, the intensity (counts.s^{-1}) of a polyatomic ion is divided by intensity obtained from a solution containing the interfered element (conc. analyte) at $10 \mu\text{g L}^{-1}$. For selenium and iron isotopes the BEC was estimated after subtracting the background ion signal from the intensity of the analyte signal.

The signals of the Cl-based interferences $^{35}Cl^{16}O^+$, $^{35}Cl^{16}O^+H^+$ and $^{40}Ar^{35}Cl^+$, Fig. 2 (a, b and d), were obtained when 1% HCl (approx. 4200 mg L^{-1} chlorine) was aspirated. This high chlorine concentration does not reflect the composition of most water samples, but was used just to exploit the CC efficiency in removing those interfering polyatomic species.

In ordinary water samples analyzed in our laboratory (drinking, river and groundwater), the chlorine content is measured by ion chromatography before ICP-MS analysis. Most samples have Cl concentration below 200 mg L^{-1} . At this chlorine level, BEC values of $^{51}V^+$, $^{52}Cr^+$ and $^{75}As^+$ in CC mode using H_2/He at 4 mL/min are 0.1, 0.005 and $0.003 \mu\text{g L}^{-1}$, respectively. While BEC values for $^{52}Cr^+$ and $^{75}As^+$ are low enough for accurate determination of these elements in water samples at the sub $\mu\text{g L}^{-1}$ (ppb) level, for $^{51}V^+$ it is still relatively high, and could produce inaccurate results. To reduce the interference of $^{35}Cl^{16}O^+$ on $^{51}V^+$ to a negligible level, a gas flow of 6 mL/min must be used. This yields a BEC of $0.004 \mu\text{g L}^{-1}$, meaning an overall improvement of 530 times, when the gas flow is changed from 0 to 6 mL/min.

The effective removal of the interfering polyatomic ions on $^{51}V^+$ and $^{75}As^+$ is visualized in Fig. 3. When the measurements are made without gas or at low gas flow the $ArCl^+$ contribution to $^{75}As^+$ is about 10% and the signal of V^+ is fully hidden by the ClO^+ . With standard ICP-MS conditions that contribution, indicated by the (x), is even greater. With proper gas flows these interferences are reduced to less than 2 count.s^{-1} .

The data in Fig. 2 and 3 can be used to estimate of the necessary gas flow rate to account for a specific chlorine level. For instance, when samples with 500 mg L^{-1} of Cl are analyzed, the BEC values of $^{51}V^+$, $^{51}Cr^+$ and $^{75}As^+$ can be kept below $0.005 \mu\text{g L}^{-1}$, if the gas flows indicated above are

