TECHNICAL NOTE

Vladislav Chrastný · Michael Komárek ·
Martin Mihaljevič · Jana Štíchová

Vanadium determination in chloride matrices using ICP-MS: finding the optimum collision/reaction cell parameters for suppressing polyatomic interferences

Abstract Efficiencies of He/NH$_3$ and He/H$_2$ collision gases were compared in a conventional type of hexapole cell of an inductively coupled plasma mass spectrometer (ICP-MS). The optimum conditions [hexapole and quadrupole bias voltage (V$_H$ and V$_Q$) and collision/reaction gas flow rates] were tested for vanadium determination (^{51}V) in chloride matrices. When the He/H$_2$ mixture was used, the optimum values of V$_H$ and V$_Q$ were −10.0 and −8.0 V, respectively. This set-up corresponds to the kinetic energy discrimination effect. When the He/NH$_3$ mixture was used, the optimum values of V$_H$ and V$_Q$ were +10.0 and −7.0 V, respectively. Positive V$_H$ values correspond to the ion kinetic energy effect, which allows the reactivity of the ions entering the collision/reaction cell with the reaction gas to be controlled. The obtained results showed that the He/H$_2$ mixture is not optimal for V determination in samples containing chlorides due to the insufficient suppression of the polyatomic interference of ^{35}Cl^{16}O$^+$. Data obtained from vanadium determination using the He/NH$_3$ mixture were consistent for all selected Cl$^-$ concentrations, and the results were acceptable. The detection limit was comparable with detection limits obtained from ICP-MS equipped with a dynamic reaction cell. Analyses of elements forming interfering molecules, e.g., iron (^{56}Fe), arsenic (^{75}As) and selenium (^{80}Se), were in good agreement with the certified values for both studied collision/reaction gas mixtures.

V. Chrastný (✉)
Department of Chemistry, University of South Bohemia,
Studentská 13,
370 05 České Budějovice, Czech Republic
e-mail: vladislavchrastny@seznam.cz

M. Komárek
Department of Agrochemistry and Plant Nutrition,
Czech University of Agriculture in Prague,
Kamýcká 129,
165 21 Prague 6, Czech Republic

M. Mihaljevič
Institute of Geochemistry, Mineralogy and Mineral Resources,
Charles University,
Albertov 6,
128 43 Prague 2, Czech Republic

J. Štíchová
Applied Ecology Laboratory, University of South Bohemia,
Studentská 13,
370 05 České Budějovice, Czech Republic

Introduction

Vanadium is an element found in different types of samples, e.g., sea water [1], soils [2], and biological fluids including serum and urine [3, 4]. The main advantage of mass spectrometry with inductively coupled plasma (ICP-MS) is the multielemental high-precision trace element determination. The problem of isobaric and polyatomic overlaps is one of the most important limitations, however, the overlaps are not as problematic as non-spectral interferences, limited matrix tolerance, etc. During vanadium determination in samples containing chlorides, there is evidence of interference in the mass-to-charge ratio 51 due to the formation of the polyatomic ion ^{35}Cl^{16}O$^+$ [1]. A collision/reaction cell, which has been comprehensively reviewed by Tanner et al. [5], presents an effective tool for suppressing these polyatomic interferences in ICP-MS techniques.

There are two different approaches for suppressing polyatomic overlaps using a collision/reaction cell. The first, the classical approach of distinguishing the analyte and the interferent, is based on differences in axial kinetic energy. All the ions derived from the plasma are accelerated due to the expansion of the plasma in the vacuum interface and by negative voltages of ion lenses. Polyatomic ions are subjected to more collisions with the collision gas than monoatomic ions of the analytes. Therefore, the axial kinetic energy of polyatomic interference ions decreases more significantly than in the case of monoatomic ions of the analyte [6]. The interfering polyatomic ions can be eliminated using kinetic energy discrimination (KED), in other words, by creating a

potential barrier for ions with lower kinetic energy. The operating conditions of the collision cell multipole used in this approach are set for a large transmission of a wide m/z range and cannot be changed. ICP-MS instruments from Thermo Electron Corporation and Agilent use this first approach. These instruments use a radio-frequency (rf)-only hexapole or octapole as rf device of the cell and are typically operated with He and/or H_2 as the collision/reaction gas. This configuration enables kinetic energy discrimination for removal of in-cell ions by biasing the pole bias of the collision cell negatively relative to the mass analyser rod offset. This effect requires a sufficient number of collisions to create a wide difference in the axial kinetic energies of analyte and interfering ions.

The second approach, used by Perkin Elmer-SCIEX instruments (dynamic reaction cell, DRC), is based on the possibility of selectively changing the ion transmission conditions of the reaction cell (Mathieu parameters a and q). This approach allows the use of relatively heavy reaction gases, such as NH_3, CH_4, O_2, and CH_3, at pressures providing near-thermal conditions [5].

The determination of vanadium in chloride matrices and determination of other elements that are difficult to analyse (mainly As, Se and Fe) using a collision cell and NH_3 as the reaction gas have been well documented in literature only for the multipole with mass bandpass [4, 7]. According to our knowledge there is no information about using NH_3 as a reaction gas in the classical type of collision/reaction cell. The reaction gases typically used include He and/or H_2. The optimisation of operating conditions using He/H_2 has been studied by several authors [8–10].

