

Multivariate quantification of spectroscopic interferences caused by sodium, calcium, chlorine and sulfur in inductively coupled plasma mass spectrometry

Marco Grotti,^{*a} Cinzia Gnecco^a and Fabio Bonfiglioli^b

^aDipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, I-16136 Genova, Italy

^bAzienda Mediterranea Gas e Acqua, Genova, Italy

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A new method for quantification of spectral interferences in ICP-MS, based on empirical modelling and experimental design, is presented. The relationship between interfering effect and matrix composition is deduced by performing a multiple linear regression analysis and taking into account linear and quadratic effects of matrix elements and all the potential interactions between them. In order to separate spectroscopic from non-spectroscopic interferences, analyte isotope ratio measurements were performed, except for monoisotopic elements for which the signal ratio (ratio between signal measured with and without matrix) was considered and internal standardization applied. Spectral interferences caused by sodium, calcium, chlorine and sulfur species, at the m/z of interest for the determination of several isotopes (^{51}V , ^{52}Cr , ^{53}Cr , ^{58}Ni , ^{60}Ni , ^{62}Ni , ^{59}Co , ^{64}Zn , ^{66}Zn , ^{68}Zn , ^{63}Cu , ^{65}Cu , ^{75}As , ^{111}Cd , ^{114}Cd , ^{207}Pb and ^{208}Pb) were modelled and are discussed.

Introduction

The accuracy of analytical results obtained with low-resolution inductively coupled plasma mass spectrometry (ICP-MS) is often limited by spectral and non-spectral interferences caused by matrix elements, such as Na, Ca, Cl and S, which are present in several types of environmental and biological samples, at high concentration levels. Many papers have appeared in literature dealing with the problem of interferences in ICP-MS, either exclusively or in conjunction with a particular application.^{1,2} In order to separate mathematically the information corresponding to the analyte from that of the overlapping species, Vaughan and Templeton³ studied the spectral interferences due to calcium species in the mass region of interest for nickel determination. They found that ^{61}Ni is the isotope most severely affected by the presence of calcium, because of the formation of $^{44}\text{Ca}^{16}\text{O}^1\text{H}$; also at m/z 58, 60 and 62, the signal is increased by the overlap of calcium oxide and hydroxide species, such as $^{42}\text{Ca}^{16}\text{O}$, $^{43}\text{Ca}^{16}\text{O}^1\text{H}$, $^{44}\text{Ca}^{16}\text{O}$ and $^{46}\text{Ca}^{16}\text{O}$. Moreover, they stated that, when considering the determination of Ni in urine, the situation is worsened by two further interferences at m/z 58 and 62, due to the formation of $^{23}\text{Na}^{35}\text{Cl}$ and $^{23}\text{Na}^{39}\text{K}$, respectively.

Lu and co-workers⁴ studied the effects of NaCl and $\text{Mg}(\text{NO}_3)_2$ on the $^{63}\text{Cu}/^{65}\text{Cu}$, $^{114}\text{Cd}/^{111}\text{Cd}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios. They found that Na and Mg matrix elements do not affect the isotopes of Cd and Pb, whereas they drastically altered the $^{63}\text{Cu}/^{65}\text{Cu}$ ratio, because of the interferences from $^{40}\text{Ar}^{23}\text{Na}$ at m/z 63 and $^{41}\text{Ar}^{24}\text{Mg}$ at m/z 65. Flow injection analysis reduced the amount of the interfering species only partly, so that a separation of Na and Mg before the determination of Cu in biological and environmental samples was necessary.

