Talanta 86 (2011) 241–247

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Performance evaluation of collision–reaction interface and internal standardization in quadrupole ICP-MS measurements

Rodrigo F.S. Salazar, Marcelo B.B. Guerra, Edenir R. Pereira-Filho, Joaquim A. Nóbrega*

Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, Washington Luiz Hwy, km 235 – P.O. Box 676 – 13.565-905 – São Carlos, SP, Brazil

ARTICLE INFO

Article history:
Received 29 May 2011
Received in revised form 6 September 2011
Accepted 8 September 2011
Available online 28 September 2011

Keywords:
Internal standardization
Polyatomic ions
Transport effects
Collision–reaction interface (CRI)

ABSTRACT

The combined use of internal standardization with collision and reaction interface in an inductively coupled plasma quadrupole mass spectrometer (ICP-QMS-CRI) was evaluated. The behavior of several elements (Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Pb, Sb, V and Zn) was studied by introducing H_2 or He through the skimmer and sampler cones of the CRI device and by using In, Rh and Sc as internal standards. Certified reference material of trace elements in water (NIST 1643e) was used to evaluate the performance of the method. A vinegar sample and mixed food diet standard reference material were directly introduced into the equipment as complex matrices for Cr and V determinations. Improvements in accuracy and precision were attained combining both strategies. The introduction of H_2 through the skimmer cone was the best way to overcome polyatomic ions formation and to improve SBR and BEC values for several elements. The use of Sc as internal standard improved the performance of ICP-QMS-CRI.

1. Introduction

Nowadays, inductively coupled plasma mass spectrometry (ICP-MS) is one of the most widely used spectroanalytical techniques. Due to its multi-elemental capability and low limits of detection, ranging from $\mu g\,L^{-1}$ to $ng\,L^{-1}$ for some elements, ICP-MS is applied in different fields, such as petrochemical, clinical and environmental areas [1,2]. However, some drawbacks, such as the occurrence of ionic suppression effects and isobaric interferences are commonly related to this technique. The later are observed mainly for elements with mass to charge ratio (m/z) between 20 and 80 and the accuracy for quantification of various analytes is negatively affected [1,3,4].

Since the emerging of the first commercial ICP-MS equipment, many instrumental or sample preparation strategies have been adopted to minimize, eliminate or circumvent spectral and non-spectral interferences [3,5–9]. Sometimes, these drawbacks can cause difficulties for routine applications of ICP-MS [3]. In this sense, in the 90s it was proposed a device called collision cell technology (CCT). The CCT was designed as a chamber located between the ion lenses region and the mass analyzer with temperature and pressure control. Its main task is to promote collisions, reactions and charge transfer processes in the ion stream induced by gases injected in [3,10,11]. Afterwards, other devices were proposed such as dynamic reaction cell (DRC) and, more recently the collision–reaction interface (CRI). The CRI is composed by a sampler and skimmer cones that supply collision and reaction gases directly into the plasma and ion beam before the ion lens region without requiring a pressurized chamber. In DRC device, a reaction cell is positioned between the ion lenses and the mass analyzer similarly to the CCT technology, but with reduced number of magnetic poles (octopole or hexapole in CCT device and quadrupole in DRC). In the case of CCT and DRC several studies dealt with their performance, fundaments and applications for complex matrices whereas for CRI device there are few papers that discuss about its use and mechanism involved with. This trend is due to the recent proposal of the CRI device (around 9 years later than CCT and DRC commercially available devices) [12]. Until now, it was not reported any study that compare the performance of the former strategies (CCT and DRC) and CRI technology. These instrumental strategies were responsible for the greater popularization and implementation of the ICP-MS with quadrupole mass filter (ICP-QMS) in the last decade [3,11,13,14]. The popularity achieved by ICP-QMS as a tool for routine analysis in quality control and processes monitoring was due to its greater versatility, robustness, and lower operational complexity when compared with high resolution and sector field inductively coupled plasma mass spectrometer (HR-ICP-MS). However, ICP-QMS is the arrangement most strongly affected by spectral and non-spectral interferences [15–17].

Spectral interferences can occur during the analytical signal acquisition by overlapping due to polyatomic species, double charge ions and isobaric interferences. As commented by Ferguson and co-workers, plenty of papers describe fundamental aspects of polyatomic production in different parts of ICP-MS, mainly at

---

* Corresponding author. Tel.: +55 16 3351 8088.
E-mail address: djan@terra.com.br (J.A. Nóbrega).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.09.009

plasma, interface and ion lenses extraction regions [18]. Polyatomic species can arise from the reagents employed in the sample preparation step, from the sample matrix or due to physicochemical characteristics of the plasma [4,18–21].

Non-spectral interferences can occur due to: (i) physico-chemical characteristics of the samples and their influences on nebulization and transport to the plasma; (ii) dissolved solids resulting from sample digestion; (iii) generation, modification and extraction of ions in the plasma; (iv) transference of ions to the mass analyzer and mainly by (v) space charge effects [1,3,4,6]. These interferences may either increase or decrease analytical signals and these effects can be more severe due to matrix complexity. Consequently, the application of external calibration and the accuracy of the results may become a difficult target [1,4]. Some analytical strategies as the standard additions method, isotope dilution, matrix matching and internal standardization can be used to improve reproducibility and circumvent random and systematic errors inherent to analytical measurements [13,22,23]. The matrix matching would be one of the most interesting strategies, but its practical applicability is restricted to samples with low matrix complexity and high homogeneity. These requirements reduce the applicability of this strategy in routine analysis [23]. The standard additions method is not applicable to solve problems of signal acquisition and introduces additional steps in the analytical sequence being more time consuming and creating problems related to contamination and waste generation [13,22]. Isotope dilution is other feasible strategy, but it is not applicable for monoisotopic elements such as As, Mn, and P. On the other hand, internal standardization is a strategy employed to offset the loss of a particular analyte signal due to effects of ion suppression and transport, being employed in multi-element determination in different ICP-MS arrangements for different purposes [8,15,22–26].