The voltage of hexapole bias (V_H) has been shown to be a very important setup parameter [8]. Unfortunately, recommendations from literature concerning hexapole bias setup are often contradictory. Boulyga et al. [8] refer to attenuation of background ion intensities caused by argon-based molecular ions [e.g., $^{41}(ArH)^+$, $^{54}(ArN)^+$, $^{56}(ArO)^+$ and $^{80}(Ar_2)^+$] using a collision cell pressurised with He/H_2 mixture. A reduction of three orders of magnitude in these Ar-based molecular ion intensities was observed with V_H set to 0 V, and a decrease of five orders of magnitude with V_H set to +1.6 V. The optimum V_H for multielemental determination was set at 1.5 V [8]. At a voltage of more than +2.0 V, a strong decrease in analyte intensity was observed. The observed reduction in background ion intensities is attributed to the effect of kinetic energy discrimination. However, this interpretation seems to be problematic.

Niemelä et al. [10] presented similar results concerning hexapole bias setup used for determination of arsenic (^{75}As), iron (^{56}Fe) and selenium (^{80}Se) in samples of moss. The authors found the optimum operational conditions for the hexapole collision cell using a He/H_2 gas mixture. The optimum voltage of V_H was found to be +4.0 V. When the voltage was set to positive values, a retardation of the ions entering the collision cell occurred and therefore the reactivity of ions present in the collision cell increased. On the other hand, Yamada et al. [6] studied mechanisms for reducing interferences in an octapole collision cell ICP-MS and found KED as the most efficient tool. The use of KED suppressed water cluster ions formed within the cell, and KED was also found to reduce the amount of polyatomic ions that do not react with the reaction gas. Kinetic energy discrimination was obtained by setting the bias voltage of the octapole to −15 V and the bias voltage of the quadrupole (V_Q) to −14 V.

Optimising input ion energy by applying appropriate hexapole bias potential and using kinetic energy discrimination in a hexapole cell pressurised with a mixture of He/H_2 were studied in detail by Dexter et al. [9]. The authors confirmed that increasing V_H influenced the suppression of polyatomic interferences, but this phenomenon was attributed to the initial ion kinetic energy effect (IKEE). This is based on the fact that the kinetic energy of ions entering the cell with changes in the potential between the plasma and the hexapole and thus alters the reactivity of the ions with the reaction gas in the cell. Increasing hexapole bias voltage increases the rate of exothermic reactions and increases the efficiency of Ar^+ ion removal by reaction with hydrogen. Under the same conditions, maximum efficiency for analyte transmission was achieved. Achieving the optimum balance between analyte sensitivity and maximum interference suppression is specific for each analytical determination [9].

The main objective of this work was to evaluate the use of He/NH_3 mixture as the collision gas used in a classical collision cell during determination of V and other elements and to compare its efficiency with the use of He/H_2 gas mixture based on V_H and V_Q setup.

Experimental

Instrumentation of ICP-MS

A PQExCell instrument with a hexapole collision cell (Thermo Electron, Winsford, UK) was used throughout this study. For solution introduction, a Meinhard nebuliser with spray chamber cooled to 3 °C was used. Operating conditions are given in Table 1. The ion lens setting,

Table 1 Instrumental and experimental conditions used

Instrument conditions	
RF power	1,350 W
Reflected power	<2 W
Cool gas flow	13.1 L min^{-1}
Auxiliary gas flow	0.60 L min^{-1}
Nebuliser gas flow	0.91 L min^{-1}
Quadrupole bias	−15.0 to 9.0 V
Hexapole bias	−10.0, −5.0, 0.0, +5.0, +10.0 V

Experimental conditions	
Sweeps	50
Channels per mass	3
Dwell time	10 ms
No. of repeats	3

nebuliser gas-flow rate and torch position of the instrument were optimised daily to obtain the maximum [115]In count rate. Typical sensitivity in standard mode and in mode with collision cell was 30,000 counts s^{-1} ng mL^{-1} for In. Before optimising collision cell parameters, the cell was flushed with collision gas (10 mL min^{-1}) for at least 30 min in order to obtain the equilibration state within the cell. For the comparison study of collision cell gas efficiency, two premix gases (both 99.999%) were used; 7% H_2 in He was the first gas mixture and 1% NH_3 in He was the second gas mixture. Stainless steel tubing was used throughout. Flow rates of the collision/reaction gases varied between 0.5 and 8 mL min^{-1} for the study of optimum cell conditions. Nonzero gas flow at the lowest point was used due to automatic switch of hexapole bias voltage in the unpressurised state of the collision cell.

Reagents

For all measurements presented, quantification using multielement standard stock solution was performed (Merck VI, CertiPUR, Darmstadt, Germany). A solution containing 100 µg L^{-1} of V, As, Se and Fe (single-element ICP-standard solutions, CertiPUR, Merck, Germany) was prepared to obtain the analytical signal needed for collision/reaction gas flow rate optimisation and for construction of "stopping-curves" of vanadium. A solution of 0.5 M HCl (ultrapure grade, Merck, Germany) was used to obtain the comparable signal of interference on mass-to-charge ratios of 51 and 75 (due to the formation of polyatomic ions of $^{35}Cl^{16}O^+$ and $^{40}Ar^{35}Cl^+$ respectively).