One of the most studied matrix element in ICP-MS is chlorine, because of its presence in several kind of samples and the serious spectral interferences due to chlorine-containing species. The most common example is the inter-

ference of $^{40}\text{Ar}^{35}\text{Cl}$ on monoisotopic ^{75}As . Gregoire and de Lourdes Ballinas⁵ studied the production of $^{40}\text{Ar}^{35}\text{Cl}$ in argon plasma by monitoring $^{40}\text{Ar}^{37}\text{Cl}$ and using both electrothermal vaporization (ETV) and solution nebulization for sample introduction. They found that for solution nebulization sample introduction, the production of ArCl is substantial (5500 counts s^{-1}) at an NaCl concentration of $100 \mu\text{g ml}^{-1}$. ETV sample introduction greatly reduced the amount of $^{40}\text{Ar}^{35}\text{Cl}$, allowing direct determination of As in waters containing up to $10\,000 \mu\text{g ml}^{-1}$ of Na, while for the analysis of highly saline waters, chloride must be eliminated from the sample before the high temperature vaporization step. Severe spectral interferences from chloride species were also reported by Krushevskaya and co-workers⁶ for the determination of ^{53}Cr and ^{51}V in biological materials, due to the formation of $^{37}\text{Cl}^{16}\text{O}$ and $^{35}\text{Cl}^{16}\text{O}$, respectively.

Sulfur is another matrix element causing severe interferences in ICP-MS. The most interfering species are SO_2 , S_2 and SO_2H , affecting the m/z region from 64 to 68.⁷

Bjorn and co-workers⁸ remarked on the importance of the accurate quantification of spectroscopic interferences and the risk of underestimating them if the analyte signal suppression caused by non-spectroscopic interferences has not been taken into account. For this purpose they proposed a new method for quantification of spectral interferences based on analyte isotope ratio measurements. Within this method, a tolerance level (TL) was defined as the matrix concentration at which the ratio between analyte isotopes with and without interferences is altered by 10% compared with a pure water reference standard, normalized with respect to the analyte concentration in the solution. Then, TLs were used to quantify the spectral interferences caused by simple matrices, such as sodium chloride or calcium, on the signal of several analyte isotopes (^{53}Cr , ^{58}Ni , ^{60}Ni , ^{61}Ni , ^{62}Ni , ^{63}Cu and ^{77}Se).

Moreover, they found that spectral interference from $^{42}\text{Ca}^{16}\text{O}$ on ^{58}Ni is reduced in the presence of phosphate, showing that the formation of interfering species is dependent

on the entire matrix composition and the knowledge of the individual effects of some of the interfering elements is not sufficient to predict interference effects in samples. In contrast, the quantification of the interferences due to a specific matrix should be performed considering all the elements of a matrix and the potential interactions between them.

A multivariate approach, based on the empirical modelling and experimental design concepts, was successfully applied for investigation and quantification of interferences in electrothermal atomic absorption spectrometry.^{9–11}

In this paper, a similar method was applied to ICP-MS in order to obtain a multivariate quantification of interferences caused by Na, Ca, Cl and S when these matrix elements are present together in the sample, at concentration levels ranging from 0.5 to 1000 µg ml⁻¹. According to the method proposed by Bjorn and co-workers,⁸ the spectroscopic interferences were studied by monitoring the changes in the isotope ratio (signal ratio for monoisotopic analytes) with varying matrix composition.

Experimental

Apparatus

The experiments were carried out on a Perkin-Elmer SCIEX Elan (Thornhill, ON, Canada) Model 6000 ICP mass spectrometer, equipped with a sample introduction system composed of an AS-91 autosampler, a Gilson (Worthington, OH, USA) Model 212 peristaltic pump, cross-flow nebulizer and Scott spray chamber. The operating parameters are given in Table 1.

Reagents

Standard solutions of 1 or 10 mg ml⁻¹ Na and Ca (BDH, Poole, Dorset, UK) and 1 or 10 mg ml⁻¹ standard solutions of S and Cl, prepared from 96% sulfuric acid and 30% hydrochloric acid of Suprapur grade (Merck, Darmstadt, Germany), respectively, were used as matrix stock standard solutions. A 10 µg ml⁻¹ multi-element standard solution (Perkin-Elmer, Norwalk, CT, USA) was used as an analyte stock standard solution.

Standard solutions of 1 mg ml⁻¹ Sc and Rh (Merck) were used as internal stock standard solutions. Synthetic samples and standards were prepared daily by the addition of the appropriate aliquots of the above standard solutions and by dilution with Milli-Q water (Millipore, Bedford, MA, USA). All solutions were in 0.1 mol l⁻¹ HNO₃ of Suprapur grade (Merck).