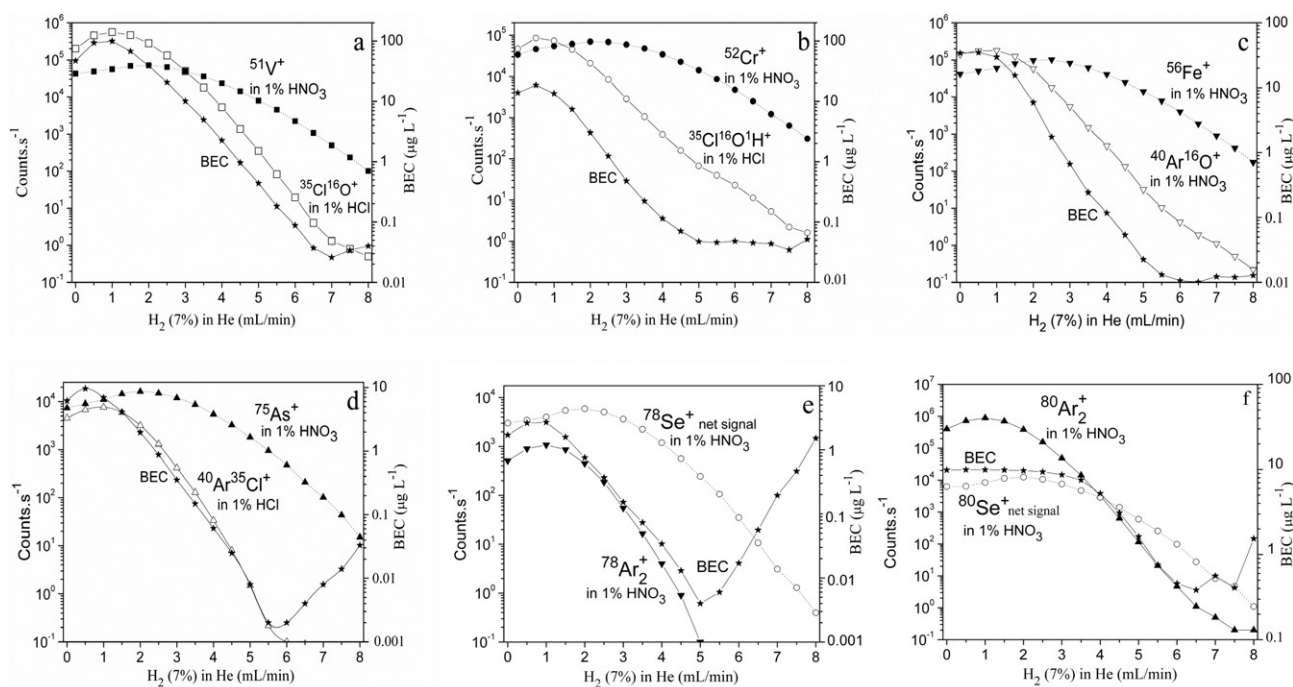


Fig. 2 Effect of the increase of the gas flow rate in polyatomic interferences attenuation, analyte ion signal ($10 \mu\text{g L}^{-1}$) and background equivalent concentration (BEC), with $\text{KED} = 3\text{V}$. Symbols: BEC (*); a) $^{51}\text{V}^+$ (■) and $^{35}\text{Cl}^{16}\text{O}^+$ (□); b) $^{52}\text{Cr}^+$ (●) and $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ (○); c) $^{56}\text{Fe}^+$ (▼) and $^{40}\text{Ar}^{16}\text{O}^+$ (▽); d) $^{75}\text{As}^+$ (▲) and $^{40}\text{Ar}^{35}\text{Cl}^+$ (△); e) $^{78}\text{Se}^+$ (○) and $^{78}\text{Ar}_2^+$ (▼); f) $^{80}\text{Se}^+$ (○) and $^{80}\text{Ar}_2^+$ (▲). The net signals for iron and selenium isotopes correspond to the total counts at the specific mass after background subtraction: $^{78}\text{Se}^+$ ($10 \mu\text{g L}^{-1}$ solution) = total counts at m/z 78 – $^{78}\text{Ar}_2^+$ (in 1% HNO_3).

increased by 0.5 mL/min. Thus, the method may be easily adapted to samples with different Cl content. But, above that Cl level, the use of higher gas flow rates implies in significant loss in sensitivity and specifically turns $^{51}\text{V}^+$ measurement difficult. In such case, a reactive gas (1% NH_3 in He), as recommended by Chrastný *et al.*,⁴² is more effective to accomplish the removal of ClO^+ .

The attenuation of the chlorine hydroxide ($^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$) that hampers the quantification of Cr with its most abundant isotope $^{52}\text{Cr}^+$ (83.8%), is shown in Fig. 2 (b). The overall improvement of $^{52}\text{Cr}^+$ BEC surpasses 120 times when the gas flow increases from 0 to 4 mL/min. The subsequent change in the slope of the $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ line when gas flow reaches 5 mL/min, indicates a possible contamination of Cr in the 1% HCl (suggested since the lines of $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ and $^{52}\text{Cr}^+$ take the same slope), hence further improvement in BEC was not possible. In a similar way, the measurement of $^{40}\text{Ar}^{16}\text{O}^+$ (Fig. 2 c) at high gas flows (> 6 mL/min) seems to be affected due the presence of Fe in the blank.

The occurrence of $^{40}\text{Ar}^{23}\text{Na}^+$ was investigated by introducing a solution with 500 mg L^{-1} of Na. The results (not presented) showed significant formation of ArNa^+ and consequently serious interference on $^{63}\text{Cu}^+$ when no gas was added to CC. This interference was fully removed by adding a gas flow of 4 mL/min.

