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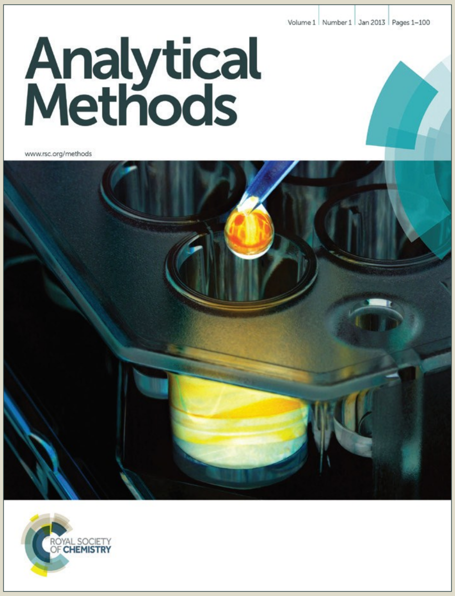

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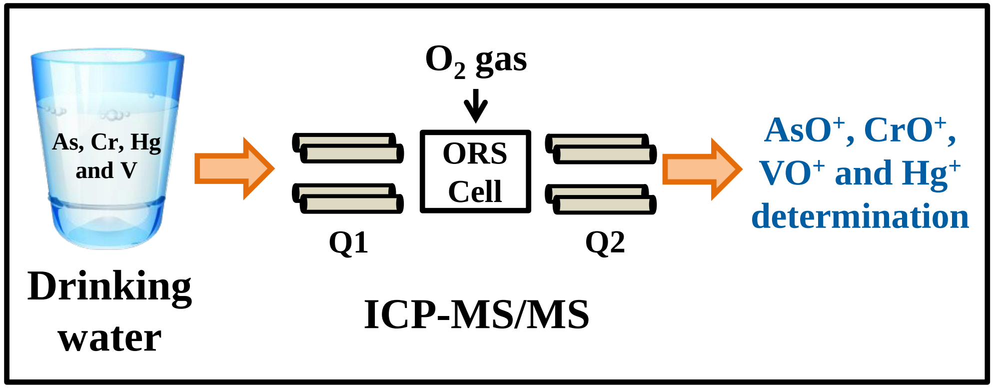
As, Cr, Hg and V
Drinking water
O_2 gas
ORS Cell
Q1
Q2
ICP-MS/MS
AsO^+, CrO^+, VO^+ and Hg^+ determination

A novel strategy to determine As, Cr, Hg and V in drinking water by ICP-MS/MS

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Abstract

This work demonstrates the potentiality of inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) on trace element analysis. Aiming Hg determination in water analysis, sample preservation requires chloride addition, which presents formation of polyatomic interfering ions as a drawback for determination of other analytes (e.g. As and V). Thus, the effect of chloride on As, Cr, V and Hg determinations and the feasibility of using ICP-MS/MS to circumvent the interferences were evaluated. A standard reference material (NIST SRM 1643e) and recoveries from tap water spiked with As, Cr, Hg and V were used for accuracy assessment and for evaluation of matrix effects. The reaction between Hg and oxygen gas is not favorable in the octopole reaction system (ORS^3). Therefore, Hg was accurately determined as a single atom ion ($^{202}Hg^+$) in the same analytical condition adopted for As, Cr and V determination by monitoring $^{75}As^{16}O^+$, $^{52}Cr^{16}O^+$ and $^{51}V^{16}O^+$ while the ORS^3 was pressurized with oxygen gas. The oxygen reaction mode significantly improved accuracy for As, Cr and V, especially at the lowest spiked level, which is strongly affected by matrix effects. The signal gain in m/z 75 for a solution containing 1 μg L^{-1} As in 0.48 mol L^{-1} chloride medium was 1974% when employing single quadrupole mode. On the other hand, the signal increased only 7% when 0.75 mL min^{-1} O_2 was used in mass shift mode proving the efficiency of the MS/MS mode. Thus, ICP-MS/MS and ORS^3 pressurized with O_2 gas effectively reduced interferences, and enhanced accuracy and sensitivity for some specific isotopes in a complex medium. Limits of detection for V ($^{51}V^{16}O^+$), Cr ($^{52}Cr^{16}O^+$), As ($^{75}As^{16}O^+$) and Hg ($^{202}Hg^+$) were estimated at 2, 3, 1.6 and 38 ng L^{-1} at the 99.7% confidence level, respectively.

Keywords: tandem mass spectrometry, multielemental determination, spectral interferences, water analysis, chloride.