The choice of an element as internal standard is usually a compromise between the proximity of its mass with the analyte and the closeness between both first ionization energies (I.E.) [22,27]. The ideal internal standard is that whose intensity and changes due to different disturbances are directly related to the analyte in study, i.e. the signal intensity ratio between analyte/internal standard must remain constant for any change in sample composition and equipment performance [22,23,25]. On the other hand, there are few studies reporting analytical determinations employing CRI technology since the emerging of first commercial ICP-QMS-CRI in 2005/2006 [14,28,29]. Only one of these studies has shown the CRI performance for As and Se determination [14] and there are no investigations related to the combination of CRI with internal standardization for correcting interferences. Thus, the aim of this study was to evaluate the application of In, Rh and Sc as internal standards as an auxiliary tool for improving performance of an ICP-QMS-CRI. The collisional and reactive gases were He and H_2, respectively. Barium, Cd, Co, Cr, Cu, Li, Mn, Mo, Pb, Sb, V and Zn were determined in a certified reference material of trace elements in water (NIST 1643e) to evaluate the accuracy and precision of the proposed method. As complex samples for Cr and V determination, a mixed food diet and a synthetic vinegar reference sample, prepared by spiking a vinegar sample with the NIST 1643e Trace Elements in Water Standard Reference Material, were directly introduced into the ICP-MS.

2. Material and methods

2.1. Instrumentation

An inductively coupled plasma quadrupole mass spectrometer was used in all experiments (Varian 820-MS, Mulgrave, Australia, nowadays been produced by Bruker Corp., Billerica, MA, USA). This equipment has a collision–reaction interface (CRI) that allows gas introduction (either H_2 or He) through sampler and skimmer cones. For ion extraction and focalization, this equipment has a double off-axis setup in 90° after ion lenses. Table 1 shows the operating conditions for this ICP-QMS-CRI. An automatic sampler (Varian SPS3, Mulgrave, Australia) was used for sample introduction. The sample introduction system employed was a concentric nebulizer, connected to a standard quartz Scott spray chamber, operated at 3 °C to minimize the presence of water vapor in the gas stream.

Table 1
Operating conditions and parameters for ICP-QMS-CRI system.

Radio frequency – applied power	1400 W
Argon flow rate ($L\,min^{-1}$)	
Plasma	18.0
Auxiliary	1.80
Sheath	0.15
Nebulizer gas flow rate	0.95
Sampling depth	5.5 mm
Sampler cone	Nickel, 0.8 mm (ϕ)
CRI gas flow rate (H_2 or He) through the sampler cone	80; 120; 160; 200; 240; 280; 320; 360; 400; 440; 500; 800 $mL\,min^{-1}$
Skimmer cone	Nickel, 1.2 mm
CRI gas flow rate (H_2 or He) through the skimmer cone	4; 8; 12; 16; 20; 24; 28; 32; 36; 40; 50; 80 $mL\,min^{-1}$
Ionic lens voltage (V)	
1st extractor	−10
2nd extractor	−120
3rd extractor	−242
Corner lens	−210
Quadrupole	
Detector voltage	2900 V
High/low resolution	0.80 AMU/0.78 AMU
Dwell time	10 ms
Replicates/sample	5
Uptake delay	60 s
Stabilization delay	10 s

2.2. Reagents, analytical solutions and samples

All solutions were prepared using analytical grade reagents and ultra pure water (resistivity of 18.2 MΩ cm) obtained with a Milli-Q system (Millipore Corp., Billerica, MA, USA). Nitric and hydrochloric acids (Merck, Darmstadt, Germany) distilled in quartz sub-boiling still (Milestone, Sorisole, Italy) were used. Analytical grade sulfuric acid was also used (Merck). To avoid contamination, glassware and polypropylene flasks were washed with soap, soaked in 10% (v/v) HNO_3 solution overnight and rinsed thoroughly with deionized water prior to use. Reference and internal standards solutions, used for external calibration, were prepared by suitable dilution of stock solutions containing 1000 $mg\,L^{-1}$ of investigated elements: Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Pb, Sb, V and Zn (Tec-Lab, Hexis, São Paulo, SP, Brazil) in 0.014 $mol\,L^{-1}$ HNO_3. Indium, Rh and Sc were employed as internal standards (I.S.). Diluted solutions of sub-boiling HNO_3 and HCl were used for spectral interference studies.

Standard reference material of trace elements in water (NIST-1643e) were used for evaluating the method accuracy when the following conditions were employed: (i) CRI with I.S.; (ii) CRI without I.S.; (iii) mathematical equation correction with I.S. and (iv) mathematical equation correction without I.S. Helium and H_2, both 99.995% of purity (White Martins, Sertãozinho, SP, Brazil), were used as collision and reaction gases at several flow rates ($mL\,min^{-1}$) through the sampler and skimmer cones aiming elimination of interferences caused by polyatomic ions (see flow rate range in Table 1). Liquid argon (99.995% purity) was provided by the same supplier.

A vinegar sample was directly introduced into the equipment after a 10-fold dilution and addition of the studied internal standards in order to evaluate the CRI and the combined use of CRI with I.S. In order to verify the system performance with a