For quantification purposes, the isotope $^{78}\text{Se}^+$ was preferred instead of $^{80}\text{Se}^+$, as the former has a BEC 150 times smaller than the last, at 4 mL/min (Fig. 2 e and f). With this gas flow rate the BEC of $^{78}\text{Se}^+$ and $^{56}\text{Fe}^+$ are 0.03 and $0.12 \mu\text{g L}^{-1}$, respectively, and are appropriate to the intended application. If desired, those BEC can be reduced to 0.004 and $0.02 \mu\text{g L}^{-1}$ using 5 mL/min. However, 4 mL/min was preferred to measure $^{78}\text{Se}^+$ and $^{56}\text{Fe}^+$,

because it is the same gas flow established for $^{75}\text{As}^+$, $^{63}\text{Cu}^+$ and $^{52}\text{Cr}^+$. This simplifies the instrument tuning and implies in higher speed of analysis.

The signals of selenium isotopes present the most severe loss in intensity with gas flow increase, possibly due to hydride formation as pointed out by Boulyga and Becker.³⁵ Sloth and Larsen⁵³ also reported the formation of SeH^+ , but with methane as reaction gas. The quantification of Se in CC mode with H_2/He mixture is a good example of chemical mitigation of undesired ions, where polyatomic ($^{78,80}\text{Ar}_2^+$) and analyte ions react with the gas, but the reaction is faster with the former, leading to an improvement in the value of Se^+ BEC.

3.2 Trueness

The assessment of trueness requires the comparison of averaged measurement results with a reference value (RV). Ideally it should be tested at three concentration levels in order to check if any observed difference is a function of the analyte content.⁵⁴ However, few water certified reference materials are available. Thus our method validation was limited to two NIST reference materials (SRM 1640 and 1643e) that possess certified or reference values with low uncertainties for a wide trace element suite. These certified reference materials contain different matrix and levels of trace elements. SRM 1640 contains higher sodium and lower trace elements level than SRM 1643e, while the opposite occurs for calcium concentration.

Bias, uncertainty of bias, as defined by Linsinger,⁵⁵ and z-score were evaluated by analysis of the two CRM during a period of few months, characterizing intermediate precision. The mean

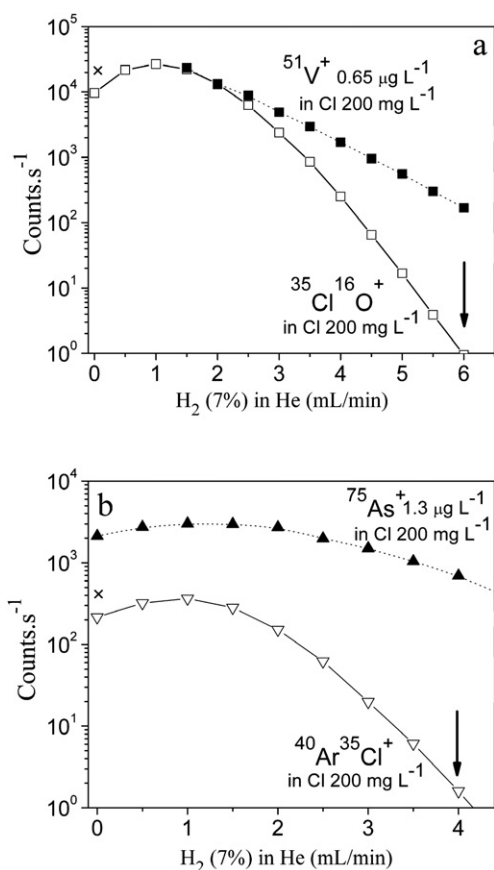


Fig. 3 Attenuation of Cl-based interferences corresponding to a sample with high chlorine content in 20-fold diluted NIST SRM 1640 spiked with 200 mg L⁻¹ of Cl. KED = 3V. a) ³⁵Cl¹⁶O⁺ (□) and ⁵¹V⁺ (■); b) ⁴⁰Ar³⁵Cl⁺ (△) and ⁷⁵As⁺ (▲). The arrows indicate the recommended gas flow rate and (x) at the y-axis corresponds to the production of polyatomic ion in standard mode.

results and respective standard deviation (s) obtained for 10-fold diluted aliquots are presented in Tables 2 and 3 and are compared with respective certified or reference value (*RV*) and uncertainties (*U_{CRM}*). The next columns include bias, calculated as the relative difference (%) between the mean of results for each analyte and the respective *RV*, followed by uncertainty of bias and z-score in the last two columns.