Introduction

Trace elements in plants, animals, body tissues and fluids are those found in low concentrations, whether the element is essential or not.[1] Elements in drinking water may be either essential or toxic for human health depending on their chemical forms and concentrations[2] and several agencies around the world have established threshold levels. In this context, the Brazilian Ministry of Health recently approved a national regulation for inorganic constituents in drinking water destined to human consumption.[3] Particularly, the determination of highly toxic elements (e.g. As and Hg) in environmental samples is important as an issue for environmental preservation and human health, even in trace concentration (µg L^{-1} or even ng L^{-1}).[4-6] Thus, sensitive and reliable analytical procedures are required for their determinations in drinking water.

Inductively coupled plasma mass spectrometry (ICP-MS) is an attractive alternative due to the typically low detection limits achieved, wide linear response range, high sample throughput and capability for both multielementar and isotopic analysis.[7] Despite all these advantages and the widespread use, it may suffer severe physical, matrix and spectral interferences. Matrix induced interferences comprises transport effecst, space-charge interferences and those caused by concomitants at ionization conditions of the plasma. It is usually caused by differences in physico-chemical properties of the solvent being aspirated, organic matrices and dissolved solids. Some strategies to overcome physical/matrix interferences are internal standardization, optimization of the ion lens voltages, diminution of total dissolved solids below 0.2% and even the standard additions method.[7,8]

Spectral overlaps caused by atomic or polyatomic species with similar mass/charge ratios of the analytes are, however, the most serious interferences in ICP-MS. Spectral interferences are associated to either the argon plasma itself, components of the sample matrix, including the solvent, isotope overlaps, or oxygen or nitrogen gases from the surrounding air. Different strategies have been proposed to overcome such problems, including cool plasma condition, matrix separation, mathematical correction equations, and high resolution mass spectrometers, but in most cases interferences may not be completely eliminated.[7-9]

Polyatomic interferences affecting $^{52}Cr^+$ determination in a rich-carbon medium (*i.e.* formation of $^{40}Ar^{12}C^+$) was overcome by collision-reaction interface (CRI) by introducing 60 mL min^{-1} of H_2 through the skimmer cone. The authors emphasized the need for CRI, once matrix matching calibration and ICP-MS operation in standard mode did not suffice to improve accuracy, especially in ammonium acetate medium.[10]

Collision/reaction cells are also efficient alternatives to overcome spectral interferences. These pressurized cells are located before the quadrupole analyzer and gases such as O_2, NH_3 and H_2, are introduced into the cell promoting collision or reaction processes.[7,8] Taking into account vanadium determination in complex environmental matrices, O_2 was introduced into the reaction cell to form $^{51}V^{16}O^+$ for measurements in the gas shift mode.[11] Dynamic reaction cell was used for Cr and Fe determination in environmental samples, such as soil, rock and water.[12] However, different from the previously cited study, the reaction gas (NH_3) reacted with interfering polyatomic ions, thus improving signal-to-noise ratio on Cr and Fe determinations. Based on the kinetic energy discrimination (KED) technology, H_2 and He were used as cell gas and effectively attenuated polyatomic interferences on, among other elements, As, Cr and V determinations.[13] Chrastný et al. evaluated mixtures of He/NH_3 and He/H_2 for reducing chloride interferences on V determination. According to the authors, He/H_2 mixture associated to KED technology sufficed to eliminate $^{35}Cl^{16}O^+$ interferences on V determination in matrices containing up to 0.1 mol L^{-1} Cl^-. On the other hand, using the mixture of 1% NH_3 in He was consistent and provide accurate vanadium determination.[14]

In spite of the successful examples previously mentioned, occurrence of unexpected reactions in the reaction cell, formation of new interfering species, and difficulty of using internal standardization have also been reported.[15] These drawbacks are pronounced in some cases, such as for ^{80}Se determination in biological matrices. The m/z of its oxide ion ($^{80}Se^{16}O^+$) overlaps with that of ^{96}Mo isotope thus hindering its accurate determination.[9]

