



Reactivity and analytical performance of oxygen as cell gas in inductively coupled plasma tandem mass spectrometry

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ABSTRACT

The reactivity and analytical performance of O₂ as cell gas in inductively coupled plasma tandem mass spectrometry was investigated. Selected analytes in a wide mass range were divided in three groups according to their reactivity: G1 represents elements with high oxygen affinity (Ce, La, P, Sc, Ti, and Y), G2 contains elements that may partially react with oxygen (As, Ba, Mo, Si, Sr, and V), and G3 comprises elements expected to be less reactive towards oxygen (Al, Bi, Cu, Mg, Pb, and Pd). On-mass and mass-shift modes were evaluated by monitoring atomic and metal oxide ions, respectively. Analytical signal profiles, oxide percentages, sensitivities and limits of detection for oxygen flow rates varying from 0.1 to 1.0 mL min⁻¹ were also studied. Group 1 elements plus As and V presented better sensitivities and LODs when measuring oxides, which were the major species for all flow rates evaluated. Molybdenum and Si oxides presented intermediate behavior and MoO fraction was up to 47% and limit of detection was the same as that obtained in on-mass mode. For others G2 and G3 elements, on-mass mode presented higher sensitivity and better LODs, with estimated oxide contents lower than 10%. In most cases, increasing oxygen flow rates led to lower sensitivities and worse LODs.

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1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most used techniques for determination of trace and ultra-trace elements in a wide variety of samples due to the combination of its unique features such as high sensitivity, sample throughput, multi-element capability and isotopic analysis [1]. Despite the advantages, ICP-MS with quadrupole mass spectrometer is prone to severe spectral overlaps caused by the formation of polyatomic, isobaric and doubly-charged species into the plasma. Some of these interferences can be overcome either by using high-resolution technology or by using quadrupole-based instruments with collision-reaction cell devices. Many different instrumental designs have been proposed along the last decades [1,2].

The recently proposed ICP-tandem mass spectrometry (ICP-MS/MS) presents an innovative instrumental configuration to deal with challenging spectral interferences. The instrument is composed by an octopole reaction system in-between two independent quadrupole mass filters (Q1 and Q2). As different mass-to-charge ratios can be selected in each quadrupole, collision and especially reaction processes may take place in a more selective and controlled process [3]. The use of reaction gases, such as H₂, NH₃, N₂O, O₂, and CH₃F, into the octopole cell

has been studied, but O₂ has been extensively used and shown interesting performance in ICP-MS/MS [4,5]. Oxygenation reactions may be limited by thermodynamic aspects and the prediction of possible reactions and its extent according to gas flow rate in the cell allows a better understanding of the chemical processes and the potential for driving oxidation reactions for reaching better selectivity [6,7].

Sulfur determination by ICP-MS is highly affected by polyatomic interferences of ¹⁶O₂⁺ in the main isotope (³²S⁺) and it is an example of practical application of O₂ reaction. The analytical performance of the ICP-MS/MS operating in single quadrupole mode (i.e. no oxygen reaction) and in bandpass and MS/MS modes for the determination of ³²S⁺, ³³S⁺ and ³⁴S⁺ in organic matrices were compared [8]. Better results were obtained when ³²S⁺ reacted with O₂ to form ³²S¹⁶O⁺ (*m/z* = 48), thus overcoming ¹⁶O₂⁺ overlaps. When MS/MS was used, better selectivity was achieved since possible interfering elements such as ⁴⁸Ca⁺ and ⁴⁸Ti⁺ on ³²S¹⁶O⁺ can be eliminated by setting Q1 = 32 and thus allowing only ³²S⁺ and ¹⁶O₂⁺ to reach the octopole cell. Sulfur and other challenging elements as P and Si in biodiesel, diesel and lubricating oil were determined by ICP-tandem mass spectrometry [9]. In addition to the spectral overlaps already mentioned for ³²S⁺, ³¹P⁺ and ²⁸Si⁺ are prone to interferences caused by ¹⁴N¹⁶OH⁺ and ¹⁴N₂⁺, respectively. The reaction with oxygen and the use of MS/MS and mass-shift modes led to better accuracy, sensitivities and limits of detection (LODs). Alternatively, oxygen gas can be introduced into the octopole

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cell aiming its reaction with interfering ions. The conversion of MoO^+ to MoO_2^+ enabled accurate Cd determination free of interferences in milk samples by operating ICP-MS/MS in on-mass mode [10]. In this case, Mo concentration was also determined by monitoring its dioxide ion in the same run.