Uncertainty of bias (*u_b*), was obtained by combining standard uncertainty of the mean value ($u = s/\sqrt{n}$, where *s* is the standard deviation of the number *n* of available results) and the standard uncertainty of the certified/reference value (U_{CRM}/k , where *k* is the coverage factor), as shown:

$$u_b = \sqrt{\frac{s^2}{n} + \frac{U_{CRM}^2}{k}}$$

The certificate of the SRM 1643e informs the values of the coverage factor used to expand the uncertainty of each certified value, while in the certificate of SRM1640 that information is absent, so *k* = 2 was adopted to calculate the uncertainty of bias for SRM1640. The uncertainty in the concentration of the commercial standard solutions (0.5%) used to prepare the

Table 2 Results (μg L⁻¹) for 10-fold diluted SRM 1640, certified/reference values (*RV*), bias, uncertainty of bias (*u_b*) and z-score

Analyte	Mean ± 1s (n = 8)	RV ± U _{SRM}	bias (%)	<i>u_b</i>	z-score
Li	50.3 ± 3.4	50.8 ± 1.4	-1.0	1.4	-0.4
Be	36.20 ± 2.32	34.99 ± 0.41	3.5	0.84	1.4
B	295.7 ± 18.0	301.6 ± 6.1	-2.0	7.1	-0.8
Na	28366 ± 1588	29394 ± 310	-3.5	582	-1.8
Mg	5661 ± 357	5828 ± 56	-2.9	129	-1.3
Al	55.1 ± 8.4	52.1 ± 1.5	5.8	3.1	1.0
Si	4863 ± 374	4737 ± 120	2.7	145	0.9
K	995 ± 142	995 ± 27	0.0	52	0.0
Ca	7073 ± 368	7056 ± 89	0.2	138	0.1
V	13.28 ± 0.85	13.01 ± 0.37	2.1	0.35	0.8
Cr	39.3 ± 2.0	38.7 ± 1.6	1.6	1.1	0.6
Mn	123.6 ± 6.1	121.7 ± 1.1	1.6	2.2	0.9
Fe	35.1 ± 2.7	34.4 ± 1.6	2.0	1.2	0.6
Co	21.00 ± 0.94	20.31 ± 0.31	3.4	0.37	1.9
Ni	28.1 ± 1.8	27.4 ± 0.8	2.6	0.8	0.9
Cu	87.4 ± 3.2	85.3 ± 1.2	2.5	1.3	1.6
Zn	56.9 ± 5.6	53.3 ± 1.1	6.8	2.1	1.8
As	27.61 ± 1.85	26.71 ± 0.41	3.4	0.69	1.3
Se	23.00 ± 1.36	21.99 ± 0.51	4.6	0.54	1.9
Rb	2.16 ± 0.26	2.00 ± 0.02	8.0	0.09	1.7
Sr	125.1 ± 5.8	124.4 ± 0.7	0.6	2.1	0.3
Mo	47.17 ± 1.78	46.82 ± 0.26	0.7	0.64	0.5
Ag	7.60 ± 0.42	7.63 ± 0.25	-0.4	0.19	-0.2
Cd	23.64 ± 0.82	22.82 ± 0.96	3.6	0.56	1.5
Sb	13.78 ± 0.50	13.81 ± 0.42	-0.2	0.27	-0.1
Ba	150.7 ± 5.1	148.2 ± 2.2	1.7	2.1	1.2
Pb	28.70 ± 1.33	27.93 ± 0.14	2.8	0.48	1.6

Table 3 Results (μg L⁻¹) for 10-fold diluted SRM 1643e, certified/reference values (*RV*), bias, uncertainty of bias (*u_b*) and z-score