The instrumental strategy evaluated in the present work, the tandem mass configuration (ICP-MS/MS) features an additional quadrupole mass analyzer (Q1) in front of the 3rd generation of the octopole reaction/collision system (ORS^3 cell) and a second quadrupole mass analyzer (Q2). Q1 operates as a mass filter, allowing only the target analyte mass to enter the cell and rejecting all other masses. The main advantage of MS/MS is the breakthrough performance improvement when operated in reaction mode.[16,17] Arsenic and selenium at ultra-trace levels were determined as $AsCH_2^+$ and $SeCH_2^+$ employing CH_3F/He as reaction gas in ICP-MS/MS. This approach provided interference-free conditions, high accuracy and precision.[18] Low levels of S in organic matrices were also accurately determined as SO^+ exploiting MS/MS mode and isotope dilution.[19] However, in some cases the purpose is to determine an analyte that reacts poorly with oxygen, with other reactive elements that in fact need this reaction to be accurately determined. This was the focus of this work, in which the goal is to determine at the same condition, Hg without any reaction, and elements that need the reaction with O_2 to eliminate severe spectral interferences. The magnitude of such interferences was observed when chloride was added to the solution to make feasible Hg determination. The determination of As, which is a monoisotopic element ($^{75}As^+$), and the main isotopes of Cr and V ($^{52}Cr^+$ and $^{51}V^+$) may be hindered by chloride due to the formation of $^{40}Ar^{35}Cl^+$, $^{35}Cl^{16}OH^+$ and $^{35}Cl^{16}O^+$. On the other hand, Hg determination in water requires addition of chloride for the preservation of dissolved mercury as well as to avoid memory effects when solutions are introduced by pneumatic nebulization in ICP-MS.[12] Thus, the determination of the trace elements As, Cr, Hg and V in a medium containing chloride in the same run is quite difficult. The present work then present a novel strategy for the multi-elemental ICP-MS/MS determination of Hg as single atom ion, as well as As, Cr and V in mass shift mode in drinking water enriched with chloride. It was also evaluated the effect of chloride addition on As net analytical signal at m/z 75.

Experimental

Instrumentation

All measurements were carried out using an Agilent 8800 ICP-MS/MS instrument (Agilent Technologies, Japan) equipped with an octopole-based collision/reaction cell (ORS^3) located in-between two quadrupole analyzers. Pure oxygen (≥99.999%, Air Products, São Paulo-SP, Brazil) was used to pressurize the ORS^3 aiming to form the oxide polyatomic species for analytes quantification on MS/MS mode. Measurements without O_2 were carried out on the single quadrupole mode. Plasma operating conditions are shown in Table 1.

Reagents and standard solutions

Ultrapure water (resistivity > 18.2 MΩ cm, Milli-Q, Millipore, Bedford, MA, USA), concentrated nitric and hydrochloric acids (Merck, Darmstadt, Germany) purified in a sub-boiling distillation system (Milestone, Sorisole, Italy) were employed to prepare all solutions. Working standard solutions (0.5 – 50 $\mu g\ L^{-1}$) were prepared by dilutions of 1000 mg L^{-1} As, Cr, Hg and V stock solutions (Quimis, São Paulo, SP, Brazil) in 0.14 mol L^{-1} HNO_3. The cleaning of the sample introduction system with 0.06 mol L^{-1} HCl after the calibration step is required for avoiding memory effects.

Procedures

Trace elements in water standard reference material (NIST SRM 1643e, Gaithersburg, MD, USA) diluted (1:1 v v^{-1}) in 0.06 mol L^{-1} HCl was used for accuracy assessment. Tap water (1:1 v v^{-1}) in 0.06 mol L^{-1} HCl was spiked with the analytes in two different concentrations to evaluate interferences by polyatomic interferences in chloride medium. In order to obtain net signals for the spikes, the concentrations found in tap water were subtracted from an unspiked real sample. Limits of detection (LOD) were calculated according to IUPAC recommendations.[20] The slopes of analytical calibration curves and the standard deviation for 10 consecutive measurements of blank solutions (0.06 mol L^{-1} HCl) were considered.

The effect of $^{40}Ar^{35}Cl^+$ interference on $^{75}As^+$ net signal was evaluated for solutions containing 1 μg L^{-1} As in the absence and containing 0.012, 0.06, 0.12, 0.24, 0.36, or 0.48 mol L^{-1} HCl. Instrumental measurements were carried out either using single quadrupole mode or pressuring the ORS^3 with 0.30, 0.50 and 0.75 mL min^{-1} O_2 when operating in the MS/MS mode. For comparison purposes, the analytical signal of $^{75}As^+$ and $^{75}As^{16}O^+$ in the solution without Cl^- was normalized to 100%, and then percentages of signal gain in solutions containing increasing concentrations of chloride were calculated based on it.