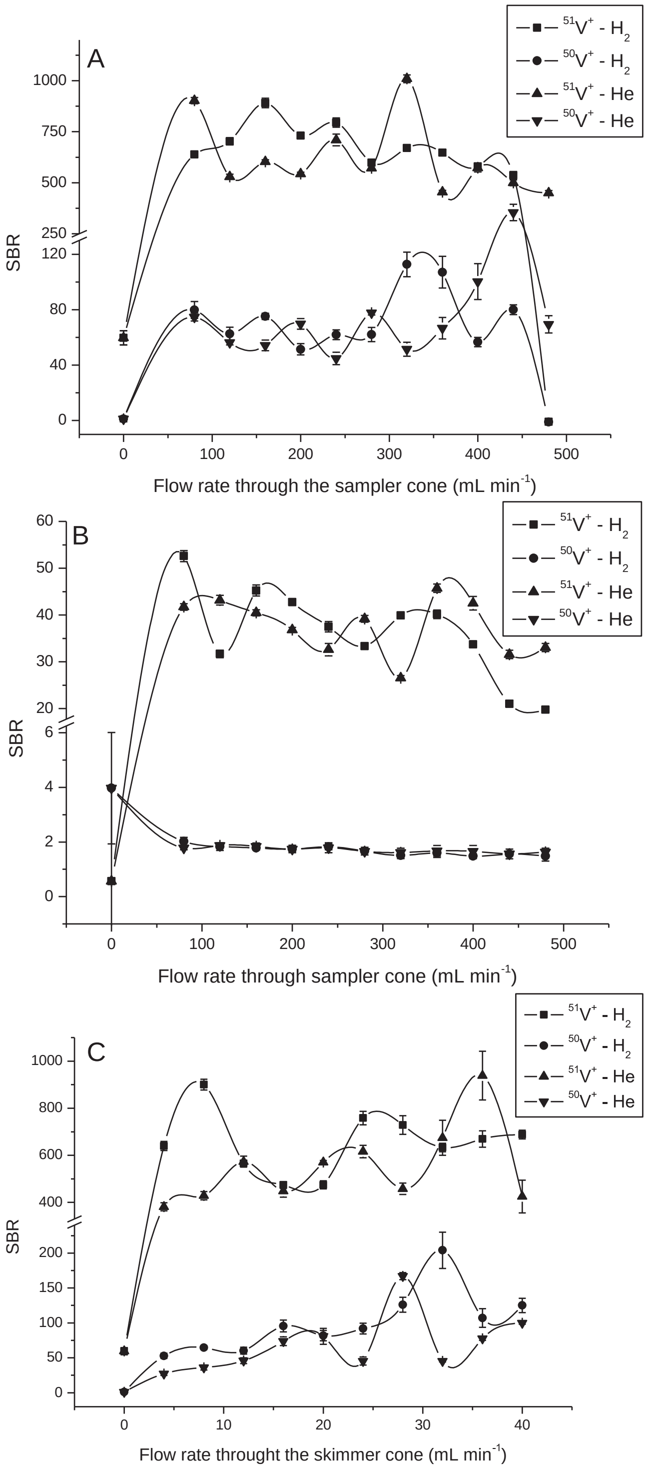

Fig. 1. (A) Evaluation of SBR for quantification of 50 ng mL^{-1} V in 1.0% (v/v) HNO_3 at different flow rates of H_2 and He through the sampler cone. (B) Evaluation of SBR for quantification of 50 ng mL^{-1} V in HCl (1.0%, v/v) at different flow rates of H_2 and He through the sampler cone. (C) Evaluation of SBR for quantification of 50 ng mL^{-1} V in HNO_3 (1.0%, v/v) at different flow rates of H_2 through the skimmer cone. (D) Evaluation of SBR for quantification of 50 ng mL^{-1} V in HCl (1.0%, v/v) at different flow rates of H_2 through the skimmer cone.

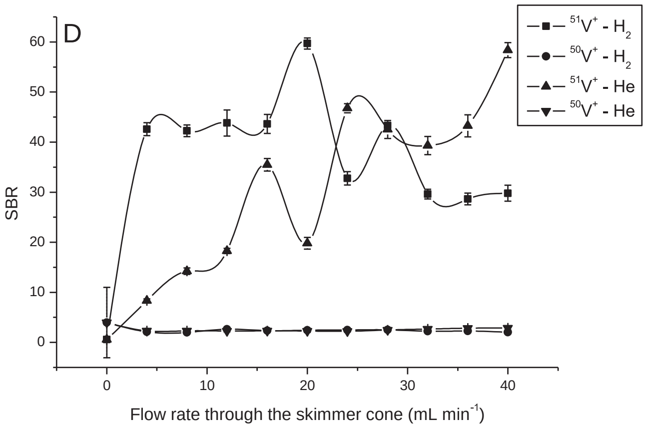

Fig. 1. *Continued.*

complex sample, a synthetic reference vinegar sample was prepared (as proposed by Liu [30]) by the addition of 1 mL of SRM NIST 1643e (trace elements in water) to 1 mL of vinegar sample and the final volume was made up to 10 mL. As vinegars contain around 4.0% (v/v) of acetic acid, with a 10-fold dilution, these samples can reach 1600 mg L^{-1} of dissolved carbon, just from this carbon-based compound. Solutions diluted 5-fold of High Purity Standards (Charleston, SC, USA) of trace element in mixed food diet (CRM-MFD) were also employed in order to check the performance of CRI with internal standardization.

2.3. Procedures

A solution composed of 5 μg L^{-1} of Ba, Be, Ce, In and Th in 1.0% (v/v) HNO_3 was used to check the equipment performance. Sensitivity in low, medium and high m/z was verified by monitoring the following species: ^{9}Be, ^{115}In and ^{232}Th, respectively. To evaluate double charge formation and to optimize the system considering oxide formation, the ratios between $^{138}Ba^{++}/^{138}Ba^{+}$ and $^{140}Ce^{16}O^{+}/^{140}Ce^{+}$ were monitored.

2.4. Interference studies

The spectra of background plasma for deionized water, HNO_3 and HCl solutions both 2.0% (v/v) were obtained. For this purpose, the ICP-QMS-CRI was operated with and without He or H_2 introduction through the interface. In this step, it was evaluated which ion signals would be reduced and/or eliminated and which new ions would be generated. For skimmer cone it was employed flow rates of 20, 50 and 80 mL min^{-1} whereas for sampler cone were 200, 500 and 800 mL min^{-1}.