Organic matrices are also sources of interferences in ICP-MS determinations. Isotopes such as $^{52}\text{Cr}^+$ and $^{28}\text{Si}^+$ are highly affected by carbon-based polyatomic ions as $^{40}\text{Ar}^{12}\text{C}^+$ and $^{12}\text{C}^{16}\text{O}^+$, respectively. An analytical procedure developed for the direct analysis of ethanol fuel demonstrated that the atomic ions react with oxygen to give their oxides and dioxides ions in ICP-MS/MS, proper accuracies were achieved and analytical performance was improved [11]. Interferences caused by doubly-charged species of $^{150}\text{Nd}^{2+}$ and $^{150}\text{Sm}^{2+}$ on $^{75}\text{As}^+$ and $^{156}\text{Gd}^{2+}$ and $^{160}\text{Gd}^{2+}$ on $^{78}\text{Se}^+$ and $^{80}\text{Se}^+$ determinations have also been solved by using O_2 reactions to give AsO^+ and SeO^+ , respectively [12]. Arsenic and Se were displaced to $m/z + 16$, and both were determined in food samples free from double-charge interferences.

It is important to consider that O_2 played a major role for overcoming spectral interferences and in all cited analytical procedures different optimal oxygen gas flow rates were used to obtain accurate and sensitive analysis. However, there is a lack of experimental studies describing a systematic evaluation of O_2 reactivity and selectivity into the octopole cell and a critical discussion of its impact on the performance of the analytical procedure. In the present study the effects of O_2 flow rates on Al, As, Ba, Bi, Ce, Cu, La, Mg, Mo, P, Pb, Pd, Sc, Si, Sr, Ti, V, and Y signals in ICP-MS/MS with on-mass and mass-shift modes were evaluated. Experimental data were interpreted considering thermodynamic data and it was demonstrated that the behavior of these elements can be rationalized based on their chemical reactivities towards O_2 .

2. Experimental

2.1. Instrumentation

All experiments were carried out using an Agilent 8800 ICP-MS spectrometer (Agilent Technologies, Japan) equipped with an octopole cell in-between two quadrupole mass analyzers (Q1 and Q2). Ultrapure oxygen gas ($\geq 99.999\%$, Air Products, São Paulo, SP, Brazil) at different flow rates was used into the octopole to promote atomic ions reactions and oxide ions formation. The instrument operation in MS/MS mode and on-mass ($Q1 = Q2$) and mass-shift ($Q2 = Q1 + 16$ or $Q1 + 32$) analysis modes were carefully evaluated. The ICP-MS/MS operating parameters and monitored masses are shown in Table 1.

2.2. Reagents, standard solutions and samples

All analytical solutions were prepared using distilled-deionized water (resistivity $> 18.2 \text{ M}\Omega \text{ cm}$) obtained from a Milli-Q system (Millipore, Bedford, MA, USA) and nitric acid (Merck, Darmstadt, Germany) purified using a subboiling distillation system (Milestone, Sorisole, Italy). Standard solutions were prepared by adequate dilution of 1000 mg L^{-1} Al, As, Ba, Bi, Ce, Cu, La, Mg, Mo, P, Pb, Pd, Sc, Si, Sr, Ti, V and Y stock solutions (Fluka Analytical, St. Gallen, Switzerland) in $1\% \text{ v v}^{-1} \text{ HNO}_3$.

3. Results and discussion

3.1. Evaluation of gas flow rates and reactivity

One of the main conditions to O_2 gas phase reactions into collision-reaction cells is the dissociation of the O_2 molecule. Oxides formation into the octopole cell generally involves an atomic oxygen transfer with the analyte (X^+) according to Eq. (1).



Table 1
Agilent 8800 ICP-MS/MS operating parameters.