Results and Discussion

Determination of Hg as single atom ion and As, Cr and V as oxide ions at same analytical conditions

According to Louie et al.[21] the presence of chloride has a stabilizing effect on Hg ions in water samples and it also avoids memory effects in ICP-MS determinations. The recommended acid combination is HNO_3 0.14 mol L^{-1} plus HCl 0.0012 mol L^{-1}. However, the resulting chloride concentration is high enough to cause interference in the determination of other elements, so the potential of ICP-MS for solving polyatomic overlaps and permit the multielement determination was evaluated. The chloride concentration adopted in the present study was 0.06 mol L^{-1} in order to infer the behavior of diluted solutions of seawater, biological fluids or digests obtained by using hydrochloric acid.

The results of the determination of As, Cr, Hg and V in a medium containing 0.06 mol L^{-1} HCl are presented in Table 2. The overlaps of $^{35}Cl^{16}O^+$, $^{35}Cl^{16}OH^+$ and $^{40}Ar^{35}Cl^+$ on m/z 51, 52 and 75, respectively, were effectively corrected by pressuring the ORS^3 with 0.30 mL min^{-1} O_2 combined with determination based on the corresponding oxide ions. This performance was achieved by setting Q1 at m/z 51, 52, 75 and 202 and Q2 at m/z 67, 68, 91, 202 and 218. Because the spiked concentrations were lower than those found in the SRM 1643e and the effects of polyatomic interferences on accuracy were more pronounced, recoveries were not adequate when using single quadrupole mode in addition and recovery experiments. On the other hand, by mass shift mode and pressuring the ORS^3 with 0.30 mL min^{-1} O_2, accurate results were obtained for SRM 1643e and tap water, both in 0.06 mol L^{-1} chloride medium. Arsenic, Cr and V recoveries in SRM 1643e were not quite different comparing single quadrupole mode and MS/MS mode, ranging from 92 to 106%, probably due to the higher concentrations of the analytes in the SRM and the lower chloride concentration when compared to tap water. Mercury concentration is not certified in the SRM NIST1643e.

It can be seen in Table 2 that when the analyte concentration increases, the need of using MS/MS mode decreases. This is due to the higher analyte/interfering specie ratio and demonstrates the matrix effect. In addition, when using single quadrupole mode no strategies were adopted to correct the spectral interferences.

As expected, the accuracy for Hg determination was better as a single atom ion than by mass shift mode because the formation of HgO^+ is not thermodynamically favorable. In single quadrupole mode the recovery of 0.5 µg L^{-1} was 84% and, for the addition of 10 µg L^{-1}, the recovery was appreciably better (96.2%). A significant improvement of accuracy for Hg determination at low concentrations was observed when 0.5 µg L^{-1} Hg was determined as single atom ion in MS/MS mode with ORS^3 pressurized with oxygen gas (100% recovery). It can also be seen in Table 2 that it was possible to select the same m/z ratio (202) in both quadrupoles (Q1 and Q2) and carried out Hg determination as elemental species even under oxygen gas flow rate into the ORS. Although it was not possible to determine Hg as $^{202}Hg^{16}O^+$ in concentrations as low as 0.5 µg L^{-1} in spiked tap water, the calibration curve at reaction mode was linear. From these results, it may be inferred a partial reaction of Hg^+ with O_2 in the pressurized ORS^3. Relatively high limit of detection (0.57 µg L^{-1}) was observed for Hg determination as $^{202}Hg^{16}O^+$ which explains the accuracy observed in spiked tap water at 10 µg L^{-1} Hg and not for 0.5 µg L^{-1} Hg in this analytical condition.

This proposed strategy presents an important aspect when considering multielement determinations. Accurate determinations were observed at low and high concentration levels (0.5 and 10 µg L^{-1}) with the advantage of determine As, Cr and V as oxide ions and Hg as single atom ion ($^{202}Hg^+$) at the same run and all elements with ORS^3 pressurized with oxygen. Moreover, the Hg determination by the strategy here proposed is simpler when compared to strategies that use the addition of gold chloride to avoid memory effects and to ensure stability.[22,23]

The LOD for $^{202}Hg^{16}O^+$ under 0.30 mL min^{-1} O_2 is ca. 17-fold higher than in the single quadrupole mode (without oxygen gas flow rate). However, when $^{202}Hg^+$ was selected in both quadrupoles (Q1 and Q2) and Hg determination was carried out as single atom ion even pressuring the ORS^3 with oxygen, the limit of detection was similar to that found in single quadrupole mode (33.6 and 38.1 ng L^{-1}, respectively), thus confirming the feasibility and advantages of As, Cr, Hg and V determination on MS/MS mode in the same run.