In order to verify the optimum operational conditions of the collision cell, a standard reference material (SRM) solution, NIST 1640 (Trace Elements in Natural Water, National Institute of Standards and Technology, Gaithersburg, MD, USA) with the addition of 0.5 M HCl, was analysed. All the reagents were diluted with deionised Milli-Q water (Milli-Q-Plus, Millipore, Molsheim, France).

Methodology

For selected V_H values (−10.0, −5.0, 0.0, +5.0, +10.0 V), the analytical signal was determined for the mass-to-charge ratio of 51 (model solution of 100 µg V L^{-1}), dependent on the changes in V_Q (from −15.0 to +9.0 V). The model solutions were chosen to have approximately the similar analytical sensitivities. The same procedure was applied during a simulation of interferences for the mass-to-charge ratios 51 and 75 using 0.5 M HCl. The signal obtained from Ar interferences on the mass-to-charge ratios 56 and 80 (polyatomic ions $^{40}Ar^{16}O^+$ and $^{80}Ar_2^+$) was systematically subtracted at the appropriate V_Q value in order to obtain a "clean" analytical signal. The collision/reaction gas flow was set to 2.8 mL min^{-1} throughout the whole experiment. The obtained data were plotted into graphs as stopping-curves for both tested gas mixtures. The optimum analytical conditions were selected as a compromise

between the maximum analytical signal and a minimum interference signal. Different set-up conditions for V_H and V_Q were found for separate gas mixtures. Under these conditions, the levels of analytical and interference signals, dependent on changes in collision gas flow, were tested in the same manner. Hexapole bias voltage was changed manually on the trimmer resistor of the cell control section using a screwdriver and was monitored against ground via a multimeter.

The verification of optimum conditions was performed using SRM NIST 1640 spiked with HCl in order to simulate the chloride matrix (concentration gradient: 0.005, 0.01, 0.025, 0.05, 0.1 M HCl). The results were evaluated for both collision gases, different V_H and V_Q values and different collision/reaction gas flows (Table 2).

Results and discussion

The results are presented in Figs. 1, 2 and 3. The first part of the experiment was focused on finding the optimum set-up conditions for V_H and V_Q for the tested collision-gases mixtures (Figs. 1 and 2); the second part dealt with finding the optimum collision/reaction gases flows (Fig. 3). In the third part of the experiment, the optimum conditions were tested using a standard reference material spiked with HCl (Table 2). The limits of detection obtained for these two tested mixtures are given in Table 3.