Procedure

The samples were prepared according to the experimental design reported in Table 2 and analysed by ICP-MS, using

Table 1 Operating parameters for ICP-MS measurements

Rf frequency	40 MHz
Rf power	1 kW
Outer gas flow rate	15 l min ⁻¹
Auxiliary gas flow rate	0.8 l min ⁻¹
Nebulizer gas flow rate	0.9 l min ⁻¹
Sampler cone orifice diameter	1.1 mm
Skimmer cone orifice diameter	0.9 mm
Lens voltage	7.25 V
Vacuum pressure	2.33 × 10 ⁻⁵ Torr
Sweeps per reading	30
Readings per replicate	1
Number of replicates	3
Scanning mode	Peak hopping
Integration time	3000 ms
Dwell time	100 ms

aqueous standard solutions. Isobaric interferences of ⁵⁸Fe on ⁵⁸Ni and ⁶⁴Ni on ⁶⁴Zn were corrected by means of mathematical equations. ⁴⁵Sc at 10 ng ml⁻¹ was added to standards and samples and used as a reference isotope for analytes having *m/z* 51–68 and ¹⁰³Rh at 20 ng ml⁻¹ was added for heavier isotopes.

Multiple linear regression analysis and the other statistical calculations were performed using the package of programs Parvus 1.2.¹²

Results and discussion

In order to obtain an accurate estimation of expected spectral interferences due to a specific matrix, it is necessary to investigate the relationship between interfering effect and concentrations of all the elements composing the matrix.⁸ For interferences caused by simple matrices, the relationship is normally linear; in contrast, when considering more complex matrices, deviations from linearity may occur and more general mathematical functions must be considered. Such a relationship should also include all the potential interactions between matrix elements, owing to their importance in the formation of polyatomic species. Therefore, the following equation was postulated:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i \neq j, i, j=1}^n b_{ij} x_i x_j \quad (1)$$

where *Y* is the parameter used to quantify the spectral interferences, *x_i* are the concentrations of the *i* elements which compose the matrix and *b_i* are the coefficients of the model.

The present study considered four common matrix elements (Na, Ca, Cl and S) and investigated their spectral interferences on several analyte isotopes, listed in Table 3 together with the potential interfering species. For this matrix, eqn. (1) can be expressed as follows:

$$\begin{aligned} Y = & b_0 + b_1 (\text{Na}) + b_2 (\text{Ca}) + b_3 (\text{Cl}) + b_4 (\text{S}) + b_{11} (\text{Na})^2 \\ & + b_{22} (\text{Ca})^2 + b_{33} (\text{Cl})^2 + b_{44} (\text{S})^2 + b_{12} (\text{Na})(\text{Ca}) \\ & + b_{13} (\text{Na})(\text{Cl}) + b_{14} (\text{Na})(\text{S}) + b_{23} (\text{Ca})(\text{Cl}) + b_{24} (\text{Ca})(\text{S}) \\ & + b_{34} (\text{Cl})(\text{S}) \end{aligned} \quad (2)$$

where (*X*) are the concentrations of matrix elements, expressed as coded values.

To quantify the spectral interferences, two different parameters were considered. For the isotopes of Cr, Ni, Zn, Cu, Cd and Pb, isotope ratio measurements were performed. Since ratios between different isotopes of an element are poorly affected by non-spectral matrix effects, a good separation of spectroscopic from non-spectroscopic interferences is expected. For monoisotopic ⁷⁵As and ⁵⁹Co and for ⁵¹V (isotopic abundance 99.75%), signal ratios (ratios between the signal measured with and without matrix) were calculated and non-spectroscopic interferences were corrected by internal standardization.

An internal standard was also used in the isotope ratio measurements, to minimize the experimental variance during the experiments.