2.5. Skimmer and sampler performance

Different flow rates of He and H_2 were introduced through the skimmer (from 4 to 80 mL min^{-1}) and through the sampler (from 80 to 800 mL min^{-1}) cones in order to evaluate the CRI performance to overcome polyatomic ions formation. Aqueous solutions containing 50 ng mL^{-1} of V in different acid media (HCl, HNO_3 and H_2SO_4, all them 1.0%, v/v) were employed in these studies. This element was selected in this systematic study because its determination is difficult due to polyatomic species commonly formed in ICP-MS analysis such as: $^{35}Cl^{16}O^{+}$, $^{38}Ar^{13}C^{+}$ on $^{51}V^{+}$; $^{35}Cl^{16}O^{1}H^{+}$, $^{35}Cl^{17}O^{+}$, $^{40}Ar^{12}C^{+}$ on $^{52}Cr^{+}$; and $^{37}Cl^{16}O^{+}$, $^{40}Ar^{13}C^{+}$, $^{40}Ar^{12}C^{1}H^{+}$ on $^{53}Cr^{+}$ [31,32]. Results were reported as function of signal-to-background ratio (SBR) and background equivalent concentration (BEC) for each condition. In this case we aimed to attain compromise conditions that allow improvement in SBR (higher values) and BEC (lower values).

Table 2
Collision reaction interface (CRI) evaluation employing different flow rates of H_2 or He through sampler or skimmer cones by monitoring the minimization/formation of polyatomic interferences in the ratios m/z 51, 52 and 53 in deionized water and acid solutions.

	Gas	m/z 51 (cps)			m/z 52 (cps)			m/z 53 (cps)		
		H_2O	HCl	HNO_3	H_2O	HCl	HNO_3	H_2O	HCl	HNO_3
Without – CRI	–	1.7×10^5	1.5×10^6	1.8×10^5	3.6×10^4	5.3×10^4	4.1×10^4	4.2×10^3	4.3×10^5	6.3×10^3
CRI – Skimmer (mL min^{-1})										
20	H_2	3.1×10^3	6.6×10^5	3.3×10^3	6.2×10^3	2.2×10^4	7.4×10^3	1.1×10^3	2.6×10^5	1.5×10^3
	He	1.8×10^5	4.2×10^5	1.9×10^5	8.1×10^3	1.9×10^4	9.3×10^3	4.6×10^4	1.5×10^5	7.4×10^4
50	H_2	7.1×10^2	1.7×10^5	7.4×10^2	1.4×10^2	4.4×10^3	1.9×10^2	0	5.2×10^4	0
	He	2.2×10^3	1.1×10^5	2.2×10^3	1.9×10^3	3.3×10^3	2.0×10^3	3.5×10^3	3.8×10^4	5.6×10^2
80	H_2	0	8.9×10^4	0	0	1.9×10^2	0	0	3.3×10^3	0
	He	1.5×10^2	1.6×10^4	1.9×10^2	0	1.7×10^3	0	0	6.3×10^3	0
CRI – Sampler (mL min^{-1})										
200	H_2	1.5×10^4	4.1×10^6	1.5×10^4	1.2×10^4	8.3×10^4	1.5×10^4	5.2×10^3	1.5×10^6	5.6×10^3
	He	1.2×10^4	1.7×10^6	1.2×10^4	1.6×10^4	4.8×10^4	1.9×10^4	5.6×10^3	5.6×10^5	6.3×10^3
500	H_2	1.9×10^4	6.0×10^6	1.9×10^4	4.6×10^3	1.1×10^5	5.2×10^3	6.2×10^3	2.1×10^6	7.2×10^3
	He	1.1×10^4	1.4×10^6	1.1×10^4	1.1×10^4	4.3×10^4	1.2×10^4	3.0×10^3	4.2×10^5	3.1×10^3
800	H_2	7.6×10^3	3.3×10^6	7.8×10^3	1.9×10^3	9.9×10^4	2.0×10^3	2.7×10^3	1.1×10^6	2.8×10^3
	He	1.1×10^4	1.3×10^6	1.1×10^4	1.2×10^4	4.5×10^4	1.4×10^4	2.9×10^3	4.6×10^5	3.3×10^3

3. Results and discussion

3.1. Relationship between CRI and polyatomic destruction/formation

Aqueous and acid solutions are well known as one of main sources for polyatomic formation in different parts of the ICP-MS system [18]. Acid solutions were object of study because they are generally employed in various types of sample preparation. Table 2 presents the effects of different He or H_2 flow rates through the skimmer and sampler cones on specific mass/charge ratios.

It could be observed significant interference signal reduction (cps) as the flow rate of the gas injected through the skimmer cone increased. This effect was more pronounced when H_2 was employed instead of He. Analyte ion losses were reported by Koppenaal et al. [11] in a paper about the performance of ICP-MS equipped with collision cell technology (CCT), however improvements in SBR and BEC values were obtained for different analytes. According to these authors the acceptable signal loss should be proportional to the SBR increase in order to compensate this apparent loss of sensitivity.

However, it could be verified in previous studies the increment of SBR values and improvements for BEC values for some elements that suffer isobaric interference problems in the 40–80 m/z range when an ICP-QMS-CRI was employed for analytical determinations [14,28,29]. Fig. 1A–D presents the SBR values for V solutions in HNO_3 and HCl media employing different gas flow rates through the CRI. It was needed to introduce He or H_2 at flow rates 10-fold higher than those used for the skimmer cone for evaluating the performance of the sampler cone. A higher CRI gas flow rate into the plasma could be restrictive because it can adversely affect the interface region which is kept under vacuum and it can disturb the plasma stability [1]. Even so, there were no reductions in the analyte signal intensities neither polyatomic minimization by using He and H_2 flow rates up to 1 L min^{-1} as reported by Pereira et al. [14] for As and Se determinations. The data presented in Table 2 indicate the efficiency of the skimmer on the minimization of polyatomic ions effects in different media when compared with the sampler cone. This behavior could be confirmed with BEC values improvement for Cr and V measurements when skimmer cone was used instead of sampler cone. Similar performance was achieved by Pereira et al. [14] for As and Se measurements. A detailed discussion of these data will be presented in the next section.

3.2. Skimmer and sampler performance

The performance of the CRI was evaluated by determining SBR when either the sampler (Fig. 1A and B) or skimmer cones (Fig. 1C and D) were used. For this purpose, aqueous solutions containing 50 ng mL^{-1} of V in HNO_3 and HCl, both 1.0% (v/v), were used. Background equivalent concentrations (BEC) were also acquired for CRI performance evaluation (see Table 3). For these same experiments, BEC values for V were also calculated in three different media (HCl, HNO_3 and H_2SO_4, all 1.0%, v/v) by monitoring of $^{50}V^+$ and $^{51}V^+$ using different gas flow rates through the CRI cones (Table 3).