In some experiments with synthetic solutions containing 1 µg L^{-1} Cr and V in different HCl concentrations interferences were observed on the determination of Cr and V caused by chloride concentrations higher than 0.06 mol L^{-1} in both single quadrupole and mass shift mode. Probably it is due to the formation of the $^{35}Cl^{16}O^+$ and $^{35}Cl^{17}O^+$ species, both selected in Q1 and, because the formation of $^{35}Cl^{16}O_2^+$ and $^{35}Cl^{16}O^{17}O^+$ is possible into the ORS^3, both dioxide ions were selected in Q2 causing the positive interference. However, the formation of these polyatomic ions did not occur when working with the certified reference material and tap water probably because other elements interact with chloride and this anion was not available for gas phase reactions in the ORS^3.

Effect of chloride addition on As net analytical signal

The effect of chloride concentrations on As determination was evaluated by monitoring $^{75}As^+$ in single quadrupole mode and $^{75}As^{16}O^+$ in MS/MS mode using ORS^3 pressurized with oxygen (Figure 1). The pressurization of the ORS^3 with O_2 allowed the arsenic determination as $^{75}As^{16}O^+$. The spectral interference reduction was improved with the increase of O_2 gas flow rate from 0.30 to 0.75 mL min^{-1} into the reaction cell. The positive interference on m/z 75 ($^{75}As^+$) in 0.48 mol L^{-1} chloride medium was very significant (signal increased 1974%) employing single quadrupole mode and, when the mass shift mode was adopted and pressurized ORS^3 with 0.75 mL min^{-1} O_2 gas flow rate, this increment was only 7%, demonstrating the efficiency of MS/MS mass shift mode to form $^{75}As^{16}O^+$ and overcome polyatomic interferences. The $^{75}As^{16}O^+$ ion monitored at m/z 91 would be interfered by isobaric overlaps from $^{91}Zr^+$ when measured using a quadrupole-based conventional instrument, however this isotope is rejected by Q1 in the ICP-MS/MS, which leaves the m/z 91 free of interferences, resulting in good accuracy and detectability.

McCurdy and Woods[24] stressed that the combination of O_2 reaction mode and mass shift mode operation makes feasible the accurate determination of As in complex samples. Pereira et al.[25] also evaluated the effect of chloride concentration on As determination at m/z 75 using a quadrupole based ICP-MS equipped with a collision-reaction interface (CRI). These authors observed a complete interference correction when H_2 gas was introduced through the skimmer cone at 80 mL min^{-1}. However, sensitivity was 90% lower due to defocusing of As^+ isotope. The approach presented in this work avoided this hindrance.

Conclusions

Accurate determinations of Hg, As, Cr and V at trace levels in spiked tap water and in water standard reference material was successfully carried out, even in a matrix with high chloride concentration. The isotope $^{202}Hg^+$ isotope was accurately determined as single atom ion in the same run with $^{75}As^{16}O^+$, $^{52}Cr^{16}O^+$ and $^{51}V^{16}O^+$ under ORS^3 pressurized with O_2 gas. The limits of detection achieved by MS/MS mass shift mode were up to 35-fold improved, which is a consequence of background reduction due to the Q1 mass filter. It is clear that by using ICP-MS/MS instrument and O_2 into the reaction cell, interferences are reduced, and accuracy and sensitivities are improved. Although the Hg^+ reaction with O_2 is not thermodynamically favorable, a linear calibration curve was observed and it may be inferred that a partial reaction between these species occurs in the ORS^3 cell.

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Tables

Table1. ICP-MS operating parameters

Instrument Parameter	Operating condition			
RF applied power (kW)	1.55			
Sampling depth (mm)	7			
Auxiliary gas flow rate (L min^{-1})	1.8			
Nebulizer	Concentric nebulizer – glass			
Spray chamber	Scott type – double pass			
Makeup gas flow rate (L min^{-1})	0.15			
Carrier gas flow rate (L min^{-1})	1.05			
Mass/charge ratios monitored – Q1	51, 52, 75 and 202			
Mass/charge ratios monitored– Q2	67, 68, 91, 202 and 218			
Operating mode	Single quadrupole	MS/MS		
Cell gas	No gas	O_2	O_2	O_2
Gas flow rate (mL min^{-1})	0	0.30	0.50	0.75

Table 2. Determination of As, Cr, Hg and V (mean ±standard deviations, n = 3) in water SRM (NIST 1643e) and spiked tap water, operating in single quadrupole mode and O_2 reaction mode. Both tap water and SRM were diluted 1:1 (v/v) in 0.06 mol L^{-1} chloride medium.