In order to estimate the coefficients of the model, a multiple linear regression analysis was performed, according to the method reported previously.¹⁰ The adopted experimental design is presented in Table 2. According to this, each variable is studied at five levels (coded as $-\sqrt{5}$, -1 , 0 , $+1$, $+\sqrt{5}$); the experiments are performed on a spherical domain, at the vertices of the hypercube corresponding to a 2⁵⁻¹ fractional design (points 1–16), at the so-called 'star points' (points 17–26) and at the centre of the domain (points 27–32). The replicates at the centre point give the estimate of the experimental variance, taking into account both the instrumental pre-

Table 2 Experimental design

Run	Coded values					Real values ^a				
	Na	Ca	Cl	S	Analyte	Na	Ca	Cl	S	Analyte
1	-1	-1	-1	-1	+1	4.1	4.1	4.1	4.1	9.0
2	+1	-1	-1	-1	-1	123	4.1	4.1	4.1	5.0
3	-1	+1	-1	-1	-1	4.1	123	4.1	4.1	5.0
4	+1	+1	-1	-1	+1	123	123	4.1	4.1	9.0
5	-1	-1	+1	-1	-1	4.1	4.1	123	4.1	5.0
6	+1	-1	+1	-1	+1	123	4.1	123	4.1	9.0
7	-1	+1	+1	-1	+1	4.1	123	123	4.1	9.0
8	+1	+1	+1	-1	-1	123	123	123	4.1	5.0
9	-1	-1	-1	+1	-1	4.1	4.1	4.1	123	5.0
10	+1	-1	-1	+1	+1	123	4.1	4.1	123	9.0
11	-1	+1	-1	+1	+1	4.1	123	4.1	123	9.0
12	+1	+1	-1	+1	-1	123	123	4.1	123	5.0
13	-1	-1	+1	+1	+1	4.1	4.1	123	123	9.0
14	+1	-1	+1	+1	-1	123	4.1	123	123	5.0
15	-1	+1	+1	+1	-1	4.1	123	123	123	5.0
16	+1	+1	+1	+1	+1	123	123	123	123	9.0
17	$+\sqrt{5}$	0	0	0	0	1000	22.4	22.4	22.4	7.0
18	$-\sqrt{5}$	0	0	0	0	0.5	22.4	22.4	22.4	7.0
19	0	$+\sqrt{5}$	0	0	0	22.4	1000	22.4	22.4	7.0
20	0	$-\sqrt{5}$	0	0	0	22.4	0.5	22.4	22.4	7.0
21	0	0	$+\sqrt{5}$	0	0	22.4	22.4	1000	22.4	7.0
22	0	0	$-\sqrt{5}$	0	0	22.4	22.4	0.5	22.4	7.0
23	0	0	0	$+\sqrt{5}$	0	22.4	22.4	22.4	1000	7.0
24	0	0	0	$-\sqrt{5}$	0	22.4	22.4	22.4	0.5	7.0
25	0	0	0	0	$+\sqrt{5}$	22.4	22.4	22.4	22.4	11.5
26	0	0	0	0	$-\sqrt{5}$	22.4	22.4	22.4	22.4	2.5
27–32	0	0	0	0	0	22.4	22.4	22.4	22.4	7.0

^aConcentrations are expressed as $\mu\text{g ml}^{-1}$ for matrix elements and ng ml^{-1} for analytes.

Table 3 Isotopes analysed and main spectral interferences expected in the investigated system