Table 3
Evaluation of CRI effects on BEC values (ng mL^{-1}) for different acid solutions containing 50 ng mL^{-1} of V.

	Gas	$^{50}V^+$ (ng mL^{-1})			$^{51}V^+$ (ng mL^{-1})		
		HNO_3	HCl	H_2SO_4	HNO_3	HCl	H_2SO_4
Without – CRI	–	43.0	12.6	115.2	0.838	88.3	16.8
CRI – Skimmer (mL min^{-1})							
10	H_2	0.773	25.2	167.8	0.056	1.18	1.48
	He	1.38	21.6	175.1	0.117	3.52	7.68
20	H_2	0.611	20.4	122.6	0.105	0.838	0.937
	He	0.619	21.9	129.1	0.088	2.52	3.43
40	H_2	0.400	24.7	152.4	0.073	1.68	2.03
	He	0.500	17.5	96.9	0.118	0.857	1.20
CRI – Sampler (mL min^{-1})							
100	H_2	0.626	24.8	149.2	0.078	0.951	0.885
	He	0.670	28.0	138.1	0.055	1.20	1.07
200	H_2	0.972	28.7	149.6	0.068	1.17	0.983
	He	0.717	28.7	173.5	0.092	1.36	1.19
400	H_2	0.883	33.8	126.8	0.086	1.48	1.18
	He	0.499	30.2	130.4	0.087	1.18	1.19

Table 4
Recoveries of investigated elements in water certified reference material (CRM – NIST), in percentage values (%), by inductively coupled plasma mass spectrometry (ICP-QMS-CRI) in different conditions ($n = 3$).

	Without I.S.		Sc		Rh		In	
	Rec.	RSD	Rec.	RSD	Rec.	RSD	Rec.	RSD
Employing correction equation (CE) and internal standard (I.S.)								
^{7}Li	252.2	58.3	113.1	6.2	235.2	14.2	250.7	26.1
^{51}V	232.0	35.2	113.5	7.0	220.3	8.5	224.5	2.7
^{75}As	180.9	36.2	110.9	3.4	163.1	5.2	185.6	10.9
^{121}Sb	91.2	7.0	45.2	8.2	91.6	13.0	77.7	8.8
^{207}Pb	97.4	7.3	179.4	70.8	182.5	53.8	168.4	39.4
Employing internal standard (I.S.) and CRI – skimmer H_2								
^{7}Li	224.8	13.0	93.4	3.3	160.0	8.3	168.3	7.9
^{50}V	164.9	12.9	61.2	10.6	140.1	11.7	117.7	8.8
^{51}V	228.8	4.6	101.2	7.8	180.4	1.2	190.6	4.8
^{50}Cr	348.2	23.7	100.6	12.3	2485.5	217.3	265.2	16.3
^{53}Cr	331.2	43.2	96.4	6.9	300.0	43.7	27.1	4.4
^{55}Mn	226.9	6.5	94.3	8.0	160.0	1.4	168.1	5.5
^{59}Co	212.8	5.4	96.0	4.7	151.7	5.9	177.0	5.8
^{63}Cu	187.4	9.7	84.0	2.4	100.1	7.5	152.0	6.6
^{66}Zn	190.6	22.6	97.4	4.4	202.5	27.7	7.7	0.9
^{68}Zn	239.1	18.2	93.8	0.5	200.0	17.8	216.1	19.1
^{75}As	176.4	5.9	97.4	6.1	135.0	1.8	109.2	4.1
^{98}Mo	148.3	4.6	59.5	3.5	116.7	2.6	111.5	3.0
^{95}Mo	154.3	2.5	62.5	4.7	110.6	1.3	129.9	2.9
^{114}Cd	113.5	3.0	43.6	5.1	85.1	4.1	90.7	2.5
^{138}Ba	90.4	0.9	32.7	2.8	64.1	0.8	68.8	1.1
Employing internal standard (I.S.) and CRI – Skimmer He								
^{7}Li	222.2	31.7	93.0	2.8	182.2	9.4	207.6	9.7
^{51}V	207.2	24.1	101.2	3.1	183.2	4.3	194.2	3.7
^{55}Mn	220.2	27.2	101.5	2.3	170.4	5.5	187.0	5.0
^{59}Co	220.8	18.6	106.1	6.3	190.0	2.5	200.7	3.2
^{68}Zn	163.3	42.4	97.2	12.9	207.3	37.4	212.8	36.2
^{121}Sb	102.0	9.0	47.7	4.5	86.8	4.9	91.0	5.5

By evaluating the SBR distribution for V isotopes it could be observed that the gas introduction through the skimmer cone was more efficient to reduce the interference generated in the plasma (Fig. 1C and D) when compared to the sampler cone. Another advantage of gases introduction through the skimmer cone refers to the lower flow rates of gas injected to destroy polyatomic ions when compared with the gas flow rates introduced through the sampler cone. In addition, previous data about the evaluation of the sampler performance in different media (acid and organic solutions) have shown that there was an increase of the background spectra complexity in the m/z range from 40 to 80. Thus, the skimmer cone was chosen as the gateway for destroying polyatomic ions and carrying out in the analysis of certified water sample and evaluate its performance when combined with the use of internal standard.

Background EC values for $^{51}V^+$ (99.76% natural abundance) isotope were better than those observed for $^{50}V^+$ (0.24% natural abundance) in different media when using the CRI (Table 3). As expected $^{51}V^+$ suffers more severe polyatomic interferences caused by signal overlap of $^{35}Cl^{16}O^+$ and it was evident the need of the CRI in order to minimize polyatomic interferences and to improve the BEC (Table 3) and SBR values in HNO_3 solution (Fig. 1C) or in HCl solution (Fig. 1D). It can be mentioned that SBR and BEC values were improved for most isotopes when the skimmer was employed. These findings are consistent with the data obtained by Bednar [33]. In this study it was demonstrated that chloride concentration above 840 mg L^{-1} is quite enough to cause significant overlap on the ^{53}Cr signal due to the $^{37}Cl^{16}O^+$ formation. This behavior was confirmed by the discrepancies observed between the results provided by ^{52}Cr and ^{53}Cr isotopes. Then, Bednar [33] concluded that this chloride concentration could affect V determination as well, being necessary the use of a polyatomic strategy correction. In our study the combined employment of internal standardization with CRI devices was proposed.