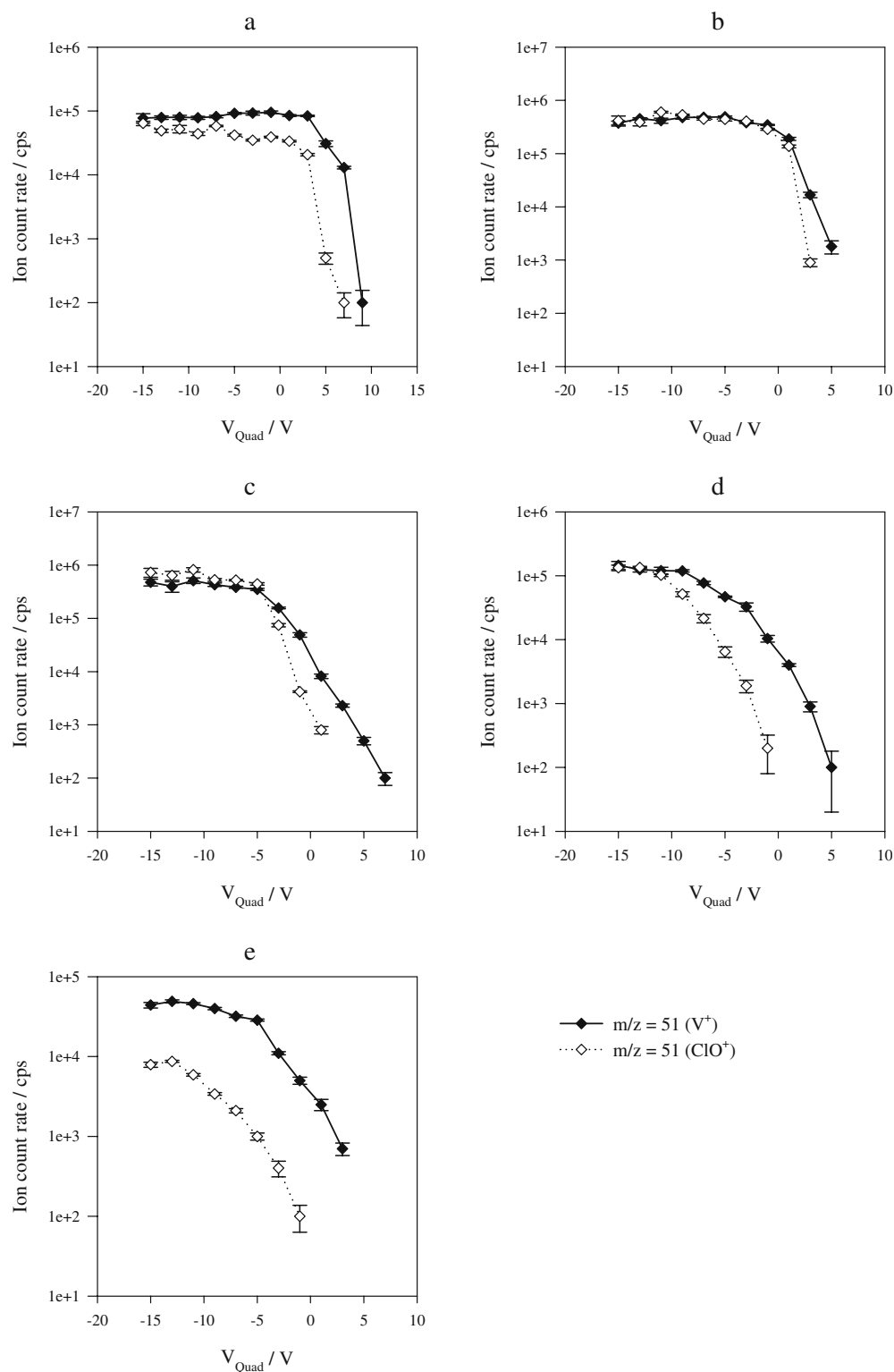Hexapole and quadrupole bias set-up

He/H₂ as the reaction gas

Signal values of the analysed mass-to-charge ratio 51 (100 µg V L^{-1}) and the interference signal ($^{35}Cl^{16}O^+$ using

Table 2 Determination of V and As in NIST 1640 spiked with CI

Cl^- (mol L^{-1})	V		As	
	(µg L^{-1})[a]	(%)	(µg L^{-1})	(%)
He/H₂ as the collision/reaction gas				
0.000	13.1±0.27	101	24.4±0.57	91.4
0.005	17.9±0.81	138	25.6±0.23	95.8
0.010	23.2±0.49	178	26.8±0.42	100
0.025	32.3±1.51	248	27.1±0.61	101
0.050	49.3±1.45	379	26.8±0.32	100
0.100	85.4±1.82	656	27.2±0.38	102
He/NH₃ as the collision/reaction gas				
0.000	13.7±0.38	105	25.5±0.34	95.5
0.005	13.4±0.38	103	26.1±0.31	97.7
0.010	13.4±0.26	103	26.7±0.29	100
0.025	13.5±0.30	104	26.9±0.44	101
0.050	13.5±0.42	104	25.9±0.52	97.0
0.100	13.5±0.33	104	26.7±0.58	100

Recoveries (mean±SD and %; n=5) were calculated for certified values of V and As (13.0±0.37 and 26.71±0.41 µg L^{-1}, respectively)

Fig. 1a–e Signal intensities of V^+ (*closed marks*) and ClO$^+$ (*open marks*) at different quadrupole bias voltages (V_Q) with He/H$_2$ used as the collision/reaction gas. Graphs **a**–**e** correspond to hexapole bias voltages (V_H) of +10.0, +5.0, 0.0, −5.0 and −10.0 V, respectively. Each *point* represents mean±SD (*n*=3)

0.5 M HCl) in dependence on the hexapole and quadrupole bias set-up using He/H$_2$ mixture are summarized in Fig. 1. These graphs were constructed for selected model solutions (see Methodology); it is therefore impossible to deduce conclusions concerning signal values alone but rather the focus should be on signal trends. Figure 1a–e represents V_H values of +10.0, +5.0, 0.0, −5.0 and −10.0 V respectively,

and V_Q values ranging from −15.0 to +9.0 V. In general, it is possible to assume that increasing quadrupole bias potential leads to a decrease in both the analytical and the interference signal. A significant decrease in the analytical and the interference signal was observed from a certain V_Q value. Over a specific interval of V_Q values, the signal remained constant (plateau area) (Fig. 1a–e). Decreasing