Instrument Parameter	Operating condition
RF applied power (kW)	1.55
Sampling depth (mm)	8.0
Plasma gas flow rate (L min^{-1})	12.0
Carrier gas flow rate (L min^{-1})	1.08
Auxiliary gas flow rate (L min^{-1})	1.8
Nebulizer	Concentric nebulizer - glass
Spray chamber	Scott type - double pass
Isotopes selected - Q1	^{24}Mg , ^{27}Al , ^{28}Si , ^{31}P , ^{45}Sc , ^{48}Ti , ^{51}V , ^{63}Cu , ^{75}As , ^{88}Sr , ^{89}Y , ^{98}Mo , ^{106}Pd , ^{137}Ba , ^{139}La , ^{140}Ce , ^{208}Pb , ^{209}Bi
Operating mode	MS/MS
Cell gas	O_2
O_2 flow rate (mL min^{-1})	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0
Analysis mode	On-mass Mass-shift
Isotopes selected - Q2	The same as Q1 $^{24}\text{Mg}^{16}\text{O}$, $^{27}\text{Al}^{16}\text{O}$, $^{28}\text{Si}^{16}\text{O}$, $^{28}\text{Si}^{16}\text{O}_2$, $^{31}\text{P}^{16}\text{O}$, $^{45}\text{Sc}^{16}\text{O}$, $^{48}\text{Ti}^{16}\text{O}$, $^{51}\text{V}^{16}\text{O}$, $^{63}\text{Cu}^{16}\text{O}$, $^{75}\text{As}^{16}\text{O}$, $^{88}\text{Sr}^{16}\text{O}$, $^{89}\text{Y}^{16}\text{O}$, $^{98}\text{Mo}^{16}\text{O}$, $^{98}\text{Mo}^{16}\text{O}_2$, $^{106}\text{Pd}^{16}\text{O}$, $^{138}\text{Ba}^{16}\text{O}$, $^{139}\text{La}^{16}\text{O}$, $^{140}\text{Ce}^{16}\text{O}$, $^{208}\text{Pb}^{16}\text{O}$, $^{209}\text{Bi}^{16}\text{O}$

The enthalpy for this reaction (D^0) is the difference between the dissociation energy of the O_2 molecule (ca. 5.1 eV) [6] and the dissociation energy of the oxide specie (XO^+), also known as the analyte affinity for oxygen (Eq. 2) [13].

$$D^0 = D^0_{\text{O}_2} - D^0_{\text{XO}^+} \quad (2)$$

During the collision process between the analyte and oxygen, if the former has great affinity by O (i.e. dissociation energy for $\text{XO}^+ > 5.1 \text{ eV}$) then the enthalpy would be negative, thus the reaction is exothermic and the process spontaneous [13]. Moreover, analyte limited affinity for oxygen and lower dissociation energy for XO^+ lead to endothermic and less extent reactions. In addition to oxygen atom transfer, charge transfer and secondary oxygen transfer may also occur into the octopole cell according to Eqs. (3) and (4), respectively [4,14]. The occurrence of these parallel reactions may impair oxides formation and reduce analytical signals for monitored species in mass-shift mode. It is important to point out that these reactions may be dependent on the amount or gas flow rate through the octopole cell.



For the studies of reactivity at different gas flow rates, 18 analytes in a wide mass range were evaluated and separated in three groups (G1–G3) according to their oxygen affinity, as shown in Table 2 [13]. Group 1 is composed by ^{31}P , ^{45}Sc , ^{48}Ti , ^{89}Y , ^{139}La , and ^{140}Ce which are expected to easily react with oxygen (i.e. $D^0_{\text{XO}^+} > D^0_{\text{O}_2}$). Group 2 is composed by intermediate reactive elements, such as ^{28}Si , ^{51}V , ^{75}As , ^{88}Sr , ^{98}Mo , and ^{138}Ba , with XO^+ dissociation energies about 1.0 eV lower or higher than $D^0_{\text{O}_2}$ and Group 3 comprised elements that are expected to be less reactive due to their low XO^+ dissociation energy (i.e. $D^0_{\text{XO}^+} \ll 5.1 \text{ eV}$), such as ^{24}Mg , ^{27}Al , ^{63}Cu , ^{106}Pd , ^{208}Pb , and ^{209}Bi . Analytical solutions containing all analytes at $10 \mu\text{g L}^{-1}$ were prepared in $1\% \text{ v v}^{-1} \text{ HNO}_3$ and a blank solution was prepared in this same acid medium. On-mass and mass-shift modes were evaluated in the same run for different oxygen gas flow rates and in each case (Figs. 1 to 3), blank signals were subtracted and the intensities for CeO^+ and MoO^+ were divided by 10 for scale purposes.

Signal profiles for ionic and oxide species for G1 are shown in Fig. 1. In general, metal oxide ion signals were 5 to 50-fold higher than the respective atomic ion signals, thus demonstrating the high affinity of Ce, La, P, Sc, Ti and Y by O_2 and high O-transfer reaction rate. When the

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