Best SBR and BEC values were observed at flow rates up to 20 mL H_2 min^{-1} and around 20 and 40 mL He min^{-1} when using the skimmer cone. Consequently, studies about internal standards were carried out by keeping a gas flow rate of 20 mL min^{-1} through the skimmer cone as a compromise condition between SBR (higher values) and BEC (lower values) improvements.

3.3. *Effect of internal standardization*

The efficiency of internal standardization was evaluated when employing it with: (i) He flow rate (20 mL min^{-1}) through the skimmer, (ii) H_2 flow rate (20 mL min^{-1}) through the skimmer or (iii) by combining with mathematical correction equations. Table 4 presents recovery values (%) for investigated analytes in the standard reference material of trace elements in water (NIST-1643e).

It was possible to demonstrate the accuracy for the determination of 32 elements in 4 conditions (CRI with or without I.S. and mathematical equation correction with or without I.S.). Six isotopes (^{7}Li, ^{51}V, ^{55}Mn, ^{59}Co, ^{68}Zn and ^{121}Sb) were accurately determined when inserting He through the skimmer cone, whereas with H_2 it was possible to determine 15 isotopes (^{7}Li, ^{50}V, ^{51}V, ^{50}Cr, ^{53}Cr, ^{55}Mn, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{68}Zn, ^{75}As, ^{98}Mo, ^{95}Mo, ^{114}Cd and ^{138}Ba). When using only mathematical correction equation, elements with the highest mass values, such as ^{121}Sb, ^{138}Ba and ^{207}Pb, could be determined. Internal standardization combined with CRI minimized polyatomic interference effects, especially when using H_2 as reaction gas that allowed best recoveries, mainly for those elements between m/z 30 and 80.

Obviously, neither the use of mathematical correction equations nor internal standardization could overcome the overlap caused by polyatomic interferences for most elements. It was possible to demonstrate the accuracy for 32 isotopes quantification in the CRM – NIST 1643e. Nearly 87.5% of all determined isotopes (28 of 32) required the combination of I.S. and CRI in order to improve the accuracy. This fact demonstrates the efficiency of internal standardization for most elements and the need for using the CRI. Scandium (^{45}Sc) improved the recovery for 18 of 28 quantified isotopes,

Table 5
Evaluation of combined use of collision-reaction interface with internal standardization for Cr and V determination.