Fig. 2a–e Signal intensities of V^+ (*closed marks*) and CIO$^+$ (*open marks*) at different quadrupole bias voltages (V_Q) with He/NH$_3$ used as the collision/reaction gas. Graphs **a**–**e** correspond to hexapole bias voltages (V_H) of +10.0, +5.0, 0.0, −5.0 and −10.0 V, respectively. Each *point* represents mean±SD (*n*=3)
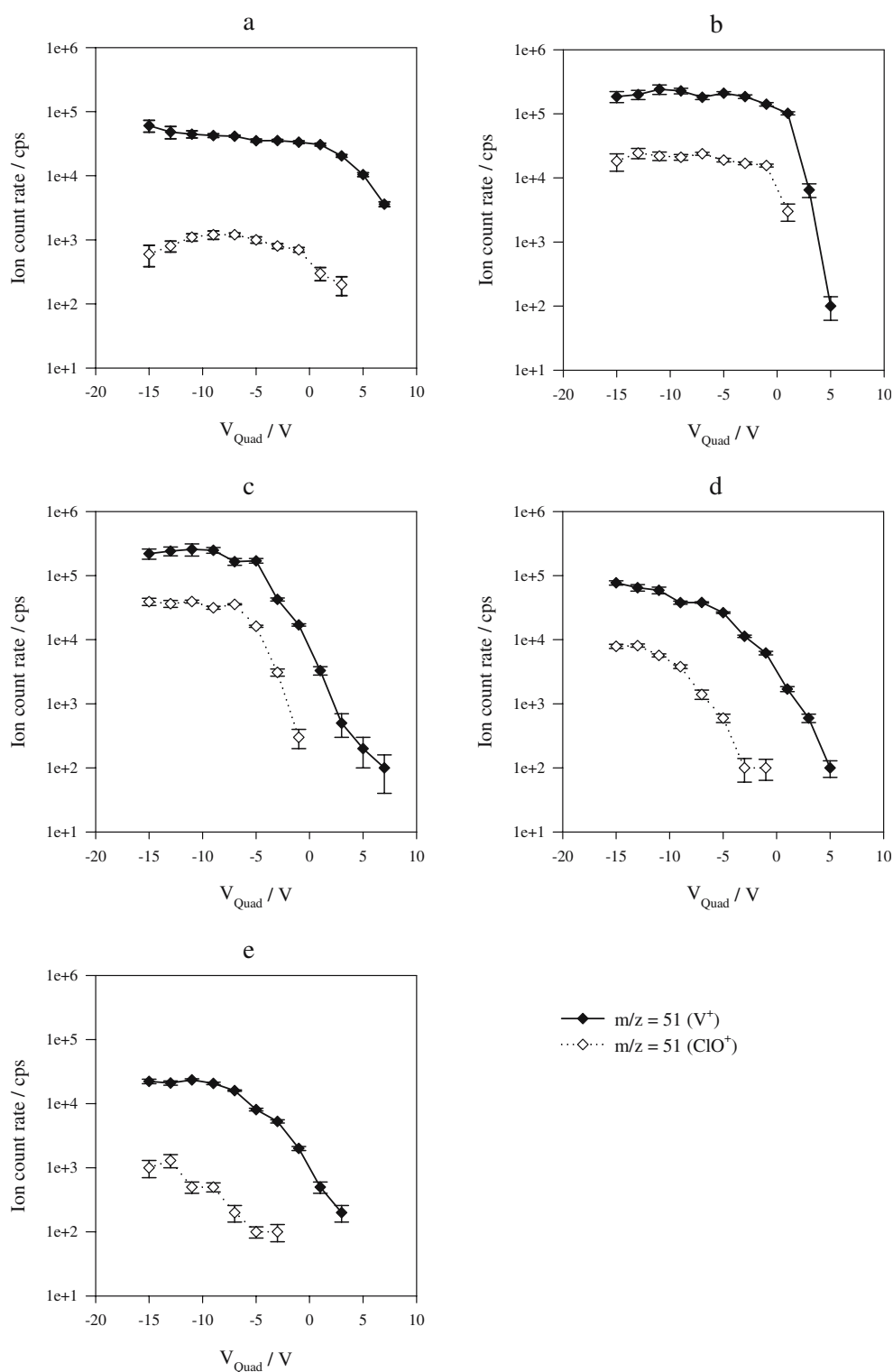
the V_H value led to a shortening of the plateau area, therefore, a significant drop in the analytical and interference signal was observed at V_H= +10.0 V and V_Q>+4.0 V. At V_Q values ranging from −15.0 to +4.0 V, the analytical signal was almost constant (Fig. 1a). For V_H=+5.0 V the quadrupole potential "breakpoint" was already at V_Q=0.0 V (Fig. 1b), and for V_H=0.0 V a significant signal decrease was observed already at V_Q=−3.0 V (Fig. 1c). The trends in the analytical signal and the interference signal were identical at V_H=+10.0 and +5.0 V. The plateau area in the case of the interference signal shortened according to the decrease in the hexapole bias potential. At V_H=0.0 V and V_Q>−3.0 V, it was possible to distinguish clearly between the signal of the analyte and the interference.