Analyte	Mean ± 1s (n = 6)	RV ± U _{SRM}	bias (%)	<i>u_b</i>	z-score
Li	17.4 ± 1.4	17.4 ± 1.7	0.0	0.8	0.0
Be	13.82 ± 0.74	13.98 ± 0.17	-1.1	0.31	-0.5
B	162.3 ± 17.8	157.9 ± 3.9	2.8	7.4	0.6
Na	20378 ± 988	20740 ± 260	-1.7	424	-0.9
Mg	8036 ± 365	8037 ± 98	0.0	157	0.0
Al	139.3 ± 18.3	141.8 ± 8.6	-1.8	7.9	-0.3
K	1996 ± 111	2039 ± 29	-1.9	47	-0.9
Ca	31793 ± 1110	32300 ± 1100	-1.6	600	-0.8
V	36.91 ± 1.13	37.86 ± 0.59	-2.5	0.54	-1.8
Cr	20.79 ± 1.29	20.40 ± 0.24	1.9	0.54	0.7
Mn	37.70 ± 1.88	38.97 ± 0.45	-3.3	0.80	-1.6
Fe	99.7 ± 5.2	98.1 ± 1.4	1.6	2.24	0.7
Co	26.70 ± 1.14	27.06 ± 0.32	-1.3	0.49	-0.7
Ni	60.91 ± 2.36	62.41 ± 0.69	-2.4	1.02	-1.5
Cu	22.48 ± 0.97	22.76 ± 0.31	-1.2	0.42	-0.7
Zn	76.5 ± 5.1	78.5 ± 2.2	-2.2	2.2	-0.9
As	59.14 ± 3.13	60.45 ± 0.72	-2.2	1.33	-1.0
Se	11.78 ± 1.37	11.97 ± 0.14	-1.6	0.56	-0.3
Rb	14.14 ± 0.71	14.14 ± 0.18	0.0	0.30	0.0
Sr	331.2 ± 22.5	323.1 ± 3.6	2.5	9.4	0.9
Mo	121.7 ± 5.6	121.4 ± 1.3	0.2	2.4	0.1
Ag	1.02 ± 0.04	1.062 ± 0.075	-4.0	0.029	-1.5
Cd	6.45 ± 0.34	6.568 ± 0.073	-1.8	0.14	-0.8
Sb	58.17 ± 2.08	58.30 ± 0.61	-0.2	0.90	-0.1
Ba	543.2 ± 14.4	544.2 ± 5.8	-0.2	6.6	-0.2
Tl	7.44 ± 0.28	7.445 ± 0.096	-0.1	0.12	0.0
Pb	19.59 ± 0.70	19.63 ± 0.21	-0.2	0.30	-0.1

calibration solutions was not included in the combined uncertainty, as it is negligible in comparison with the other components considered.

The handbook for calculation of measurement uncertainty in environmental laboratories⁵⁴ requires that if CRM are used to estimate the bias, these should be analyzed in at least 5 different analytical series before the values are used. This requirement was obeyed because data from more than 6 different runs were used. The averaged relative standard deviation for all analytes is 6.5% for SRM 1640 and 5.6% for SRM1643e. And no difference in precision was observed between elements measured in standard and CC mode.

All elements were determined with relative bias smaller than 8% and mostly show opposite deviation from RV for the two reference materials. In general, the agreement between results and reference values is better for SRM 1643e than SRM 1640. The largest deviations from RV were observed for Al, Zn and Rb measured in SRM 1640. However the results of these trace elements in SRM 1643e are in good agreement with RV. The difference observed in SRM 1640 may be associated to environmental contamination because dilutions were not made in clean-room conditions and the certificates of these water standard reference materials recommend their manipulation in a Class-100 clean hood. Despite that, the bias of the vast majority of elements is <5%.

To assess if the difference between mean values and RV is significant from an uncertainty point of view, the z-score was also calculated.⁵⁶ In simple terms, the z-score is absolute bias divided by the uncertainty of the bias:

$$z\text{-score} = \frac{(\text{Mean} - \text{RV})}{u_b}$$

Significant bias is defined as z-score >|2|. ⁵⁶ Most z-score values (56% for SRM 1640 and 85% for SRM 1643e) lie within the -1 to +1 range, reflecting the close agreement between mean and RV, and all other elements present z-score within ± 2 . So these results are free of significant bias.