Isotope/ Specie	**Found ($\mu g\ L^{-1}$)**	**Rec. (%)**	**Added ($\mu g\ L^{-1}$)**	**Found ($\mu g\ L^{-1}$)**	**Rec. (%)**	**LOD ($ng\ L^{-1}$)**
SRM NIST(1643e)			**Tap Water**			
Single quadrupole mode						
$^{51}V^+$	38±2	101±6	0.5	1.26±0.27	252±54	61
			10	14.6±1.49	121±15	
$^{52}Cr^+$	20.9±1.3	102±6	0.5	0.48±0.04	95±8	4.2
			10	10.7±0.51	107±5	
$^{75}As^+$	54±3	90±5	0.5	1.09±0.21	219±42	56
			10	11.7±1	117±10	
$^{202}Hg^+$	-	-	0.5	0.42±0.01	84±2	34
			10	9.62±0.48	96.2±4.8	
MS/MS mode 0.30mL min^{-1} O_2						
$^{51}V^{16}O^+$	39.2±0.8	103±2	0.5	0.44±0.06	88±12	2
			10	9.7±0.3	97±4	
$^{52}Cr^{16}O^+$	20.0±0.4	98±2	0.5	0.49±0.02	98±4	3
			10	10.1±0.1	101±1	
$^{75}As^{16}O^+$	56.4±0.9	94±2	0.5	0.57±0.01	114±2	1.6
			10	10.9±0.3	109±3	
$^{202}Hg^+$	—	—	0.5	0.50±0.01	100±2	38
			10	9.79±0.13	98±1	
$^{202}Hg^{16}O^+$	—	—	0.5	—	—	566
			10	10±2	97±23	

Certified values in NIST SRM 1643e ($\mu g\ L^{-1}$): V – 37.86 ± 0.59, Cr – 20.40 ± 0.24 and As – 60.45 ± 0.72

Figures

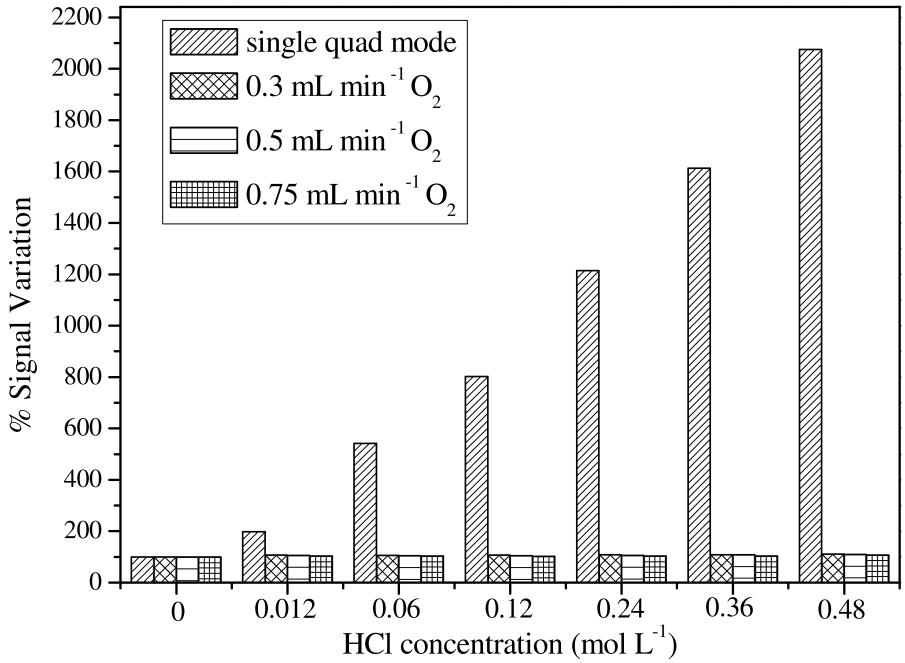

Figure 1. Effect of O_2 gas introduction into the ORS^3 on chloride interferences at As determination in solution containing 1 µg L^{-1} As and different HCl concentrations. The $^{75}As^+$ isotope was monitored by single quadrupole (▭) mode while $^{75}As^{16}O^+$ was monitored at m/z 91 by MS/MS mode using ORS^3 pressurized with oxygen gas (▭, ▭, ▭).