Fig. 3 Analytical ion intensities (*closed marks*) and interference ion intensities (*open marks*) as a function of He/H_2 (graphs **a** and **b**) and He/NH_3 (graphs **c** and **d**) gas flow rates under found optimum conditions of $V_Q=-8.0$ V, $V_H=-10.0$ V and $V_Q=-7.0$ V, $V_H=+10.0$ V, respectively. Each *point* represents mean±SD ($n=3$)
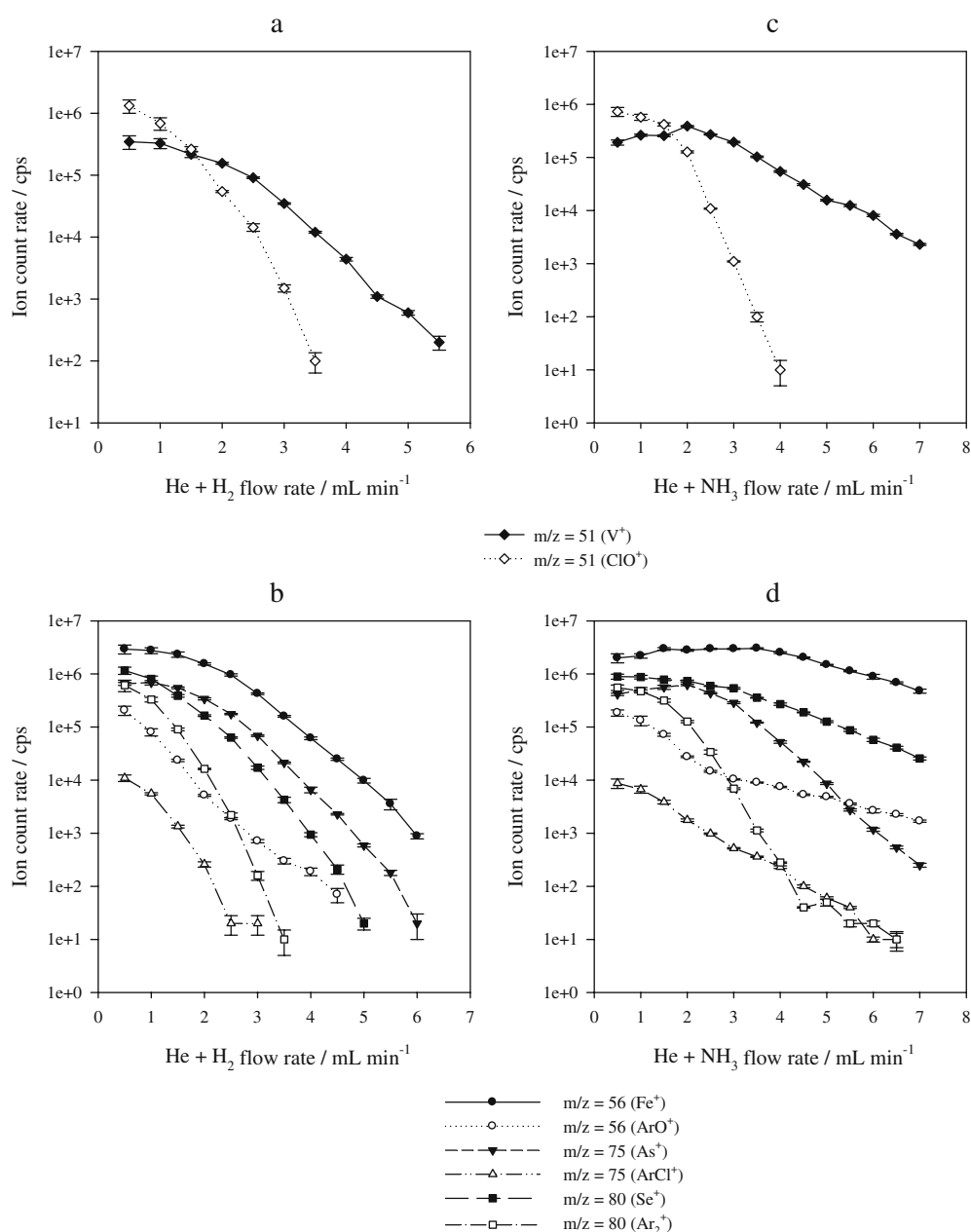
Above $V_Q > -3.0$ V, the decrease in the interference signal was significantly steeper than the analytical one. When setting up $V_H < 0.0$ V, the interference signal steepness grew compared to the analytical signal (Fig. 1d,e). At $V_H=$ −10.0 V, the area of a constant interference signal was minimal compared to the analytical signal (V_Q ranging from −15.0 to −12.0 V). At $V_Q > -12.0$ V there was a steep drop in the interference signal; on the other hand, the analytical signal remained constant at V_Q values ranging from −15.0 to −8.0 V. At $V_Q=-5.0$ V, a slow decrease in the analytical signal was observed whilst the interference signal decreased by more than one order of magnitude (Fig. 1e). Figure 1e best demonstrates the possibility of distinguishing between the analytical signal and the interference signal. When using a He/H_2 gas mixture as the collision/reaction gas, the optimum hexapole and quadrupole bias set-up is in accordance with set-ups used by other authors [6] and is related to the kinetic energy discrimination of the ions.

Table 3 Detection limits (ng L^{-1}) for different collision/reaction gas mixtures under optimum V_Q, V_H and collision/reaction gas flow rate

Analyte	Detection limit (ng L^{-1})[a]	
	He/H_2	He/NH_3
[51]V	36	12
[56]Fe	40	30
[75]As	27	27
[80]Se	30	11

[a]$LOD=3\rho_{blank}$

He/NH₃ as the collision/reaction gas

The values of the analytical signal on the mass-to-charge ratio 51 (100 μg V L^{-1}), together with the values of the interference signal (0.5 M HCl) in dependence on V_H (Fig. 2a–e) and V_Q (values from -15.0 to $+9.0$ V) using the He/NH₃ mixture as the collision/reaction gas are summarised in Fig. 2.