Analyte isotope	Isotopic abundance (5)	Interfering species
⁵¹ V	99.75	³⁵ Cl ¹⁶ O
⁵² Cr	83.79	¹ H ³⁵ Cl ¹⁶ O
⁵³ Cr	9.50	³⁷ Cl ¹⁶ O
⁵⁸ Ni	68.27	⁴² Ca ¹⁶ O, ⁴¹ Ca ¹⁶ O ¹ H, ²³ Na ³⁵ Cl
⁵⁹ Co	100	⁴³ Ca ¹⁶ O, ⁴² Ca ¹⁶ O ¹ H
⁶⁰ Ni	26.10	⁴⁴ Ca ¹⁶ O, ⁴³ Ca ¹⁶ O ¹ H
⁶² Ni	3.59	²³ Na ² ¹⁶ O
⁶³ Cu	69.17	⁴⁰ Ar ²³ Na
⁶⁴ Zn	48.6	⁴⁸ Ca ¹⁶ O, ³² S ¹⁶ O ₂ , ³² S ₂
⁶⁵ Cu	30.86	³³ S ¹⁶ O ₂ , ³² S ³³ S, ⁴⁸ Ca ¹⁶ O ¹ H, ³² S ¹⁶ O ₂ ¹ H
⁶⁶ Zn	27.9	³⁴ S ¹⁶ O ₂ , ³³ S ₂ , ³³ S ¹⁶ O ₂ ¹ H
⁶⁸ Zn	18.8	³⁴ S ₂ , ³⁶ S ¹⁶ O ₂ , ³⁵ Cl ¹⁶ O ₂ ¹ H
⁷⁵ As	100	⁴⁰ Ar ³⁵ Cl, ⁴³ Ca ¹⁶ O ₂
¹¹¹ Cd	12.80	—
¹¹⁴ Cd	28.73	—
²⁰⁷ Pb	22.1	—
²⁰⁸ Pb	52.4	—

cision and the sample preparation procedure. It should be noted that, in order to consider a more realistic situation, the concentration of the analyte was considered as a variable; however, it was not included in the model, as we were interested in evaluating the dependence of *Y* only on matrix elements.

By fixing the ranges of the variables (0.5–1000 $\mu\text{g ml}^{-1}$ for the interfering elements and 2.5–11.5 ng ml^{-1} for the analytes) and the scale (a logarithmic scale for the interfering elements and a linear scale for the analyte), the coded values were replaced by real values and the experimental plan was obtained (Table 2). According this, 32 standard solutions were prepared and analysed by ICP-MS. The results of the multiple linear regression analysis, considering isotope ratios and signal ratios values as dependent variables, are reported in Tables 4 and 5, respectively. The calculated effects are expressed as mean

values and 95% confidence intervals (only significant terms are reported).

The quality of the models was tested by performing the ‘cross-validation’ procedure. According to this, each experiment was removed from the training set and the model recalculated. Then, the predicted value of the missing experiment was computed by the new model and compared with the true one. This procedure was repeated for all the experiments and the explained variance (EV) was calculated:

$$\text{EV} = 100 \frac{\sum_i^N (\hat{y}_i - y_i)^2}{\sum_i^N (\bar{y} - y_i)^2} \times 100 \quad (3)$$

where y_i is the experimental value of the experiment *i*, \hat{y}_i the predicted value and *N* the number of experiments.

From the EV values, reported in Tables 4 and 5, it was concluded that the models are able to predict efficiently the response inside the experimental domain, particularly when considering the isotope ratio as the response.

By comparing the b_0 coefficient (corresponding to the estimate of the response at the central point, when all the matrix elements are present at a concentration of 22.4 $\mu\text{g ml}^{-1}$, coded as 0) and the theoretical value of response, an evaluation of the mean interfering effect of the whole matrix can be obtained. Further, the coefficients of the models allow one to estimate all the individual and mutual effects, providing a multivariate quantification of spectral interferences arising from the considered matrix elements.

The only limitation in quantifying interference effects arises when both the considered analyte isotopes are interfered with by the same matrix element, as for the interferences due to chlorine on chromium isotopes, to calcium on nickel isotopes and to sulfur on zinc isotopes. In these cases, the models

Table 4 Multivariate effects of sodium, calcium, chlorine and sulfur on isotope ratios (mean values and 95% confidence intervals)