Samples	Vanadium		Chromium	
	^{51}V	^{50}Cr	^{52}Cr	^{53}Cr
Without CRI ($x \pm \sigma$ μg g^{-1})				
Vinegar	66 ± 5	nd	211 ± 4	21.8 ± 0.6
MFD[a]	7 ± 2	nd	26 ± 5	8 ± 5
NIST[b]	75 ± 8	26.9 ± 0.6	64 ± 1	35 ± 1
NIST + vinegar	174.2 ± 0.7	nd	332 ± 10	105 ± 4
Without CRI + Sc ($x \pm \sigma$ μg g^{-1})				
Vinegar	15 ± 7	nd	26 ± 3	13 ± 4
MFD	55 ± 3	22.3 ± 0.4	55 ± 2	37 ± 2
NIST	98 ± 2	nd	204 ± 1	86 ± 2
NIST + vinegar	67 ± 4	nd	192 ± 4	35.9 ± 0.3
Without CRI + Y ($x \pm \sigma$ μg g^{-1})				
Vinegar	60 ± 5	nd	170 ± 8	25.1 ± 0.9
MFD	14 ± 6	nd	24 ± 3	9 ± 3
NIST	55 ± 6	nd	53.9 ± 0.5	29.0 ± 0.6
NIST + vinegar	103 ± 6	nd	216 ± 5	72.6 ± 0.4
Without CRI + Rh ($x \pm \sigma$ μg g^{-1})				
Vinegar	62 ± 5	nd	173 ± 6	32.1 ± 0.8
MFD	11 ± 1	nd	24 ± 3	11 ± 4
NIST	57 ± 5	37.7 ± 0.7	54.8 ± 0.7	37 ± 1
NIST + vinegar	122.6 ± 0.5	nd	226 ± 5	92 ± 3
Isotopes	Vanadium		Chromium	
	^{51}V	^{50}Cr	^{52}Cr	^{53}Cr
Skimmer – He (20.0 mL min^{-1}) ($x \pm \sigma$ μg g^{-1})				
Vinegar	28 ± 3	113 ± 5	83 ± 5	53 ± 8
MFD	nd	nd	2.9 ± 0.7	2.6 ± 0.9
NIST	56 ± 2	25 ± 3	21.7 ± 0.5	24 ± 4
NIST + vinegar (Rec, %)[c]	97 ± 6	156 ± 18	99 ± 4 (96%)	67 ± 11 (91%)
Skimmer – He (20.0 mL min^{-1}) + Sc ($x \pm \sigma$ μg g^{-1})				
Vinegar	29 ± 1	9.46 ± 0.02	39.8 ± 0.9	14 ± 2
MFD	3.81 ± 0.02	2 ± 1	3.0 ± 0.2	2.0 ± 0.2
NIST	32.8 ± 0.8	23 ± 2	25.6 ± 0.6	27 ± 3
NIST + vinegar (Rec, %)	61.3 ± 0.4 (92%)	87 ± 8	67 ± 1	49 ± 5
Skimmer – He (20.0 mL min^{-1}) + Y ($x \pm \sigma$ μg g^{-1})				
Vinegar	13 ± 2	12 ± 6	30 ± 3	7 ± 2
MFD	1.67 ± 0.02	3 ± 1	2.7 ± 0.3	1.7 ± 0.7
NIST	37 ± 3	24 ± 2	20.1 ± 0.9	22 ± 2
NIST + vinegar (Rec, %)	66 ± 1 (130%)	102 ± 12	67 ± 14 (133%)	54 ± 8 (197%)
Skimmer – He (20.0 mL min^{-1}) + Rh ($x \pm \sigma$ μg g^{-1})				
Vinegar	29 ± 2	20 ± 7	45 ± 4	10 ± 1
MFD	4.81 ± 0.01	4.7 ± 0.6	7.5 ± 0.5	4.1 ± 0.4
NIST	33 ± 1	34 ± 2	25.9 ± 0.4	24 ± 2
NIST + vinegar (Rec, %)	74 ± 2 (111%)	141 ± 12	74 ± 11	53 ± 5
Samples	Vanadium		Chromium	
	^{51}V	^{50}Cr	^{52}Cr	^{53}Cr
Skimmer – H_2 (20.0 mL min^{-1}) ($x \pm \sigma$ μg g^{-1})				
Vinegar	31 ± 1	13 ± 4	87 ± 3	17 ± 4
MFD	3.0 ± 0.3	2.6 ± 0.4	10 ± 4	5.4 ± 0.6
NIST	70 ± 3	43 ± 2	43 ± 2	38 ± 3
NIST + vinegar	127.0 ± 0.3	142 ± 8	172 ± 7	83 ± 3
Skimmer – H_2 (20.0 mL min^{-1}) + Sc ($x \pm \sigma$ μg g^{-1})				
Vinegar	35 ± 1	30 ± 4	50.9 ± 0.9	53 ± 6
MFD	7.6 ± 0.2	2.02 ± 0.09	2.6 ± 0.4	1.9 ± 0.1
NIST	34.5 ± 0.7	25.1 ± 0.2	18.6 ± 0.9	16 ± 1
NIST + vinegar (Rec, %)	68 ± 2 (93%)	70 ± 2 (139%)	61 ± 5 (86%)	63 ± 1 (86%)
Skimmer – H_2 (20.0 mL min^{-1}) + Y ($x \pm \sigma$ μg g^{-1})				
Vinegar	27 ± 1	20 ± 4	65 ± 2	18 ± 3
MFD	4.7 ± 0.2	5.1 ± 0.4	10 ± 2	5.7 ± 0.4
NIST	45 ± 2	46 ± 1	31.3 ± 0.7	29 ± 1
NIST + vinegar (Rec, %)	81 ± 5	144 ± 2	108 ± 8	63 ± 2
Skimmer – H_2 (20.0 mL min^{-1}) + Rh ($x \pm \sigma$ μg g^{-1})				
Vinegar	25.7 ± 0.6	9 ± 2	72 ± 2	21 ± 2
MFD	2.54 ± 0.07	2.0 ± 0.2	2.3 ± 0.5	1.41 ± 0.08
NIST	35.0 ± 0.5	20.9 ± 0.2	17.8 ± 0.5	21 ± 1
NIST + vinegar (Rec, %)	56.0 ± 0.4 (88%)	70 ± 5 (238%)	97.3 ± 0.7 (105%)	64 ± 2 (154%)

nd, not detected (concentration below the LOD).

[a] MFD (mixed food diet) – [Cr] = 2 μg L^{-1} (reference value).

[b] NIST 1643e (Trace elements in water) – certified values: [Cr] = 20.40 μg L^{-1}; [V] = 37.86 μg L^{-1}.

[c] Percentage of recovery (calculated for the synthetic vinegar samples when the NIST 1643e recoveries were in adequate levels i.e. around 100%).

probably due to the proximity of its mass and/or first ionization energy values with the investigated elements [22,27,34]. The exceptions were: $^{50}V^+$ which had best results with $^{115}In^+$ (117.7%) and $^{63}Cu^+$ with $^{103}Rh^+$ (100.1%) as internal standards. These behaviors were not clearly understood yet.

More complex matrices that could provide severe polyatomic interferences for Cr and V determinations were applied as challenge samples for the CRI performance evaluation. Vinegar sample, vinegar spiked with NIST 1643e and mixed food diet were used for this purpose. In Table 5 it can be seen data obtained in different conditions considering the element used as internal standard and CRI condition. Correction equation was used for those conditions where CRI-device was not employed.

In relation to these data we can observe that the combined use of internal standardization and CRI also improved the accuracy for these complex matrices.

For V determination in the more complex matrix (synthetic vinegar sample), good recoveries were obtained using both H_2 and He through the CRI, especially when Sc and Rh were used as I.S. (see Table 5). The best four conditions attained with these combinations agreed well in terms of vanadium concentrations in the vinegar sample: 29 ± 1; 29 ± 2; 35 ± 1 and $25 \pm 0.6\,\mu g\,L^{-1}$ (see Table 5) with recoveries of 92%; 111%; 93% and 88%, respectively.

For Cr determination in the synthetic reference vinegar sample, the best conditions were attained using just He through the CRI or the combined use of Sc or Rh as I.S. with H_2 through the CRI. The best recoveries were: 96%; 91%; 86%; 86% and 105% for the combination of these conditions (see Table 5). For the mixed food diet, these conditions also led to adequate recoveries.

It is known that ICP-MS is strongly dependent on calibration strategies. In most cases either the standard additions method or the calibration with matrix-matched solutions is adopted. When comparing with other calibration strategies for obtaining more accurate and precise values in routine analysis, matrix matching calibration is the most desirable, but its application may be harder for complex samples. In this sense it was observed the possibility to use both CRI and internal standard to quantify many isotopes using non-matrix matched aqueous solutions for calibration. For these studies aqueous calibration solutions prepared in diluted acid medium were used. This calibration combined with internal standardization and CRI for minimization of polyatomic interference is a fast and easy alternative procedure. The proposed calibration method may attenuate the ICP-MS dependence for calibration with matrix matching.