When using NH₃ as the reaction gas, a greater suppression of the interference signal occurred compared to H₂ (Figs. 1 and 2). Both V_H and V_Q influenced the analytical and interference signals. Decreasing the V_H value led to a shortening of the plateau effect of both signals (analytical and interference) (Fig. 2a–e). The decreasing trends in the analytical and interference signals were identical for H₂ and NH₃ at given V_H values, but in terms of absolute signal values a greater suppression of the interference occurred with the use of NH₃. The biggest difference between the analytical and the interference signal was achieved at $V_H=$ $+10.0$ V and $V_H=-10.0$ V (Fig. 2a,e). At $V_H=+10.0$ V (Fig. 2a) the analytical signal remained constant for the range of V_Q values from -15.0 to 0.0 V. The interference signal remained constant as well but was approximately two orders of magnitude lower. At $V_Q>0$ V a steep decrease in both signals could be observed. At $V_H=-10.0$ V (Fig. 2e), the analytical signal remained constant in the range of V_Q values from -15.0 to -5.0 V; the interference signal showed a decreasing trend throughout the whole range of V_Q values. At $V_Q>-5.0$ V, a steep decrease in the analytical signal occurred.

As mentioned before, the most significant difference between the analytical and the interference signal was found to be at $V_H=+10.0$ V (Fig. 2a). This set-up has been accepted as optimal, and the V_Q value was set to -7.0 V because of the better stability of the both analytical and interference signals (middle of the plateau, Fig. 2a).

Collision/reaction gas flow optimisation

The optimum collision gas flow (He/H₂ and He/NH₃; Fig. 3a,b and 3c,d respectively) was tested for both collision/reaction gases under the optimum V_H and V_Q conditions (Fig. 1 and 2). The optimum gas flow rate determination means, in this case, finding the smallest decrease in the analytical signal together with the steepest decrease in the interference signal, which could not be optimal for creating sufficient differences between the axial kinetic energy of analyte and interferent ions. For this reason, the optimum gas flow rate is often higher but the sensitivity of the analytical signal decreases strongly due to the scattering effect. The measured signals on the mass-to-charge ratios 51, 56, 75 and 80 corresponded to the analytical signals (100 μg L^{-1} of V, Fe, As and Se) and interference signals of polyatomic ions [$^{35}Cl^{16}O^+$, $^{40}Ar^{16}O^+$, $^{40}Ar^{35}Cl^+$ and $^{80}(Ar_2)^+$]. Increasing the He/H₂ flow rate led to a decrease in the analytical signal of vanadium as well as to a decrease in the interference signal (Fig. 3a). When the He/H₂ flow rate was set to 0.5 mL min^{-1}, the interference signal was even greater than the analytical signal. At 1.5–2.5 mL min^{-1}, the decrease in the interference signal was steeper than the decrease in the analytical signal. A further increase in the flow rate led to a significant decrease in the analytical signal caused by the scattering effect (Fig. 3a).

When NH₃ was used as the collision/reaction gas (Fig. 3c), the level of the interference signal was greater than the analytical signal at a flow rate of 0.5 mL min^{-1}. A further flow rate increase led to an even decrease in the interference signal, whilst the analytical signal slightly increased. When the gas flow rate was set to 1.8 mL min^{-1}, a break point on the interference signal curve was evident (Fig. 3c). Over 1.8 mL min^{-1}, the interference signal dropped very steeply. The analytical signal increased up to its maximum value corresponding to a flow rate of 2.5 mL min^{-1}. Above this value the analytical signal dropped slightly. At 3.5 mL min^{-1}, the analytical signal reached its initial level, whilst the interference signal was approximately three orders of magnitude lower (Fig. 3c).

By comparing the two collision/reaction gas mixtures (Fig. 3) it is possible to assume that the use of the He/NH₃ mixture under optimum V_H and V_Q conditions leads to a better suppression of the interfering polyatomic ions— most significantly in the case of vanadium. The optimum gas flow for the He/H₂ mixture was found to be around 2.5 mL min^{-1} when the interference signal on the mass-to-charge ratio 51 was suppressed by one order of magnitude. Similar results were published by Dexter et al. [9]. After this value, the analytical signal of all monitored mass-to-charge ratios decreased strongly due to the scattering effect. In contrast, in the case of the He/NH₃ mixture, the optimum gas flow rate was found to be around 3.5 mL min^{-1}: during vanadium determination the interference signal was suppressed by three orders of magnitude, whilst the analytical signal remained at the initial level (Fig. 3c).

Determination of V, Fe, As and Se under optimum conditions

Under conditions found to be optimum (V_Q, V_H and collision/reaction gas flow rate) for the He/H₂ and He/NH₃ gas mixtures, V, Fe, As and Se (mass-to-charge ratios 51, 56, 75 and 80 respectively) were determined in the SRM NIST 1640 with added HCl (concentration gradient from 0.0–0.1 mol Cl$^-$ L^{-1}; Table 2). The results of V and As determination in dependence on chloride content are summarised in Table 2.

Table 3 summarises achieved limits of detection (LODs) for both collision/reaction gas mixtures. Limits of detection for V, Fe, As and Se presented in this work were computed as 3×SD from 10 replicate measurements of the instrumental blank containing only deionised water and are obtained from the optimum parameters of the collision/reaction cell during V determination in the chloride matrix. The obtained LODs for V for both studied collision/reaction gas mixtures are comparable with other published results. Nixon et al. [4] used the DRC ICP-MS instrument

and found the LOD for V to be 28 ng V L^{-1} (compared to 36 and 12 ng V L^{-1} for He/H_2 and He/NH_3 respectively; Table 3). Better LODs were obtained using the He/NH_3 gas mixture in the case of Fe and Se (Table 3). During As determination, LODs were similar for both gas mixtures (27 ng As L^{-1}) (Table 3). These LODs are fully equivalent to those reported by Niemelä et al. [10] and Feldman et al. [11]. Other authors, e.g., Boulyga et al. [8], achieved lower LODs values for Fe, As and Se, but the method used for LOD computing was not entirely clear.