Coefficient	Factor	$^{52}\text{Cr}/^{53}\text{Cr}$	$^{58}\text{Ni}/^{62}\text{Ni}$	$^{60}\text{Ni}/^{62}\text{Ni}$	$^{66}\text{Zn}/^{68}\text{Zn}$	$^{64}\text{Zn}/^{66}\text{Zn}$	$^{63}\text{Cu}/^{65}\text{Cu}$	$^{114}\text{Cd}/^{111}\text{Cd}$	$^{208}\text{Pb}/^{207}\text{Pb}$
<i>Theoretical value—</i>		8.820	19.02	7.270	1.484	1.742	2.243	2.245	2.371
<i>Intercept—</i>									
b_0	Mean	7.083 ± 0.310	15.83 ± 0.85	5.950 ± 0.807	1.513 ± 0.033	2.379 ± 0.291	2.289 ± 0.053	2.241 ± 0.008	2.363 ± 0.024
<i>Main effects—</i>									
b_1	(Na)	—	-4.623 ± 0.536	-2.389 ± 0.563	—	—	0.399 ± 0.050	—	—
b_2	(Ca)	—	1.402 ± 0.536	2.745 ± 0.691	—	0.156 ± 0.149	-0.038 ± 0.036	—	—
b_3	(Cl)	-1.558 ± 0.266	—	—	—	—	—	—	—
b_4	(S)	—	-2.817 ± 0.536	-1.306 ± 0.563	0.127 ± 0.033	1.395 ± 0.210	-0.226 ± 0.041	—	—
<i>Quadratic effects—</i>									
b_{11}	(Na) ²	—	-1.169 ± 0.420	-0.517 ± 0.441	—	—	0.168 ± 0.043	—	—
b_{22}	(Ca) ²	—	-0.555 ± 0.420	2.467 ± 0.622	—	—	—	—	—
b_{33}	(Cl) ²	-0.512 ± 0.203	—	—	—	—	—	—	—
b_{44}	(S) ²	—	-0.582 ± 0.420	—	0.150 ± 0.030	0.703 ± 0.164	-0.102 ± 0.031	—	—
<i>Two-factor interactions—</i>									
b_{12}	(Na)(Ca)	—	—	-1.006 ± 0.718	—	—	—	—	—
b_{13}	(Na)(Cl)	—	—	—	—	—	—	—	—
b_{14}	(Na)(S)	—	-1.616 ± 0.684	—	—	—	—	—	—
b_{23}	(Ca)(Cl)	—	—	—	—	—	—	—	—
b_{24}	(Ca)(S)	—	0.810 ± 0.684	—	—	—	-0.057 ± 0.053	—	—
b_{34}	(Cl)(S)	—	—	—	—	—	—	—	—
<i>Multiple linear regression coefficient—</i>		0.935	0.980	0.970	0.957	0.956	0.976	—	—
<i>Cross-validation explained variance—</i>		85%	91%	83%	76%	77%	81%	—	—

Table 5 Multivariate effects of sodium, calcium, chlorine and sulfur on signal ratios (mean values and 95% confidence intervals)

Coefficient	Factor	^{51}V	^{59}Co	^{75}As
<i>Intercept—</i>				
b_0	Mean	1.085 ± 0.032	0.975 ± 0.018	1.116 ± 0.019
<i>Main effects—</i>				
b_1	(Na)	—	—	—
b_2	(Ca)	—	0.061 ± 0.022	0.029 ± 0.016
b_3	(Cl)	0.116 ± 0.034	—	0.077 ± 0.020
b_4	(S)	-0.040 ± 0.028	-0.050 ± 0.020	—
<i>Quadratic effects—</i>				
b_{11}	(Na) ²	—	—	—
b_{22}	(Ca) ²	—	—	—
b_{33}	(Cl) ²	0.053 ± 0.030	—	0.037 ± 0.018
b_{44}	(S) ²	—	—	—
<i>Two-factor interactions—</i>				
b_{12}	(Na)(Ca)	—	—	—
b_{13}	(Na)(Cl)	—	—	—
b_{14}	(Na)(S)	—	—	—
b_{23}	(Ca)(Cl)	—	—	—
b_{24}	(Ca)(S)	—	—	—
b_{34}	(Cl)(S)	—	—	—
<i>Multiple linear regression coefficient—</i>		0.836	0.819	0.861
<i>Cross-validation explained variance—</i>		63%	60%	54%

provide a quantification of the isotope ratio changes with varying element concentration but not absolute data.