4. Conclusions

Internal standardization proved to be a good analytical auxiliary tool for analysis by ICP-QMS-CRI. The combined effect of internal standardization with CRI brings improvements in accuracy and precision when either matrix matching or the standard addition methods are less practicable. This association led to: (i) determination of elements in the m/z between 50 and 75 with good accuracy, (ii) employment of less abundant isotopes for analytical determination, i.e. ^{50}V (0.24%), ^{50}Cr (4.35%), ^{53}Cr (9.51%), ^{66}Zn (27.81%) and ^{68}Zn (18.57%), and improvement in the accuracy for determination of monoisotopic elements such as As, Co, and Mn.

The introduction of H_2 through the skimmer cone was the best alternative to overcome polyatomic ions formation, with the resulting gains in BEC and LOD values for several studied elements. Improvements of 5 to 10-fold in LOD and BEC values were observed when CRI with I.S. were employed. The BEC values for ^{75}As, ^{53}Cr, ^{51}V and ^{114}Cd were 1.62, 6.13, 0.47 and 0.053 ng mL^{-1}, respectively without I.S. and CRI use, whereas BEC values of 0.012, 1.08, 0.051 and 0.008 ng mL^{-1} were achieved by the proposed method combining both strategies.

Acknowledgements

The authors are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Grants: 2006/59083-9 and 2008/08260-3), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Grant 141737/2009-3), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for research funds and grants.

References

[1] A. Montaser, Inductively Coupled Plasma Mass Spectrometry, 1st ed., Wiley-VCH, New York, 1998, 964p.
[2] A.A. Ammann, J. Mass Spectrom. 42 (2007) 419–427.
[3] S.D. Tanner, V.I. Baranov, D.R. Bandura, Spectrochim. Acta Part B 57 (2002) 1361–1452.
[4] R. Thomas, Practical Guide to ICP-MS: A Tutorial for Beginners, 2nd ed., CRC Press, Boca Raton, 2008, 347p.
[5] D. Pozebon, V.L. Dressler, A.J. Curtius, J. Anal. At. Spectrosc. 13 (1998) 1101–1105.
[6] N. Praphairaksit, R.S. Houk, Anal. Chem. 72 (2000) 2356–2361.
[7] Z. Du, R.S. Houk, J. Anal. At. Spectrosc. 15 (2000) 383–388.
[8] E. Engström, A. Stenberg, D.C. Baxter, D. Malinovsky, I. Mäkinen, S. Pönni, I. Rodushkin, J. Anal. At. Spectrosc. 19 (2004) 858–866.
[9] J.A. Nóbrega, M.C. Santos, R.A. Sousa, S. Cadore, R.M. Barnes, M. Tatro, Spectrochim. Acta Part B 61 (2006) 465–495.
[10] R.K. Marcus, J. Anal. At. Spectrosc. 19 (2004) 591–599.
[11] D.W. Koppenaal, G.C. Eiden, C.J. Barinaga, J. Anal. At. Spectrosc. 19 (2004) 561–570.
[12] S. D'Illio, N. Violante, C. Majorani, F. Petrucci, Anal. Chim. Acta 698 (2011) 6–13.
[13] P. Masson, T. Dalix, S. Bussière, Commun. Soil Sci. Plant Anal. 41 (2010) 231–243.
[14] C.D. Pereira, E.E. Garcia, F.V. Silva, A.R.A. Nogueira, J.A. Nóbrega, J. Anal. At. Spectrosc. 25 (2010) 1763–1768.
[15] I. Rodushkin, T. Ruth, D. Klockare, J. Anal. At. Spectrosc. 13 (1998) 159–166.
[16] M.P. Field, R.M. Sherrell, J. Anal. At. Spectrosc. 18 (2003) 254–259.
[17] United States Geological Survey (USGS). Available at: http://minerals.cr.usgs.gov/icpms/intro.html (accessed January 2011).
[18] J.W. Ferguson, T.J. Dudley, K.C. Sears, S.M. McIntyre, M.S. Gordon, R.S. Houk, Spectrochim. Acta Part B 64 (2009) 690–696.
[19] R.S. Houk, N. Praphairaksit, Spectrochim. Acta Part B 56 (2001) 1069–1096.
[20] S.A. Lehn, K.A. Warner, M. Huang, G.M. Hieftje, Spectrochim. Acta Part B 57 (2002) 1739–1751.
[21] V. Colombo, E. Ghedini, P. Sanibondi, Prog. Nucl. Energy 50 (2008) 921–933.
[22] J.J. Thompson, R.S. Houk, Appl. Spectrosc. 41 (1987) 801–806.
[23] H.J. Finley-Jones, J.A. Holcombe, J. Anal. At. Spectrosc. 24 (2009) 837–841.
[24] F.A.R. Martino, M.L.F. Sánchez, A.S. Medel, J. Anal. At. Spectrosc. 15 (2000) 163–168.
[25] H.J. Finley-Jones, J.L. Molloy, J.A. Holcombe, J. Anal. At. Spectrosc. 23 (2008) 1214–1222.
[26] Y. Ogawa, S. Yamasaki, N. Tsuchiya, Anal. Sci. 26 (2010) 867–872.
[27] F. Vanhaecke, H. Vanhoe, R. Dams, Talanta 39 (1992) 737–742.
[28] P. Bélanger, P. Dumas, At. Spectrosc. 31 (2010) 175–181.
[29] L. Xing, D. Beauchemin, J. Anal. At. Spectrosc. 25 (2010) 1046–1055.
[30] Q. Liu, Spectrochim. Acta Part B 65 (2010) 587–590.
[31] T.W. May, R.H. Wiedmeyer, At. Spectrosc. 19 (1998) 150–155.
[32] V. Chrastný, M. Komárek, M. Mihaljevič, J. Štíchová, Anal. Bioanal. Chem. 385 (2006) 962–970.
[33] A.J. Bednar, Talanta 78 (2009) 453–457.
[34] Ion Chemistry Laboratory (ICL). Centre for Research in Mass Spectrometry. Available at: http://www.chem.yorku.ca/profs/bohme/research/index.html (accessed January 2011).