By comparing the Z-scores of the results obtained from the SRM NIST 1640 (with HCl added) analyses (Table 2), an evident difference in the efficiency of suppressing the polyatomic interference on the mass-to-charge ratio 51 ($^{35}Cl^{16}O^+$) was present for both tested collision/reaction gas mixtures. When the He/H_2 mixture was used, an overestimation of the signal on the mass-to-charge ratio 51 occurred with the increasing concentration of Cl^-. When the concentration of chlorides reached 0.005 mol Cl^- L^{-1}, the recovery of V determination was 138% (Table 2). At 0.01 mol Cl^- L^{-1}, the recovery value was 178%. Further increasing the chloride concentration led to a greater signal overestimation [0.1 Cl^- mol L^{-1}; recovery (V) = 656%] (Table 2). The use of the He/NH_3 gas mixture was more efficient in suppressing the polyatomic interference on the mass-to-charge ratio 51 compared to the He/H_2 mixture. The found values are in a good agreement with the certified value of 13.01 µg V L^{-1} for all selected Cl^- concentrations (Table 2). Standard deviations computed from five measurement replicates were low and similar, which points to a very stable signal even at high Cl^- contents. The suppression of the chloride interference on the mass-to-charge ratio 75 ($^{40}Ar^{35}Cl^+$) was sufficient (Table 2).

Other determined elements included Fe and Se on the mass-to-charge ratios 56 (Fe) and 80 (Se). When using the He/H_2 and the He/NH_3 gas mixtures, the concentrations obtained were 32.8±1.2 µg Fe L^{-1} (n=6) and 33.1±0.8 µg Fe L^{-1} (n=6) respectively (certified value: 34.4±1.6 µg Fe L^{-1}). The results obtained during Se determination were acceptable for both collision/reaction gas mixtures (Table 2).

Conclusions

The collision/reaction cell ICP-MS is an efficient tool for suppressing polyatomic interferences. This work was focused on the use of a 7% mixture of H_2 in He and a 1% mixture of NH_3 in He as the collision/reaction gases. The optimum set-up conditions for V_H, V_Q and collision/reaction gas flow were determined for each gas mixture (He/H_2 and He/NH_3). Furthermore, this configuration was verified by analysing SRM NIST 1640, which contains chloride ions (0.0–0.1 mol Cl^- L^{-1}).

It has been shown clearly that KED is not very efficient for suppression of the ClO^+ interference due to the wide overlaps in the axial kinetic energies of analyte and interferent ions. It would require higher collision gas pressure or a heavier collision gas to ensure applicability of

KED. The charge transfer reaction with H_2 is not possible in a thermal environment and condensation reactions show a substantial activation barrier that requires higher collision energies to proceed. The variation in the axial kinetic energy of the ions entering the cell changes not only the collision cross sections but also influences the possible reaction channels. Exothermic reactions proceed at higher rates when the ion kinetic energies are reduced either by applying a higher gas pressure or by increasing the bias of the multipole. The results show that there is no need to operate the collision/reaction cell at highly negative V_H values when using NH_3 because the reaction with ClO^+ is exothermic and has sufficiently low activation energy. Any acceleration thus reduces the reaction rate and the efficiency of the approach.

When using the gas mixture He/H_2, the optimum V_H and V_Q conditions correspond to set-up conditions when the kinetic energy discrimination of ions effect takes place due to the formation of the potential barrier. The collision/reaction gas flow was set to obtain a steeper decrease in the interference signal compared to the analytical signal. The results of the SRM NIST 1640 analyses show that using the He/H_2 mixture under optimum conditions helped to eliminate Ar-based interferences with the mass-to-charge ratios of 56 and 80 [$^{40}Ar^{16}O^+$ and $^{80}(Ar_2)^+$] and the chloride interference with the mass-to-charge ratio of 75 ($^{40}Ar^{35}Cl^+$), corresponding to the analysed isotopes ^{56}Fe, ^{80}Se and ^{75}As. Based on the obtained results, it is possible to assume that the He/H_2 gas mixture together with kinetic energy discrimination is not suitable during V determination in chloride matrices due to the insufficient suppression of the $^{35}Cl^{16}O^+$ polyatomic interference.

When the He/NH_3 was used, V_H was set to positive values. By adjusting V_H, it was possible to change the initial kinetic energy of the ions entering the collision cell (IKEE effect). During optimum collision gas flow conditions, the interference signal was significantly suppressed compared to the analytical signal, which remained almost constant. The experimental results showed that the He/NH_3 mixture, under found optimum conditions, can be used in the case of the classical multipole configuration for V, Fe, As and Se determination in chloride-containing samples. The detection limits for vanadium were comparable to published values obtained from DRC ICP-MS.

The presented analytical mode of ICP-MS analysis is applicable for the polyatomic interferences mentioned above. There is a high probability of unexpected signals as a result of clustering and condensation reactions, e.g., NH_3 is known to form cluster ions with a large number of transition elements.

References

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