Background equivalent concentrations (BECs) produced by 1000 $\mu\text{g ml}^{-1}$ standard solutions of sodium, calcium, chlorine and sulfur at each analyte isotope were also determined. The BEC values and empirical models deduced for each analyte will be now discussed separately.

Chromium isotopes

As shown in Table 4, the $^{52}\text{Cr}/^{53}\text{Cr}$ isotope ratio is sharply decreased by chlorine, whose effect increases at higher concentrations, owing to the presence of a significant quadratic term. This effect is due to the formation of $^{37}\text{Cl}^{16}\text{O}$, which overlaps the ^{53}Cr isotope and is much stronger than the interference of $^{35}\text{Cl}^{16}\text{O}^1\text{H}$ on ^{52}Cr , as reported by Krushevska and co-workers.⁶ According to this result, we found a BEC due to

1000 $\mu\text{g ml}^{-1}$ of chlorine at m/z 52 and 53 equal to 1.1 and 43.5 ng ml^{-1} , respectively.

Nickel isotopes

The mass region of interest for nickel determination (m/z 58–62) is strongly influenced by spectral interferences due to several polyatomic species containing sodium and calcium (Table 3). As shown in Table 4, the $^{58}\text{Ni}/^{62}\text{Ni}$ and $^{60}\text{Ni}/^{62}\text{Ni}$ isotope ratios are both strongly increased by calcium and its effect is more pronounced for the ^{60}Ni isotope. In agreement with this result, we found a BEC caused by 1000 $\mu\text{g ml}^{-1}$ of calcium at m/z 58, 60 and 62 equal to 2.4, 25.7 and 1.2 ng ml^{-1} , respectively. Similar values were reported by Vaughan and Templeton³ and Bjorn and co-workers.⁸ Moreover, the changes in the isotope ratio with increasing calcium concentration are different for ^{58}Ni and ^{60}Ni . In fact, $^{60}\text{Ni}/^{62}\text{Ni}$ is sharply increased by calcium, the effect of which increases at higher concentrations (owing to the presence of a significant positive quadratic effect), while the effect of calcium on $^{58}\text{Ni}/^{62}\text{Ni}$ is attenuated at higher concentrations (owing to the presence of a significant negative quadratic effect).

Concerning the effects of sodium, a sharp decrease in the $^{58}\text{Ni}/^{62}\text{Ni}$ and $^{60}\text{Ni}/^{62}\text{Ni}$ isotope ratios with increasing sodium concentration can be deduced. This effect is due to the formation of $^{23}\text{Na}_2^{16}\text{O}$, which overlaps ^{62}Ni . Chlorine did not show any significant effect on nickel isotopes, in conflict with the hypothesis³ of the formation of $^{23}\text{Na}^{35}\text{Cl}$ and in agreement with BEC measurements by Bjorn and co-workers.⁸

The effect of sulfur on nickel isotope ratios is surprising. Since nickel isotopes have no spectral overlap with sulfur species, it is probably due to non-spectroscopic effects. Finally, some significant interaction between matrix elements was found, proving the complexity of the reactions involved in the formation of interfering species. For example, the interaction between sodium and calcium on the $^{60}\text{Ni}/^{62}\text{Ni}$ isotope ratio means that the lower the concentration of sodium the higher is the effect of calcium, while the higher the concentration of calcium the greater is the effect of sodium. The significant interactions involving calcium clearly indicate the dependence of its interfering effect on matrix composition, as already found by Bjorn and co-workers.⁸

Zinc isotopes

The region from m/z 64 to 68 is drastically affected by sulfur species (Table 3). We found that the BECs caused by $1000\text{ }\mu\text{g ml}^{-1}$ of sulfur at m/z 64, 66 and 68 are equal to 27.7, 11.9 and 10.2 ng ml^{-1} , respectively. As shown in Table 4, sulfur causes an increase in both $^{66}\text{Zn}/^{68}\text{Zn}$ and $^{64}\text{Zn}/^{66}\text{Zn}$ isotope ratios, the latter being more pronounced. Therefore, the most interfering species are $^{32}\text{S}^{16}\text{O}_2$ and $^{32}\text{S}_2$. The $^{64}\text{Zn}/^{66}\text{Zn}$ isotope ratio is also increased by calcium, owing to the formation of $^{48}\text{Ca}^{16}\text{O}$.