The high quality data obtained for these two CRM indicates that the proposed method is fit for trace elements determination in common water matrices.

In additional tests, other 10-fold diluted aliquots of both CRM were spiked with 200 mg L⁻¹ of Cl (using NaCl). The relative deviation of V, Cr, Cu and As results from un-spiked samples were negligible (<0.2%), and totally insignificant considering the method precision, showing that polyatomic species are being properly attenuated. Results of other elements measured in CC mode, like Fe and Se, were also in agreement with RV, indicating that the interference attenuation is not affected in an enriched matrix.

The interference on the nominal mass of As⁺ due to formation of ⁴⁰Ca³⁵Cl⁺ in CC mode operating with KED of 3V and H₂/He at 4 mL/min was investigated introducing a solution with 100 mg L⁻¹ of Ca, prepared from CaCl₂·2H₂O. At this Ca level, none interference was detected, corroborating findings of other authors.⁴¹

Method detection limits, Table 4, are given as three times the standard deviation (3s) of eight measurements in 1% HNO₃ solution spiked with analytes at concentrations corresponding 3 to 5 times the instrumental detection limit.²¹

Method detection limits are below typical trace elements concentrations found in uncontaminated water samples, and are

Table 4 Method detection limits (MDL) in µg L⁻¹

Isotope	Mode	MDL	Isotope	Mode	MDL
⁷ Li	Standard	0.012	⁶⁰ Ni	CC	0.014
⁹ Be	Standard	0.008	⁶³ Cu	CC	0.009
¹¹ B	Standard	0.054	⁶⁶ Zn	CC	0.006
²³ Na	Standard	7.1	⁷⁵ As	CC	0.007
²⁵ Mg	Standard	3.0	⁷⁸ Se	CC	0.010
²⁷ Al	Standard	0.1	⁸⁵ Rb	Standard	0.002
²⁹ Si	Standard	50	⁸⁸ Sr	Standard	0.001
³⁹ K	CC	5.0	⁹⁵ Mo	Standard	0.003
⁴³ Ca	Standard	30	¹⁰⁷ Ag	Standard	0.003
⁵¹ V	CC	0.008	¹¹¹ Cd	Standard	0.004
⁵² Cr	CC	0.005	¹²¹ Sb	Standard	0.004
⁵⁴ Fe	CC	0.13	¹³⁷ Ba	Standard	0.004
⁵⁵ Mn	CC	0.01	²⁰⁵ Tl	Standard	0.001
⁵⁶ Fe	CC	0.07	^{206,7,8} Pb	Standard	0.003
⁵⁹ Co	CC	0.003			

generally 10 to 100 times lower than the MCLs for contaminants specified in official regulations.^{3,53}

4. Conclusions

It was demonstrated that H₂ ion-molecule chemistry and KED in a hexapole CC is efficient to improve the BEC of ⁵¹V⁺, ⁵²Cr⁺, ⁵⁶Fe⁺, ⁷⁵As⁺ and ⁷⁸Se⁺ isotopes by over two orders of magnitude. As a result reliable analysis of these elements can be accomplished by CC-ICP-MS at the low ng L⁻¹ level.

The accuracy of the proposed “multi-mode” method was confirmed by the analyses of two CRM. Even when 10-fold aliquots of both CRM were spiked with chlorine at levels usually found in typical samples, the results of interfered elements were not affected, confirming that the desired level of interference attenuation was accomplished. But, if more complex samples have to be analyzed and/or other polyatomic interferences are known or expected, the prescribed gas flow or KED, and in last instance the cell gas, may be adjusted to provide the demanded level of interference attenuation.

Method detection limits are appropriate for most hydro-geochemical studies. As low ng L⁻¹ concentrations of Cr, As and Se can be determined using the same CC conditions for concomitant ClOH⁺, ArCl⁺ and Ar₂⁺ removal, speciation of these elements may be accomplished in a single run.⁵⁷

5. Acknowledgements

Financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo (Proc. FAPESP No 2003/09916-6) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) are acknowledged.

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