Copper isotopes

As shown in Table 4, sodium causes a sharp increase in $^{63}\text{Cu}/^{65}\text{Cu}$ isotope ratio, owing to the interferences from $^{40}\text{Ar}^{23}\text{Na}$ on ^{63}Cu , in agreement with previously reported results.^{4,13} In contrast, the $^{63}\text{Cu}/^{65}\text{Cu}$ isotope ratio is decreased by Ca and S, owing to the formation of polyatomic species $^{48}\text{Ca}^{16}\text{O}^1\text{H}$, $^{32}\text{S}^{16}\text{O}_2^1\text{H}$, $^{33}\text{S}^{16}\text{O}_2$ and $^{32}\text{S}^{33}\text{S}$, overlapping ^{65}Cu . Moreover, the effect of sulfur was stronger than that of calcium. Finally, a significant interaction between calcium and sulfur was deduced.

Cadmium and lead isotopes

For $^{114}\text{Cd}/^{111}\text{Cd}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios, no significant effect due to the considered matrix elements was found, showing good efficiency of the adopted method in separating spectral from non-spectral interferences. This expected result is in agreement with analogous isotope ratio measurements by Lu and co-workers.⁴

Vanadium, cobalt and arsenic isotopes

^{51}V , ^{59}Co and ^{75}As were studied by deducing the relationships between the signal ratios (ratios between the signal measured with and without matrix) and matrix composition (Table 5). As reported in Table 5, the signal relative to ^{51}V is increased by chlorine, according to a quadratic model, and decreased linearly by sulfur. The effect of chlorine can be attributed to the formation of $^{35}\text{Cl}^{16}\text{O}$, while the decrease due to sulfur is probably due to a non-spectroscopic interference. According to this hypothesis, a BEC caused by $1000\text{ }\mu\text{g ml}^{-1}$ of chlorine at m/z 51 equal to 14.9 ng ml^{-1} was found, while no signal was detected at m/z 51 when measuring $1000\text{ }\mu\text{g ml}^{-1}$ of sulfur. The signal of ^{59}Co is linearly increased by calcium, because of the formation of polyatomic species $^{43}\text{Ca}^{16}\text{O}$ and $^{42}\text{Ca}^{16}\text{O}^1\text{H}$, and decreased by sulfur. Again, no signal was detected at m/z 59 when a $1000\text{ }\mu\text{g ml}^{-1}$ standard solution of sulfur was analyzed, whereas a BEC equal to 3.5 ng ml^{-1} was caused by $1000\text{ }\mu\text{g ml}^{-1}$ of chlorine.

Finally, it can be seen that the ^{75}As signal is sharply

increased by chlorine, according to a quadratic model, and increased linearly by calcium. While the effect of Cl is due to the well known interference from $^{40}\text{Ar}^{35}\text{Cl}$, the effect of calcium is surprising. We found that BECs caused by $1000\text{ }\mu\text{g ml}^{-1}$ of chlorine and calcium at m/z 75 are equal to 9.2 and 1.2 ng ml^{-1} , respectively, showing that both of them cause a spectral interference. A possible calcium species at m/z 75 could be $^{43}\text{Ca}^{16}\text{O}_2$, as reported by May.¹⁴

Conclusions

A new method for the quantification of spectral interferences in ICP-MS has been presented. The application of the techniques of empirical modelling and experimental design allowed us to obtain a great deal of information concerning the spectral interferences due to sodium, calcium, chlorine and sulfur species at the m/z of interest for the determination of several isotopes. All the expected interfering effects caused by the considered matrix elements were found; however, the dependence of their magnitude on matrix composition is a complex function, including significant quadratic terms and interactions between matrix elements. These results clearly indicate that a multivariate approach is particularly suitable for obtaining an accurate quantification of expected spectral interference effects.

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